

Special Issue Reprint

Advances in Mantle–Crust Interactions for Petrogenesis and Ore-Forming Processes

Edited by
Feng Huang, Liang Guo, Xiyao Li, Zhiwei Wang and Vinod O. Samuel

mdpi.com/journal/minerals

Advances in Mantle–Crust Interactions for Petrogenesis and Ore-Forming Processes

Advances in Mantle–Crust Interactions for Petrogenesis and Ore-Forming Processes

Guest Editors

Feng Huang

Liang Guo

Xiyao Li

Zhiwei Wang

Vinod O. Samuel



Basel • Beijing • Wuhan • Barcelona • Belgrade • Novi Sad • Cluj • Manchester

Guest Editors

Feng Huang

School of Earth Science
and Resources

China University
of Geosciences

Beijing

China

Zhiwei Wang

College of Earth Sciences

Hebei GEO University

Shijiazhuang

China

Liang Guo

School of Earth and
Planetary Sciences

China University
of Geosciences

Wuhan

China

Vinod O. Samuel

Department of Earth

System Sciences

Yonsei University

Seoul

Republic of Korea

Xiyao Li

College of Marine Geosciences

Ocean University of China

Qingdao

China

Editorial Office

MDPI AG

Grosspeteranlage 5

4052 Basel, Switzerland

This is a reprint of the Special Issue, published open access by the journal *Minerals* (ISSN 2075-163X), freely accessible at: https://www.mdpi.com/journal/minerals/special_issues/N3I68F184B.

For citation purposes, cite each article independently as indicated on the article page online and as indicated below:

Lastname, A.A.; Lastname, B.B. Article Title. <i>Journal Name</i> Year , Volume Number, Page Range.
--

ISBN 978-3-7258-8835-1 (Hbk)

ISBN 978-3-7258-8836-8 (PDF)

<https://doi.org/10.3390/books978-3-7258-8836-8>

© 2026 by the authors. Articles in this reprint are Open Access and distributed under the Creative Commons Attribution (CC BY) license. The reprint as a whole is distributed by MDPI under the terms and conditions of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) license (<https://creativecommons.org/licenses/by-nc-nd/4.0/>).

Contents

About the Editors	vii
-----------------------------	-----

Preface	ix
-------------------	----

Feng Huang, Liang Guo, Xiyao Li, Zhiwei Wang and Vinod O. Samuel Advances in Mantle–Crust Interactions for Petrogenesis and Ore-Forming Processes: An Introduction Reprinted from: <i>Minerals</i> 2026 , 16, 570, https://doi.org/10.3390/min16060570	1
---	---

Shashank Prabha-Mohan, Ian S. Williams and Sandeep Singh Zircon, Monazite SHRIMP U-Th-Pb and Quartz Oxygen Isotopic Results from the Higher Himalayan Crystallines (HHC) of the Sikkim Himalayas Reprinted from: <i>Minerals</i> 2024 , 14, 572, https://doi.org/10.3390/min14060572	10
---	----

Hao Zhao, Antonio Simonetti, Stefanie Simonetti, Xiaopeng Cao and Yushan Du A Geochemical and Isotopic Investigation of Carbonatites from Huangshui, Central China: Implications for Petrogenesis and Mantle Sources Reprinted from: <i>Minerals</i> 2024 , 14, 953, https://doi.org/10.3390/min14090953	37
---	----

Rui Geng, Zhenhua Fan, Zhixin Wang, Yixin Li and Bingyang Ye The Nature of the Magma Source for Jurassic Mafic Rocks in the Yanbian Area, Eastern Jilin Province: Constraints on the Subduction Process of the Paleo-Pacific Ocean Reprinted from: <i>Minerals</i> 2024 , 14, 1126, https://doi.org/10.3390/min14111126	57
--	----

Lijie Jin, Jilin Wang, Pinrui Qin, Chunjia Li, Shuang Xu, Zhixin Han, et al. Petrogenesis of Diorite-Porphyrite in the Southern Xintai Area of the Mid-Western Shandong Peninsula, North China Craton: Insights from Geochronology, Mineralogy, Geochemistry, and Sr-Nd-Hf Isotopes Reprinted from: <i>Minerals</i> 2024 , 14, 1220, https://doi.org/10.3390/min14121220	74
--	----

Jieting Ouyang, Guoyu Chen, Liya Yang, Wenqian Lu and Yun Zhou Tectonic Evolution of the Hainan Island, South China: Geochronological and Geochemical Constraints from Late Permian to Early Triassic Basalts Reprinted from: <i>Minerals</i> 2025 , 15, 293, https://doi.org/10.3390/min15030293	95
--	----

Baoqun Sun, Xinyu Wei and Huan Dong Formation Mechanism of Plagioclase–Amphibole and Amphibole–Spinel Symplectites in the Bijigou Layered Intrusion: Insights from Mineralogical and Crystallographic Constraints Reprinted from: <i>Minerals</i> 2025 , 15, 433, https://doi.org/10.3390/min15050433	114
--	-----

Yu Wang, Haoyuan Lan, Chong Jin and Yuhuang Zhang Petrogenesis of Middle Jurassic Syenite-Granite Suites and Early Cretaceous Granites with Associated Enclaves in Southwestern Zhejiang, SE China: Implications for Subduction-Related Tectonic Evolution Beneath Northeastern Cathaysia Block Reprinted from: <i>Minerals</i> 2025 , 15, 474, https://doi.org/10.3390/min15050474	130
---	-----

Didem Kiray and Oya Cengiz Petrography, Geochemistry, and Magmatic Processes of Oligocene-Miocene Tuzla Volcanics, Biga Peninsula, NW Türkiye Reprinted from: <i>Minerals</i> 2026 , 16, 23, https://doi.org/10.3390/min16010023	153
---	-----

Mohamed Zaki Khedr, Mahmoud A. Sayed, Shehata Ali, Mikhles K. Azer, Yuji Ichiyama, Eiichi Takazawa, et al. Mineralogy and Geochemistry of Jasperoid Veins in Neoproterozoic Metavolcanics: Evidence of Silicification, Pyritization and Hematization Reprinted from: <i>Minerals</i> 2024 , <i>14</i> , 647, https://doi.org/10.3390/min14070647	176
Amanda Andrade de Souza, Rogério Guitarrari Azzone, Luanna Chmyz, Lina Maria Cetina Tarazona, Fábio Ramos Dias de Andrade, José Vinicius Martins, et al. Genesis of Fe-Ti-(V) Oxide-Rich Rocks by Open-System Evolution of Mafic Alkaline Magmas: The Case of the Ponte Nova Massif, SE Brazil Reprinted from: <i>Minerals</i> 2024 , <i>14</i> , 724, https://doi.org/10.3390/min14070724	209
Liya Yang, Yongfeng Cai, Jieting Ouyang, Fang Xu, Yankun Chen and Yun Zhou Mineralogy and Geochemistry of Early Triassic Granite in South China: Insights into Source Region Characteristics and REE Mineralization Reprinted from: <i>Minerals</i> 2025 , <i>15</i> , 530, https://doi.org/10.3390/min15050530	235
Yun Zhong, Yajuan Yuan, Ye Lu and Bin Xia Origin and Tectonic Implication of Cenozoic Alkali-Rich Porphyry in the Beiya Au-Polymetallic Deposit, Western Yunnan, China Reprinted from: <i>Minerals</i> 2025 , <i>15</i> , 531, https://doi.org/10.3390/min15050531	265
Chunxia Xu, Jiantang Peng, Jianjun Gan, Chun Tang, Zhiming Yin and Cheng Huang Genesis and Mineralization Process of the Lanuoma Sediment-Hosted Pb–Zn Deposit, Sanjiang Metallogenic Belt, Southwestern China: Constraints from Zn, Pb, and S Isotopes Reprinted from: <i>Minerals</i> 2026 , <i>16</i> , 164, https://doi.org/10.3390/min16020164	291
Gao-Feng Du, Xiang-Ying Ling, Dan Wang, Wei-Jian Zhou, Liu Yang, You-Yue Lu and Zun-Zun Zhang In Situ Geochemical and Sulfur Isotopic Composition of Pyrites from the Jiepailing Tin–Beryllium Polymetallic Deposit, Southern Hunan Province, China: Implications for Ore-Forming Processes Reprinted from: <i>Minerals</i> 2025 , <i>15</i> , 312, https://doi.org/10.3390/min15030312	311
Anastassia Borisova Kinetics of Sulfide Dissolution Controlled by Sulfur Radical Diffusion: Implications for Sulfur Transport and Triggering of Volcanic Eruptions Reprinted from: <i>Minerals</i> 2025 , <i>15</i> , 989, https://doi.org/10.3390/min15090989	339
Rainer Thomas and Adolf Rericha Extreme Element Enrichment by the Interaction of Supercritical Fluids from the Mantle with Crustal Rocks Reprinted from: <i>Minerals</i> 2025 , <i>15</i> , 33, https://doi.org/10.3390/min15010033	353

About the Editors

Feng Huang

Feng Huang is a professor at China University of Geosciences (Beijing). His research focuses on petrology and isotope geochemistry, with an emphasis on the Mesozoic–Cenozoic igneous rocks exposed in the southern Tibetan orogenic belt within China. He is dedicated to elucidating the crustal and mantle compositions and their interaction processes in the Tethyan realm. He has served as Principal Investigator of three projects funded by the National Natural Science Foundation of China and was a recipient of the National Postdoctoral Program for Innovative Talents. He is also a member of the Innovation Team on “Lithospheric Evolution and Metallogenesis of the Tibetan Plateau,” a key research group supported by the Ministry of Science and Technology of China. He has published over 30 papers as first/corresponding author in international geoscience journals, including *Nature Communications*, *Geochimica et Cosmochimica Acta*, *GSA Bulletin*, and *Chemical Geology*.

Liang Guo

Liang Guo is a professor at China University of Geosciences (Wuhan). He applies a combination of petrologic, geochemical and isotopic techniques to understand the tectonic evolution of the Neo-Tethys in South Tibet and the magmatic accretion of continental crust in the subduction zone. His current research projects mainly focus on the formation and evolution of the lower crust of the Gangdese arc, and on continental relamination and its effects on mineralization during India–Asian continental convergence. He has served as Principal Investigator of three projects funded by the National Natural Science Foundation of China. He has published over 40 papers in international geoscience journals, including *Contributions to Mineralogy and Petrology*, *GSA Bulletin*, *Tectonophysics*, and *Chemical Geology*.

Xiyao Li

Xiyao Li is an associate professor at Ocean University of China. His research focuses on igneous petrology. His recent focus has been on volcanic magmatism and magma dynamics. He has served as Major Investigator of projects funded by the National Natural Science Foundation of China and the National Key R&D Program of China. He has published over 15 papers as first/corresponding author in international geoscience journals.

Zhiwei Wang

Zhiwei Wang is a Professor at the College of Earth Sciences, Hebei GEO University, China, and an Adjunct Professor and Doctoral Supervisor at China University of Geosciences, Beijing. He earned his B.S. in Geology from Jilin University in 2012 and his Ph.D. in Petrology from Jilin University in 2017. His research focuses on mantle metasomatism and the deep carbon cycle, subduction and collision processes in the Central Asian Orogenic Belt and the Arabian–Nubian Shield, genesis of magmatic-hydrothermal deposits, and supercontinent cycles (Nuna, Rodinia, Gondwana).

Vinod O. Samuel

Vinod O. Samuel is a dedicated researcher at the Structural Geology and Tectonics Lab within the Department of Earth System Sciences at Yonsei University in Seoul, South Korea. His main research topics include igneous and metamorphic petrology, geochemistry and tectonics. He has been working on magmatism, metamorphism and tectonics in a wide variety of tectonic settings in Korea, China and India. His recent works describe the stability of granitoids in the Early Earth and the role of fluids during granulite facies metamorphism/metasomatism.

Preface

This Reprint focuses on magmatic activity and metallogenesis in the context of crust–mantle interaction. It systematically presents the application of analytical techniques ranging from mineral/whole-rock element and isotope analyses to investigations of igneous rocks and ore deposits from various regions worldwide. Several contributions further constrain the deep geodynamic settings under which these igneous rocks and ore deposits formed. Experimental petrology studies also provide new insights into the modification of magmatic and metallogenic processes by sulfides, deep fluids, and melts. Collectively, the case studies presented in this Reprint offer new constraints for a better understanding of lithospheric evolution and ore formation processes. The content is intended for graduate students and early-career researchers in Earth sciences, aiming to explore the complete transfer of magmas and ore-forming materials from the deep Earth to the surface. It serves as a reference for future studies while providing petrological and geochemical clues to support and sustain human development.

Feng Huang, Liang Guo, Xiyao Li, Zhiwei Wang, and Vinod O. Samuel

Guest Editors

Advances in Mantle–Crust Interactions for Petrogenesis and Ore-Forming Processes: An Introduction

Feng Huang ^{1,*}, Liang Guo ², Xiyao Li ³, Zhiwei Wang ⁴ and Vinod O. Samuel ⁵

¹ State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Science and Resources, China University of Geosciences, Beijing 100083, China

² State Key Laboratory of Geological Processes and Mineral Resources, School of Earth and Planetary Sciences, China University of Geosciences, Wuhan 430074, China; lguo@cug.edu.cn

³ Key Lab of Submarine Geosciences and Prospecting Techniques, MOE and College of Marine Geosciences, Ocean University of China, Qingdao 266100, China

⁴ Hebei Key Laboratory of Strategic Critical Mineral Resources, College of Earth Sciences, Hebei GEO University, Shijiazhuang 050031, China; wangzw@hgu.edu.cn

⁵ Department of Earth System Sciences, Yonsei University, Seoul 03722, Republic of Korea

* Correspondence: fenghuang@cugb.edu.cn

1. Introduction

Accurately identifying the composition of crust–mantle reservoirs and deciphering the processes governing material exchange between them remain fundamental scientific issues in Earth sciences [1–3]. Mantle–crust interactions not only control the composition and evolutionary architecture of the modern lithosphere, but also profoundly influence the long-term habitability of Earth. Moreover, they represent a critical driving mechanism for the mobilization, transport, enrichment, and ultimately ore formation of metallic elements [4–8], thereby providing essential resource foundations for human civilization and societal development. Consequently, unraveling the composition, evolutionary history, and interaction mechanisms of crustal and mantle materials is of great significance for advancing petrology, geochemistry, tectonics, and economic geology.

Over the past decades, studies on crust–mantle material composition and exchange processes have evolved from early qualitative interpretations based mainly on petrographic observations toward increasingly quantitative and process-oriented investigations integrating multidisciplinary approaches. Elemental geochemistry, radiogenic isotope systems, and stable isotopes have become powerful tools for tracing the sources, evolution, and metallogenic implications of crust–mantle interactions [9–14]. During crust–mantle recycling processes, aqueous fluids and hydrous melts derived from subducting slabs or lower crustal materials can metasomatize mantle sources, whereas the upward transfer of mantle-derived heat and materials promotes continental crustal growth and reworking [15–19]. These complex crust–mantle interaction processes not only govern magma generation and evolution, but are also commonly accompanied by the activation, transport, and enrichment of critical metals, ultimately leading to the formation of diverse mineralization systems.

Despite extensive investigations into crust–mantle magmatism and fluid activity, the specific mechanisms governing crust–mantle material exchange remain incompletely understood. In particular, how crustal and mantle materials are transported, mixed, and recycled under different geodynamic settings, and how these processes further control the formation and enrichment of specific ore deposits, remain subjects of ongoing debate. Furthermore, the effects of mineral fractionation, melt–fluid evolution, and fluid metasomatism occurring during magma ascent and emplacement within the shallow crust remain insufficiently constrained, especially regarding their roles in elemental redistribution and

ore-forming processes. Therefore, systematic investigations integrating geochronology, mineralogy, elemental geochemistry, and isotope geochemistry of magmatic rocks and associated ore deposits derived from different crust–mantle reservoirs are essential for deciphering the coupling relationships among crust–mantle composition, material exchange, and metallogenesis.

This Special Issue, entitled “Advances in Mantle–Crust Interactions for Petrogenesis and Ore-Forming Processes”, focuses on key scientific questions related to crust–mantle composition and evolution, magmatism, and ore-forming processes. It aims to bridge current knowledge gaps and improve our understanding of deep Earth processes and their metallogenic consequences. The collected contributions not only highlight recent advances in petrology, geochemistry, and isotopic tracer techniques applied to igneous petrogenesis and crust–mantle interactions, but also provide important geochemical constraints on the sources of ore-forming materials, geodynamic mechanisms, and metal enrichment processes. Collectively, these studies further deepen our understanding of mantle–crust interaction processes and provide new perspectives and theoretical foundations for future investigations into the intrinsic links between deep Earth dynamics and resource–environmental systems.

2. An Overview of Published Articles

The 16 articles included in this collection address the above scientific issues from four major perspectives.

2.1. *Petrogenesis of Igneous Rocks and Mantle–Crust Interactions*

Prabha-Mohan et al. (Contribution 1) conducted a detailed investigation of oxygen isotope compositions in zircon, monazite, and quartz from the Higher Himalayan Crystallines of the Sikkim Himalayas. Their study identified source characteristics and equilibrium conditions of the melts involved, revealing the presence of multiple melt sources within the High Himalayan Crystalline Sequence. Although zircon and monazite from the same rocks display similar oxygen isotope compositions, the authors proposed that low-elevation fluid activity may have produced lighter oxygen isotope signatures in these minerals, with such fluids probably derived from metasedimentary country rocks.

Zhao et al. (Contribution 2) performed combined radiogenic Sr–Nd–Pb and stable C–O isotope studies on the Huangshuian carbonatites in central China. The results demonstrate that these carbonatites possess C–O isotope compositions comparable to primary igneous carbonatites but exhibit enriched radiogenic Sr–Nd–Pb isotope signatures. Their study suggests that the Huangshuian carbonatites represent late-stage differentiated products of mantle-derived carbonatitic magmas sourced from carbonated lithospheric mantle, with possible contamination by basement rocks.

Geng et al. (Contribution 3) carried out detailed geochronological, elemental, and isotopic investigations on Early Jurassic hornblende gabbros from northeastern China. Their results indicate that these rocks were generated through metasomatism of the mantle wedge by supercritical fluids and originated from a mixed source involving depleted mantle and approximately 10–20% terrigenous sediments. This study highlights the important role of supercritical fluids in modifying the mantle wedge during westward subduction of the Paleo-Pacific Plate.

Jin et al. (Contribution 4) evaluated diorite porphyrites from southern Xintai area in the western Shandong Peninsula, eastern China, using zircon U–Pb–Hf isotopes together with whole-rock elemental and Sr–Nd isotope geochemistry. The studied rocks exhibit pronounced adakitic geochemical affinities. The authors proposed that rollback of the Paleo-Pacific Plate during the Early Cretaceous triggered localized delamination of the lower

crust, and that interaction between lower crust-derived melts and enriched lithospheric mantle ultimately generated these diorite porphyries.

Ouyang et al. (Contribution 5) identified two types of Late Permian–Early Triassic basalts from Hainan Island, South China, characterized respectively by calc-alkaline and alkaline affinities. The early-stage basalts were derived from enriched mantle modified by subduction-related fluids, whereas the later-stage basalts originated mainly from depleted mantle and were likely contaminated by crustal materials during ascent. These basaltic suites record a tectonic transition from an island-arc setting to an intracontinental extensional environment, indicating that subduction of the Paleo-Tethyan oceanic slab persisted until at least the Late Permian and may have evolved into intraplate extension during the Middle Triassic.

Sun et al. (Contribution 6) investigated the formation mechanisms of plagioclase–amphibole and amphibole–spinel symplectites in the Bijigou layered intrusion along the northern margin of the Yangtze Block, South China. Their results demonstrate that the symplectites crystallized during the late stages of magmatic evolution, and that different mineral assemblages may preserve orientational inheritance or pseudomorphic features from earlier-formed minerals. This work refines our understanding of mineralogical evolution in layered intrusions.

Wang et al. (Contribution 7) performed geochronological, elemental, and Sr–Nd–Hf isotopic studies on Middle Jurassic to Early Cretaceous granitoids from southeastern China. Their results reveal distinct crustal and mantle source characteristics for different granitoid types. Combined with regional tectonic evolution, the study demonstrates that the region experienced significant tectonic transformation through time, evolving from a compressional regime related to Paleo-Pacific Plate subduction during the Middle Jurassic to lithospheric extension and intensified crust–mantle interaction induced by slab rollback during the Early Cretaceous.

Kiray and Cengiz (Contribution 8) investigated a complex Oligocene–Miocene volcanic assemblage in northwestern Türkiye and demonstrated that these volcanic rocks formed in a tectonic setting related to continental collision. Although the magmas were primarily derived from enriched lithospheric mantle, subsequent mineral fractional crystallization played a critical role in controlling magmatic evolution, while crustal assimilation also modified their geochemical compositions. This study provides an excellent example of crustal modification of mantle-derived magmas during ascent and emplacement.

2.2. Magmatism Related to Ore Formation

Khedr et al. (Contribution 9) conducted detailed mineralogical and geochemical studies on Neoproterozoic metavolcanic rocks and associated jasperoid veins in southern Eastern Desert of Egypt. Their results suggest that the metavolcanic rocks originated from differentiated melts derived from depleted mantle sources that were influenced by slab-derived fluids and/or melts during formation. The jasperoid veins are enriched in Fe oxides and base metals and display trace-element characteristics indicative of fluid-mobile element enrichment, suggesting formation through metasomatism by silica-rich magmatic-hydrothermal fluids.

de Souza et al. (Contribution 10) examined Fe–Ti–V oxide-bearing clinopyroxenites and magnetitites from the Ponte Nova Massif in southeastern Brazil using detailed mineralogical and geochemical approaches. Their results indicate that these rocks formed during different stages of magma chamber evolution and record distinct open-system processes. Deep magma recharge and shallow-level crustal contamination were identified as the principal controls on geochemical variations, whereas later magmatic events superimposed on these magmatic pulses contributed to sulfide formation.

Yang et al. (Contribution 11) carried out detailed geochronological and geochemical studies on granites genetically related to regolith-hosted rare-earth element (REE) deposits in South China. The granites were interpreted to have originated from sediment-derived sources. Their geochemical characteristics resemble those of granitic parent rocks associated with typical regolith-hosted REE deposits in South China, suggesting that the formation of regolith-hosted REE deposits in the Darongshan–Shiwandashan region was primarily controlled by magmatic differentiation, geomorphology, and weathering processes.

Zhong et al. (Contribution 12) investigated syenite porphyries associated with the Beiya porphyry Au-polymetallic deposit in southwestern China through geochronological and geochemical analyses. These rocks exhibit adakitic-like geochemical signatures and were interpreted to have originated from ancient thickened lower crust modified and metasomatized by upwelling mantle-derived materials. Their study highlights the significant metallogenic potential of crust–mantle interactions during magmatism and ore formation.

2.3. Geochemistry of Ore-Forming Minerals

Xu et al. (Contribution 13) conducted high-precision Zn, Pb, and S isotope analyses of ore-forming minerals (sphalerite and robinsonite) from the Sanjiang Metallogenic Belt in southwestern China. Their results indicate that Pb and Zn in the ores were derived from mixed sedimentary and crustal basement sources, whereas sulfur was likely sourced from a deep reservoir. Using a multi-isotope approach, this study provides new insights into the genesis and metallogenic processes of sediment-hosted Pb–Zn deposits in the Sanjiang Metallogenic Belt.

Du et al. (Contribution 14) performed detailed mineralogical, in situ geochemical, and sulfur isotope analyses of pyrite closely associated with Sn-polymetallic mineralization in the Jiepailing deposit, southern Hunan Province, China. Five pyrite types with distinct textures and sulfur isotope compositions were identified. Their results demonstrate that various ore bodies in the deposit were products of Late Cretaceous magmatic-hydrothermal activity and reconstruct the distinct mineralization and alteration processes involved.

2.4. Experimental Petrology and Magmatic Ore-Forming Processes

Borisova (Contribution 15) experimentally simulated the dissolution of pyrrhotite in hydrous rhyolitic melts under sulfate–sulfide transition conditions. The results demonstrate that sulfur can achieve the highest chemical diffusion rates in hybrid melts as S^{2-} or S^{3-} species under these conditions. This process may not only contribute to explosive volcanic eruptions in arc settings, but may also promote enrichment of chalcophile metals such as Au, Cu, and Pt associated with dissolved sulfide components, thereby facilitating ore formation.

Thomas and Rericha (Contribution 16) demonstrated that supercritical fluids or melts may be preserved within crustal rocks as critical high-temperature and high-pressure exotic minerals. In particular, typical fluid inclusions hosted by cassiterite are likely products of supercritical fluids. Their study suggests that mantle-derived supercritical fluids may interact with crustal rocks and become trapped within crustal lithologies.

3. Perspectives and Future Directions

The 16 contributions compiled in this collection provide systematic insights into crust–mantle material cycling and ore-forming processes. These studies not only deepen our understanding of crust–mantle compositions and exchange mechanisms under diverse tectonic settings, but also highlight the critical roles of subduction, slab rollback, lower crustal delamination, lithospheric extension, supercritical fluid metasomatism, and magmatic–hydrothermal evolution in magma generation and metallogenesis. Collectively, these

studies demonstrate that mantle–crust interaction represents one of the fundamental mechanisms controlling continental magmatic evolution and ore-forming processes. Whether in continental collision zones, active continental margins, post-collisional extensional settings, or intraplate tectonic environments, complex and multi-stage material exchange and energy transfer commonly occur between the mantle and crust [17,20–22].

Increasing evidence suggests that magmatic systems rarely originate from a single endmember source, but instead result from contributions from depleted mantle, enriched lithospheric mantle, lower crust-derived melts, sedimentary components, and slab-derived fluids/melts [18,19,23,24]. During magma ascent and storage, these systems commonly undergo fractional crystallization, crustal assimilation, deep magma recharge, and open-system evolution, further increasing their complexity.

From a regional tectonic perspective, several studies in this collection emphasize the profound influence of plate subduction and its subsequent evolution on mantle–crust interactions. For example, subduction and rollback of the Paleo-Pacific Plate are regarded as major driving forces for Mesozoic magmatism and lithospheric thinning in eastern China, whereas prolonged subduction of the Paleo-Tethyan oceanic lithosphere and its later transition into intraplate extension record a major geodynamic transformation from convergence to extension within the Tethyan realm. Meanwhile, lower crustal delamination, lithospheric extension, and asthenospheric upwelling not only modified magma source characteristics, but also facilitated upward transfer of deep heat and metal-bearing materials, thereby creating favorable conditions for mineralization.

Notably, increasing attention has been paid to the role of supercritical fluids in mantle–crust interactions within subduction zones [25,26]. Owing to their hybrid fluid–melt properties, supercritical fluids are highly efficient agents for transporting elements and isotopic signatures, and their metasomatic effects on mantle wedges may represent an important mechanism for generating unusual magmatic assemblages and metal enrichment [27–29]. Studies included in this collection concerning mantle wedge metasomatism by supercritical fluids, sulfide diffusion in melts, and supercritical fluid inclusions provide new experimental and theoretical constraints on the relationship between deep fluid activity and ore formation. These findings imply that the traditional binary distinction between “fluid metasomatism” and “melt metasomatism” may require further refinement, and that the role of deep supercritical systems in element transport and metal enrichment deserves much greater attention.

In terms of metallogenesis, the studies presented here further highlight the fundamental role of mantle–crust material exchange in controlling metal enrichment and ore formation. Whether involving adakitic magma-related Au–Cu polymetallic mineralization, regolith-hosted REE deposits, Fe–Ti–V oxide mineralization, Sn-polymetallic systems, or sediment-hosted Pb–Zn deposits, these ore-forming processes are closely associated with deep magmatic activity, mantle–crust interactions, and subsequent hydrothermal evolution. In particular, lower crustal melting coupled with interaction between crustal and mantle-derived materials is increasingly recognized as a key mechanism for generating metal-rich magmas, whereas the addition of deep volatile components and sulfur may significantly enhance metal transport and precipitation efficiency [30–32]. Collectively, these studies suggest that metallogenesis fundamentally represents the shallow crustal response to deep geodynamic processes.

This collection also demonstrates the importance of multidisciplinary and multi-scale approaches in modern geological research. The integration of high-precision geochronology, multi-isotope systems (e.g., Sr–Nd–Hf–Pb–C–O–S–Zn isotopes), in situ mineral-scale analyses, experimental petrology, and thermodynamic modeling is driving geological research from traditional lithological description toward dynamic and process-oriented

interpretations. In particular, trace-element and stable isotope records preserved at the mineral scale provide increasingly refined temporal and spatial constraints on magma evolution, fluid activity, and ore-forming processes.

Despite significant progress in recent years, several key scientific issues concerning mantle–crust interactions remain unresolved.

First, accurately distinguishing the relative contributions of different endmembers during crust–mantle material exchange remains highly challenging. In complex systems affected by multi-stage magmatic evolution and late hydrothermal overprinting, it is still difficult to quantitatively resolve the respective contributions from depleted mantle, enriched lithospheric mantle, lower crust-derived melts, sediment melts, and slab-derived fluids. Future research, therefore, requires the development of more sensitive isotopic tracers and more robust quantitative models.

Second, the mechanisms by which supercritical fluids transport deep elements remain incompletely understood. Future studies integrating high-temperature and high-pressure experiments, fluid inclusion analyses, and numerical simulations are necessary to constrain the transport and partitioning behaviors of metals, volatiles, and sulfur under supercritical conditions, thereby clarifying their actual contributions to subduction-related magmatism and ore formation.

Third, the coupling relationships between mantle–crust interactions and metallogene-sis require further investigation. At present, questions such as which types of mantle–crust interactions are most favorable for the formation of giant ore deposits and how deep geodynamic processes control metal enrichment efficiency remain poorly constrained. Future work should therefore emphasize integrated studies linking deep sources with shallow ore systems to establish cross-scale metallogenic geodynamic frameworks.

Fourth, mineral-scale investigations are expected to become a major future research direction. Increasing evidence indicates that minerals not only record magma and fluid evolution, but also preserve short-timescale dynamic processes. Greater application of in situ isotopic microanalysis, atomic-scale mineralogy, and machine learning-assisted data interpretation will enable higher-resolution reconstructions of magma–fluid system evolution.

Finally, global comparative studies should be further strengthened. Many current studies remain restricted to individual regions or tectonic systems. Future research should place greater emphasis on comparisons among different continental margins, collisional orogenic belts, and intraplate settings in order to understand mantle–crust cycling and metallogenic processes from a global geodynamic perspective, and to further explore their intrinsic links with Earth’s long-term habitability, atmospheric evolution, and resource formation.

Overall, this collection highlights recent advances in the study of mantle–crust interactions and their metallogenic consequences, while also reflecting a broader transition in deep Earth research from static compositional characterization toward dynamic process-oriented interpretations. With continued advances in high-precision analytical techniques, multi-isotope systems, experimental simulations, and big-data approaches, future studies will provide increasingly comprehensive insights into the coupling relationships among deep Earth material cycling, magmatism, and ore-forming systems, thereby establishing a stronger theoretical framework for understanding continental evolution and resource formation.

Conflicts of Interest: The Guest Editors declare no conflicts of interest.

List of Contributions:

1. Prabha-Mohan, S.; Williams, I.S.; Singh, S. Zircon, Monazite SHRIMP U-Th-Pb and Quartz Oxygen Isotopic Results from the Higher Himalayan Crystallines (HHC) of the Sikkim Himalayas. *Minerals* **2024**, *14*, 572. <https://doi.org/10.3390/min14060572>.
2. Zhao, H.; Simonetti, A.; Simonetti, S.; Cao, X.; Du, Y. A Geochemical and Isotopic Investigation of Carbonatites from Huangshuian, Central China: Implications for Petrogenesis and Mantle Sources. *Minerals* **2024**, *14*, 953. <https://doi.org/10.3390/min14090953>.
3. Geng, R.; Fan, Z.; Wang, Z.; Li, Y.; Ye, B. The Nature of the Magma Source for Jurassic Mafic Rocks in the Yanbian Area, Eastern Jilin Province: Constraints on the Subduction Process of the Paleo-Pacific Ocean. *Minerals* **2024**, *14*, 1126. <https://doi.org/10.3390/min14111126>.
4. Jin, L.; Wang, J.; Qin, P.; Li, C.; Xu, S.; Han, Z.; Wang, W.; Liu, W.; Wang, Z.; Gao, J.; et al. Petrogenesis of Diorite-Porphyrite in the Southern Xintai Area of the Mid-Western Shandong Peninsula, North China Craton: Insights from Geochronology, Mineralogy, Geochemistry, and Sr-Nd-Hf Isotopes. *Minerals* **2024**, *14*, 1220. <https://doi.org/10.3390/min14121220>.
5. Ouyang, J.; Chen, G.; Yang, L.; Lu, W.; Zhou, Y. Tectonic Evolution of the Hainan Island, South China: Geochronological and Geochemical Constraints from Late Permian to Early Triassic Basalts. *Minerals* **2025**, *15*, 293. <https://doi.org/10.3390/min15030293>.
6. Sun, B.; Wei, X.; Dong, H. Formation Mechanism of Plagioclase–Amphibole and Amphibole–Spinel Symplectites in the Bijigou Layered Intrusion: Insights from Mineralogical and Crystallographic Constraints. *Minerals* **2025**, *15*, 433. <https://doi.org/10.3390/min15050433>.
7. Wang, Y.; Lan, H.; Jin, C.; Zhang, Y. Petrogenesis of Middle Jurassic Syenite–Granite Suites and Early Cretaceous Granites with Associated Enclaves in Southwestern Zhejiang, SE China: Implications for Subduction-Related Tectonic Evolution Beneath Northeastern Cathaysia Block. *Minerals* **2025**, *15*, 474. <https://doi.org/10.3390/min15050474>.
8. Kiray, D.; Cengiz, O. Petrography, Geochemistry, and Magmatic Processes of Oligocene-Miocene Tuzla Volcanics, Biga Peninsula, NW Türkiye. *Minerals* **2026**, *16*, 23. <https://doi.org/10.3390/min16010023>.
9. Khedr, M.Z.; Sayed, M.A.; Ali, S.; Azer, M.K.; Ichiyama, Y.; Takazawa, E.; Kahal, A.Y.; Abdelrahman, K.; Mahdi, A.M. Mineralogy and Geochemistry of Jasperoid Veins in Neoproterozoic Metavolcanics: Evidence of Silicification, Pyritization and Hematization. *Minerals* **2024**, *14*, 647. <https://doi.org/10.3390/min14070647>.
10. de Souza, A.A.; Azzone, R.G.; Chmyz, L.; Tarazona, L.M.C.; de Andrade, F.R.D.; Martins, J.V.; Ruberti, E.; de Barros Gomes, C. Genesis of Fe-Ti(V) Oxide-Rich Rocks by Open-System Evolution of Mafic Alkaline Magmas: The Case of the Ponte Nova Massif, SE Brazil. *Minerals* **2024**, *14*, 724. <https://doi.org/10.3390/min14070724>.
11. Yang, L.; Cai, Y.; Ouyang, J.; Xu, F.; Chen, Y.; Zhou, Y. Mineralogy and Geochemistry of Early Triassic Granite in South China: Insights into Source Region Characteristics and REE Mineralization. *Minerals* **2025**, *15*, 530. <https://doi.org/10.3390/min15050530>.
12. Zhong, Y.; Yuan, Y.; Lu, Y.; Xia, B. Origin and Tectonic Implication of Cenozoic Alkali-Rich Porphyry in the Beiya Au-Polymetallic Deposit, Western Yunnan, China. *Minerals* **2025**, *15*, 531. <https://doi.org/10.3390/min15050531>.
13. Xu, C.; Peng, J.; Gan, J.; Tang, C.; Yin, Z.; Huang, C. Genesis and Mineralization Process of the Lanuoma Sediment-Hosted Pb–Zn Deposit, Sanjiang Metallogenic Belt, Southwestern China: Constraints from Zn, Pb, and S Isotopes. *Minerals* **2026**, *16*, 164. <https://doi.org/10.3390/min16020164>.
14. Du, G.-F.; Ling, X.-Y.; Wang, D.; Zhou, W.-J.; Yang, L.; Lu, Y.-Y.; Zhang, Z.-Z. In Situ Geochemical and Sulfur Isotopic Composition of Pyrites from the Jiepailing Tin–Beryllium Polymetallic Deposit, Southern Hunan Province, China: Implications for Ore-Forming Processes. *Minerals* **2025**, *15*, 312. <https://doi.org/10.3390/min15030312>.
15. Borisova, A. Kinetics of Sulfide Dissolution Controlled by Sulfur Radical Diffusion: Implications for Sulfur Transport and Triggering of Volcanic Eruptions. *Minerals* **2025**, *15*, 989. <https://doi.org/10.3390/min15090989>.
16. Thomas, R.; Rericha, A. Extreme Element Enrichment by the Interaction of Supercritical Fluids from the Mantle with Crustal Rocks. *Minerals* **2025**, *15*, 33. <https://doi.org/10.3390/min15010033>.

References

1. Gazel, E.; Hayes, J.L.; Hoernle, K.; Kelemen, P.; Everson, E.; Holbrook, W.S.; Hauff, F.; van den Bogaard, P.; Vance, E.A.; Chu, S.; et al. Continental crust generated in oceanic arcs. *Nat. Geosci.* **2015**, *8*, 321–327. [CrossRef]
2. Artemieva, I.M.; Shulgin, A. Making and altering the crust: A global perspective on crustal structure and evolution. *Earth Planet. Sci. Lett.* **2019**, *512*, 8–16. [CrossRef]
3. Cawood, P.A. The generation and preservation of continental crust in continental collision zones by accumelting. *Sci. China Earth Sci.* **2025**, *68*, 2746–2749. [CrossRef]
4. Stolper, D.A.; Bucholz, C.E. Neoproterozoic to early Phanerozoic rise in island arc redox state due to deep ocean oxygenation and increased marine sulfate levels. *Proc. Natl. Acad. Sci. USA* **2019**, *116*, 8746–8755. [CrossRef]
5. Clapham, M.E.; Renne, P.R. Flood Basalts and Mass Extinctions. *Annu. Rev. Earth Planet. Sci.* **2019**, *47*, 275–303. [CrossRef]
6. Nadeau, O.; Stix, J.; Williams-Jones, A.E. Links between arc volcanoes and porphyry-epithermal ore deposits. *Geology* **2016**, *44*, 11–14. [CrossRef]
7. Loucks, R.R. Deep entrapment of buoyant magmas by orogenic tectonic stress: Its role in producing continental crust, adakites, and porphyry copper deposits. *Earth-Sci. Rev.* **2021**, *220*, 103744. [CrossRef]
8. Moreira, H.; Storey, C.; Bruand, E.; Darling, J.; Fowler, M.; Cotte, M.; Villalobos-Portillo, E.E.; Parat, F.; Seixas, L.; Philippot, P.; et al. Sub-arc mantle fugacity shifted by sediment recycling across the Great Oxidation Event. *Nat. Geosci.* **2023**, *16*, 922–927. [CrossRef]
9. Hu, Y.; Teng, F.-Z. *Non-Traditional Stable Isotope Geochemistry*, in *Encyclopedia of Geology*, 2nd ed.; Alderton, D., Elias, S.A., Eds.; Academic Press: Oxford, UK, 2021; pp. 114–124.
10. Young, E.D.; Manning, C.E.; Schauble, E.A.; Shahar, A.; Macris, C.A.; Lazar, C.; Jordan, M. High-temperature equilibrium isotope fractionation of non-traditional stable isotopes: Experiments, theory, and applications. *Chem. Geol.* **2015**, *395*, 176–195. [CrossRef]
11. Liu, S.-A.; Li, S.-G. Tracing the Deep Carbon Cycle Using Metal Stable Isotopes: Opportunities and Challenges. *Engineering* **2019**, *5*, 448–457. [CrossRef]
12. Ubide, T.; McKenna, C.A.; Chew, D.M.; Kamber, B.S. High-resolution LA-ICP-MS trace element mapping of igneous minerals: In search of magma histories. *Chem. Geol.* **2015**, *409*, 157–168. [CrossRef]
13. Willbold, M.; Elliott, T. Molybdenum isotope variations in magmatic rocks. *Chem. Geol.* **2017**, *449*, 253–268. [CrossRef]
14. Tian, Y.; Huang, F.; Xu, J.; Li, J.; Zeng, Y.; McCoy-West, A.J. Missing molybdenum and the composition of the continental crust inferred from molybdenum isotopes. *Nat. Commun.* **2025**, *16*, 11436. [CrossRef]
15. Mo, X.; Hou, Z.; Niu, Y.; Dong, G.; Qu, X.; Zhao, Z.; Yang, Z. Mantle contributions to crustal thickening during continental collision: Evidence from Cenozoic igneous rocks in southern Tibet. *Lithos* **2007**, *96*, 225–242. [CrossRef]
16. Huang, F.; Zhang, Z.; Xu, J.; Li, X.; Zeng, Y.; Wang, B.; Li, X.; Xu, R.; Fan, Z.; Tian, Y. Fluid flux in the lithosphere beneath southern Tibet during Neo-Tethyan slab breakoff: Evidence from an appinite–granite suite. *Lithos* **2019**, *344–345*, 324–338. [CrossRef]
17. Huang, F.; Xu, J.F.; Zeng, Y.C.; Chen, J.L.; Wang, B.D.; Yu, H.X.; Chen, L.; Huang, W.L.; Tan, R.Y. Slab Breakoff of the Neo-Tethys Ocean in the Lhasa Terrane Inferred from Contemporaneous Melting of the Mantle and Crust. *Geochem. Geophys. Geosyst.* **2017**, *18*, 4074–4095. [CrossRef]
18. Elliott, T.; Plank, T.; Zindler, A.; White, W.; Bourdon, B. Element transport from slab to volcanic front at the Mariana arc. *J. Geophys. Res. Solid Earth* **1997**, *102*, 14991–15019. [CrossRef]
19. Woodhead, J.D.; Hergt, J.M.; Davidson, J.P.; Eggins, S.M. Hafnium isotope evidence for ‘conservative’ element mobility during subduction zone processes. *Earth Planet. Sci. Lett.* **2001**, *192*, 331–346. [CrossRef]
20. Huang, F.; Rooney, T.O.; Xu, J.-F.; Zeng, Y.-C. Magmatic record of continuous Neo-Tethyan subduction after initial India-Asia collision in the central part of southern Tibet. *GSA Bull.* **2021**, *133*, 1600–1612. [CrossRef]
21. Gómez-Frutos, D.; Castro, A.; Gutiérrez-Alonso, G. Post-collisional batholiths do contribute to continental growth. *Earth Planet. Sci. Lett.* **2023**, *603*, 117978. [CrossRef]
22. Zhang, L.; Huang, F.; Xu, J.; Liu, X.; Yang, X.; Zhang, Z.; Zhang, M.; Zeng, Y.; Zattin, M. Continental crustal growth in the post-collisional setting: Insights from the Late Triassic high-Mg andesites in the eastern Central Asian Orogenic Belt. *GSA Bull.* **2025**, *137*, 1521–1537. [CrossRef]
23. Kimura, J.-I. Modeling chemical geodynamics of subduction zones using the Arc Basalt Simulator version 5. *Geosphere* **2017**, *13*, 992–1025. [CrossRef]
24. Stolz, A.J.; Jochum, K.P.; Spettie, B.; Hofmann, A.W. Fluid- and melt-related enrichment in the subarc mantle: Evidence from Nb/Ta variations in island-arc basalts. *Geology* **1996**, *24*, 587–590. [CrossRef]
25. Cooper, L.B.; Ruscitto, D.M.; Plank, T.; Wallace, P.J.; Syracuse, E.M.; Manning, C.E. Global variations in H₂O/Ce: 1. Slab surface temperatures beneath volcanic arcs. *Geochem. Geophys. Geosyst.* **2012**, *13*. [CrossRef]
26. Chen, W.; Xiong, X.; Takahashi, E. Zircon Solubility in Solute-Rich Supercritical Fluids and Zr Transfer from Slab to Wedge in the Deep Subduction Process. *J. Geophys. Res. Solid Earth* **2021**, *126*, e2021JB021970. [CrossRef]
27. Liu, H.; Xue, Y.-Y.; Wang, K.; Sun, W.-D.; Wang, K. Contributions of slab-derived fluids to ultrapotassic rocks indicated by K isotopes. *Lithos* **2021**, *396–397*, 106202. [CrossRef]

28. Liu, S.-A.; Qu, Y.-R.; Wang, Z.-Z.; Li, M.-L.; Yang, C.; Li, S.-G. The fate of subducting carbon tracked by Mg and Zn isotopes: A review and new perspectives. *Earth-Sci. Rev.* **2022**, *228*, 104010. [CrossRef]
29. Fang, J.; Audétat, A. The effects of pressure, fO_2 , fS_2 and melt composition on the fluid–melt partitioning of Mo: Implications for the Mo-mineralization potential of upper crustal granitic magmas. *Geochim. Cosmochim. Acta* **2022**, *336*, 1–14. [CrossRef]
30. Zheng, Y.; Fu, Q.; Hou, Z.; Yang, Z.; Huang, K.; Wu, C.; Sun, Q. Metallogeny of the northeastern Gangdese Pb–Zn–Ag–Fe–Mo–W polymetallic belt in the Lhasa terrane, southern Tibet. *Ore Geol. Rev.* **2015**, *70*, 510–532. [CrossRef]
31. Hou, Z.Q.; Duan, L.F.; Lu, Y.J.; Zheng, Y.C.; Zhu, D.C.; Yang, Z.M.; Yang, Z.S.; Wang, B.D.; Pei, Y.R.; Zhao, Z.D.; et al. Lithospheric Architecture of the Lhasa Terrane and Its Control on Ore Deposits in the Himalayan-Tibetan Orogen. *Econ. Geol.* **2015**, *110*, 1541–1575. [CrossRef]
32. Lu, Y.J.; Loucks, R.R.; Fiorentini, M.L.; Yang, Z.M.; Hou, Z.Q. Fluid flux melting generated postcollisional high Sr/Y copper ore-forming water-rich magmas in Tibet. *Geology* **2015**, *43*, 583–586. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Zircon, Monazite SHRIMP U-Th-Pb and Quartz Oxygen Isotopic Results from the Higher Himalayan Crystallines (HHC) of the Sikkim Himalayas

Shashank Prabha-Mohan ^{1,2}, Ian S. Williams ³ and Sandeep Singh ^{1,*}¹ Department of Earth Sciences, Indian Institute of Technology, Roorkee 247667, India² Université Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, 63000 Clermont-Ferrand, France; shashank.mohan@uca.fr³ Research School of Earth Sciences, Australian National University, Canberra, ACT 2601, Australia; ian.williams@anu.edu.au

* Correspondence: sandeep.singh@es.iitr.ac.in or san662005@gmail.com

Abstract: Migmatites and partial melts are exposed in both the lower and upper package of the Higher Himalayan Crystallines (HHC) thrust sheet within the Sikkim Himalayas. Zircon monazite and quartz oxygen isotopic ratios from Yumthang Valley, North Sikkim, and Rathong Chuu, West Sikkim, have been used to identify their sources and equilibrium conditions. Monazites show homogeneous growth, whereas zircons show growth rings. U-Th-Pb data on monazite only indicate the latest metamorphic event. However, zircons show metamorphic rim growth between 36 and 24 Ma over their detrital core with trailing growth from 22 Ma to 15 Ma. Pervasive fluids have been interpreted in coeval development during metamorphism, as shown by monazite and zircon c. 30 Ma. The Th/U ratio of zircon is higher and variable with weak residual zoning in the samples from higher elevations. Quartz–metamorphic zircon oxygen fractionation suggests $T_{eq} > 600\text{ }^{\circ}\text{C}$, while quartz–monazite fractionation shows the same or lower temperatures. Multiple sources of melts in the HHC (even along a single valley) have been observed by $\delta^{18}\text{O}$ of 7‰ to 10‰ in zircon and 5‰ to 9‰ in monazite. Zircon and monazite generated in the same rock have similar $\delta^{18}\text{O}$ values. Monazite grown ~20 Ma in the lower elevation sample had a low $\delta^{18}\text{O}$, suggesting interaction with an external fluid.

Keywords: Sikkim Himalayas; Higher Himalayan Crystallines (HHC); oxygen isotopic compositions; zircon; monazite; mantle–crust interaction

1. Introduction

The Himalayan mountain range extends over a lateral length of more than 2400 km, confined between two syntaxial bends—Nanga Parbat in the west to Namche Barua in the east—with evident along-strike consistency in lithotectonic units as well as the tectonic boundaries (Figure 1). The Himalayan mountain chain evolved due to a continent–continent collision of the indenting Indian plate with the Eurasian plate not later than 57 Ma ago [1,2], whereas, based on various popular models of the evolution of the Himalayas, it is [3] interpreted that onset took place 59 ± 1 Ma ago.

Post-collisional metamorphism is prevalent in both the Indian Plate and the Eurasian Plate [4]. It starts with either blueschist facies metamorphism ([5] and references therein) or eclogite facies metamorphism ([1,6]; references therein) related to subduction tectonics. It is followed by regional Barrovian metamorphism in the Higher Himalayan Crystallines (HHC), which is characterized by inverted metamorphism ([6–10] and references therein) along with related main Himalayan deformational events ([8,11,12] and references therein). The Himalayan orogeny also encountered magmatism with crustal melt formation in the form of in situ melt or widespread anatectic mid-crustal melt generated from an extensive

partial melting of the migmatite zone ([13–17] and references therein). During this orogenic activity, a gap in the sedimentary records has also been interpreted by various researchers to be from after the Middle Eocene [18–23].

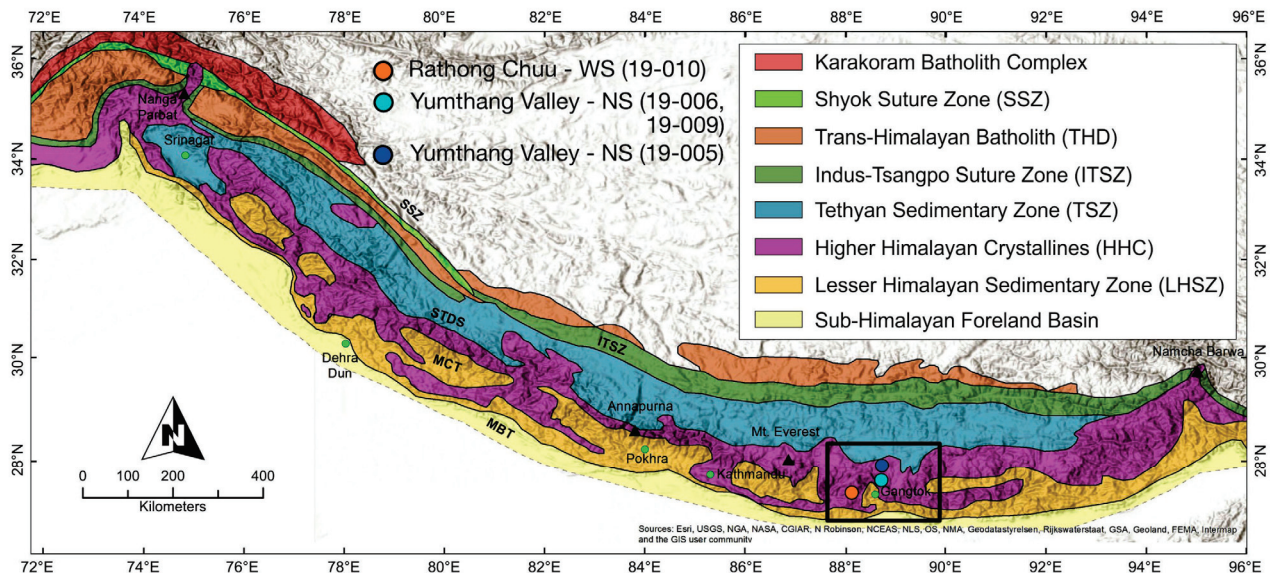


Figure 1. Geological sketch map of the Himalayas (after Singh, 2019) showing the locations where the samples were obtained. The age of the various lithotectonic units from south to north are as follows: Sub-Himalayan Foreland Basin (Neogene); Lesser Himalayan Sedimentary Zone (Late Proterozoic to Eocene); Higher Himalayan Crystallines (Proterozoic); Tethyan Sedimentary Zone (Neoproterozoic to Early Eocene); Indus Tsangpo Suture Zone (Cretaceous); Trans-Himalayan Himalayan Batholith (Early Cretaceous to Paleocene); Shoyk Suture Zone (Lower Cretaceous to Paleogene); and Karakoram Batholith Complex (Cretaceous to Eocene).

Post-collisional crustal shortening was accommodated by east–west-trending tectonic boundaries, such as the Main Frontal Thrust (MFT), Main Boundary Thrust (MBT), Main Central Thrust (MCT), South Tibetan Detachment System (STDS), Indo-Tsangpo Suture Zone (ITSZ), and their splays ([7,9]; references therein). The Higher Himalayan Crystallines (HHC), which are exposed between the MCT and the STDS, are about 15–20 km thrust sheet packages of rocks along the mountain chain and are composed of Barrovian metamorphic rocks mapped as one large unit [3,6,7,9,10,16,24]. These rocks represent the crystallines of the Greater Indian domain [3]. They are separated from the supracrustal portion, i.e., the Lesser Himalayan Sedimentary Sequence, by the MCT in the south and from the Tethyan Sedimentary Sequence by the STDS in the north [16,24–26].

Migmatite has been a source of both in situ and anatectic melt within the HHC. Migmatites are heterogeneous silicate rocks with alternating leucosome (lighter layers containing quartz, feldspar, and muscovite) resulting from partial melting and segregation of melt from the partially molten surroundings and melanosome (darker layers comprising biotite and other dark-colored minerals–residuum) layers ([27] and references therein). Migmatites of the Himalayas are mainly present within the HHC and are concentrated in a very narrow zone [16,17,24] in the NW Himalayas. However, in the eastern Himalayas, they are present from the base of the HHC to the top between the MCT and the STDS [16,17,28–35]. Their heterogeneity is evident at every scale, from a microscope to a large outcrop.

The dominant accessory phases of migmatites and granites are monazite, zircon, apatite, and minor xenotime. Zircon chronometry with monazite is a powerful tool for the temporal reconstruction of the subsolidus and anatectic process in metamorphic terrain and has been attempted using U–Th–Pb geochronology with secondary ion mass spectrometry (SIMS) in the Himalayan context [1,2,6,24,26,34,36–50]. Unlike zircon, mon-

azites show little inheritance except in a few cases [50,51] involving high-temperature diffusion that can happen close to the blocking temperature [52,53]. Zircon is an ideal chronometer for Himalayan metamorphic rocks, as they are very reactive during Barrovian metamorphism and possess the ability to preserve their chemical and isotopic composition. Researchers have also observed a discrete age population in zircon, whereas monazite dates are smoothly spread out [54]. Monazite has low solubility in the peraluminous melt [55,56] and is expected to undergo some dissolution during the dehydration melting of a metasedimentary rock and some new growth during melt crystallization [57,58]. Monazite can be consumed and produced again in a solid-state reaction [59,60]. Zircon has been known to grow in partial melt conditions [24]. Most importantly, the robust U-Pb system in zircon can survive many geological processes, including erosion, deformation, crustal anatexis, and high-grade metamorphism [61,62], and hence, can provide us with a more extended and comprehensive thermal history than monazites, which get reset during subsequent metamorphism/thermal events.

The oxygen isotopic compositions of zircon, monazite, and quartz from all the samples were measured in situ using the SHRIMP, and the zircon and monazite were also dated using the U-Th-Pb technique. The temporal evolution of oxygen isotopic composition in zircon cores and rims generally reflects the oxygen isotopic composition of the material or the environment in which they crystallized. A mantle source, a sediment-derived source, or maybe even a mixed source as well as recycling of surface-derived material/fluid into melt within the crust can be interpreted from oxygen isotopic compositions [63–65]. Many studies have proven this technique to be a reliable indicator of the source [62,64,66–68]. Combined with O isotopic analyses of quartz, zircon, and monazite, the O isotopic fractionation between the mineral pairs (Qtz-Zrn and Qtz-Mnz; [69]) gives us a first-order indication of the temperature of the final metamorphism.

This work incorporates zircon and monazite U-Th-Pb age determination along with oxygen isotopic studies on zircon, monazite, and quartz from the samples of migmatites from Yumthang Valley, North Sikkim, and Rathong Chuu, West Sikkim, in order to understand the mantle–crust interaction during Himalayan metamorphism.

2. Geological Framework

The Sikkim Himalaya are sandwiched between Bhutan (east) and Nepal (west) and are characterized by a typical mushroom-shaped window structure that is not closed on all sides [29,30,70,71]. The reason for the half-window structure appears to be the interaction of tectonic structures and erosion, resulting in a complex mushroom-shaped window (Figure 2). The complex structures have evolved due to the straight east–west trending Main Boundary Thrust (MBT) separating Siwalik rocks from the Lesser Himalayan sedimentary (LHS) sequence. At the same time, the Main Central Thrust (MCT), irrespective of its locational controversy ([72] and references therein), shows cross-folding and affects the outcrop pattern in the Sikkim Himalaya (Figure 2).

The present work is not meant to undertake mapping but to look at the relationship between migmatites and in situ melt generation with collision-related tourmaline-bearing leucogranite in the Higher Himalayan Crystallines (HHC). The HHC is a 15–20 km thick sequence of metamorphic rocks exposed along the entire Himalayas with inverted metamorphic sequences [7,9,16,73] and has been mapped as one unit. However, in the Sikkim Himalaya, the HHC has been exposed as a ~40 km-thick section in northern and a ~20 km-wide section in western Sikkim [32]. Our field observations indicate that, like the HHC of the Northwest (NW) Himalayas, the Sikkim Himalayas also have two packages, i.e., a basal package made up of Kangchenjunga gneiss/Darjeeling gneiss (equivalent to the Munisari Formation of the NW Himalayas) comprised of banded/streaky migmatite, kyanite-staurolite-sillimanite bearing biotite augen gneiss and sillimanite granite gneiss ([71] and our observations). This basal package is overlain by the Upper Chungthang Formation (equivalent to the Vaikrita Group of the NW Himalayas) and is comprised of garnet-kyanite-sillimanite biotite schist, migmatites, psammites, calc-silicate and intrusive tourmaline-

bearing granite ([71] and our observations—also see Figure 2). This has also been mapped as a suite of amphibolite to granulite facies metamorphic rocks [30,32,34,74–76] exposed between the South Tibetan Detachment System (STDS) and the MCT. The striking difference between the NW Himalayas and the Sikkim Himalayas is the presence of a migmatite zone. In the NW Himalayas, migmatites are present in a very narrow zone in an upper package of the HHC [24]. Meanwhile, in the Sikkim Himalayas, they are exposed starting close to the MCT within the basal package. These rocks have been further intruded by leucogranites emplaced between 23 and 12 Ma [16,17,31,32,34,76]. These ages have been constrained through zircon [34], monazite [31,34,35], Sm–Nd [32], and Lu–Hf aging on garnet [77].

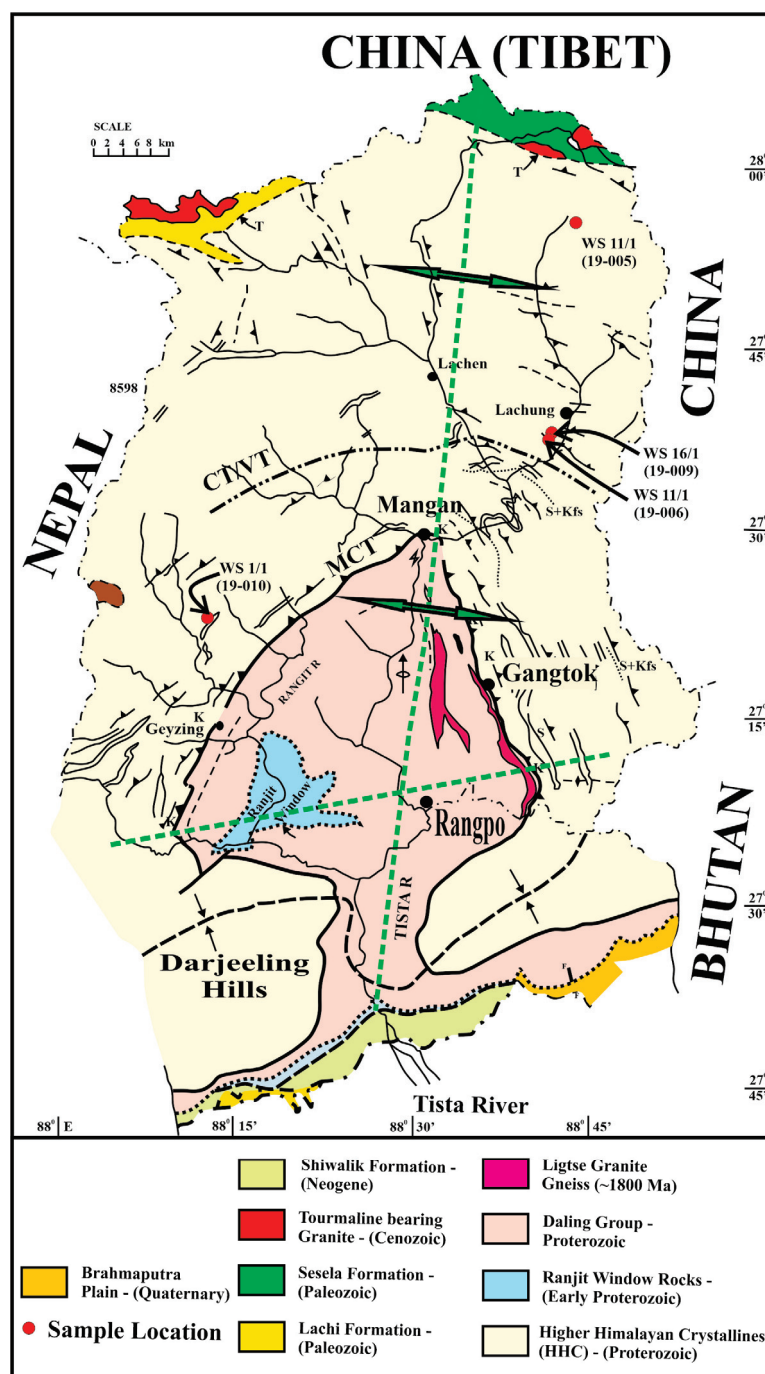


Figure 2. Geological sketch map of Sikkim marked with the sample locations after GSI Misc. Publication, 2012, and our own observations. CT/VT—Chungthang Thrust/Vaikrita Thrust; MCT—Main Central Thrust.

3. Analytical Techniques

Sample Selection: Four samples have been collected from the Sikkim Himalayas (Figure 2), with three samples—19-005 ($27^{\circ}55'38.3''$ N, $88^{\circ}43'50.8''$ E), 19-006 ($27^{\circ}37'44.8''$ N, $88^{\circ}41'20.6''$ E), and 19-009 ($27^{\circ}37'23.5''$ N, $88^{\circ}41'20.6''$ E)—having been collected along a N–S traverse of the Yumthang Valley in North Sikkim, mainly from the upper package of the HHC, and one sample—19-010 ($27^{\circ}22'07.7''$ N, $88^{\circ}12'22.0''$ E)—from West Sikkim that was collected a few kilometers down the road from Yuksom, by the Rathong Chuu river belonging to the lower package of the HHC.

Field and hand specimen observations: Migmatites from the upper package show the development of two melting phases of stromatic migmatites with the presence of kyanite (Figure 3a). At places, migmatites show distinct leucosome and melanosome layers (Figure 3b,e) or emplacement along extensional fabric both in ductile regime (Figure 3c) and brittle regime (Figure 3d) or in situ melt pods (Figure 3a,f). The tourmaline-bearing leucogranite and country rocks have very sharp contacts (Figure 3e).

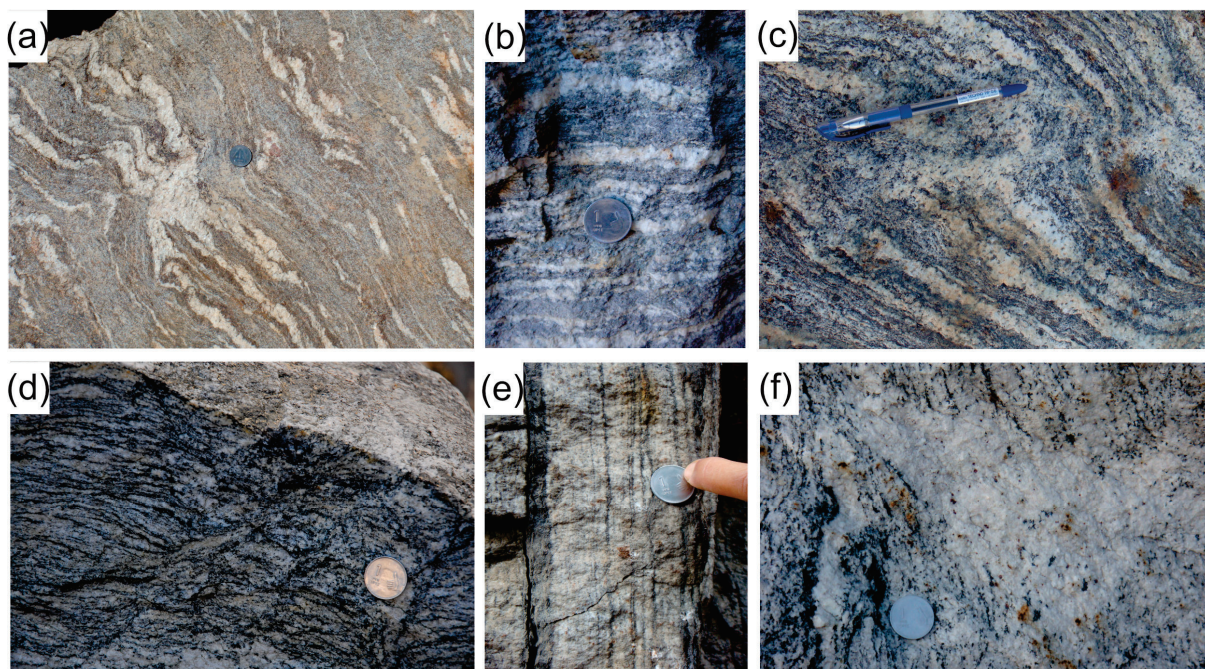


Figure 3. Field photographs showing (a) the development of in situ melt in stromatic migmatite and kyanite presence within the two melting phases of the stromatic migmatite zone; (b) development of melanosome and leucosome in migmatite; (c) migmatite with leucosome and melanosome along with in situ melt generation along the extensional fabric in a ductile zone regime; (d) migmatite with leucosome and melanosome along with in situ melt generation along the extensional fabric in a brittle zone regime; (e) sharp contact between leucogranite and country rock; (f) development of in situ melt in the form of pods within the migmatite zone.

North Sikkim 19-005: In the hand specimen, schistose banding is observed with alternating layers of leucosome (mainly quartz and plagioclase) and melanosome (mostly biotite with other dark minerals). The melanosome is more prominent, accounting for about 70% of the volume. Pink garnet porphyroblasts (up to 5 mm) can be observed at the hand specimen scale.

North Sikkim 19-006: At the hand specimen scale, schistose banding is observed with alternating layers of light (mainly quartz and plagioclase) and dark (mostly biotite with other dark minerals) layers, with the light layers being the most prominent, accounting for about 80% of the volume. Garnet porphyroblasts (up to 5 mm) can be observed at the hand specimen scale. The sample appears to be a highly metamorphosed gneiss.

North Sikkim 19-009: In the hand specimen, gneissic banding is observed with alternating layers of light (mainly quartz and plagioclase) and dark (mostly biotite with other dark minerals) layers, with the lighter layers being more prominent, accounting for about 80% of the volume. Unlike the other samples, this one does not contain any visible garnet porphyroblasts.

West Sikkim 19-010: In the hand specimen, gneissic banding is observed with alternating layers of light (mainly quartz and plagioclase) and dark (mostly biotite with other dark minerals) layers, with both the layers being present roughly in similar amounts and possessing approximately the a thickness of ~5 mm. Plenty of garnet porphyroblasts (up to 5 mm) are also observed.

Petrographic Description: *North Sikkim 19-005:* The sample under the microscope shows the presence of quartz, K-feldspar, plagioclase feldspar, biotite, garnet, and acicular sillimanite as the dominant mineral constituents, with zircon and monazite occurring as accessory phases along with the development of melt (Figure 4a,b). The plagioclase is coarse grained and exhibits polysynthetic twinning. The garnet occurs as porphyroblasts and contains a variety of inclusions, mostly accessory minerals such as monazite. A myrmekitic texture is also observed at certain locations, with intergrowths of quartz in plagioclase. The quartz is relatively coarse grained and contains some inclusions, most likely fluid. The biotite crystals are generally lath shaped and are similarly oriented. The zircon crystals are very fine grained and are observed to be rounded or slightly elongated (Figure 4a). All of the crystals present are either anhedral or, in some cases, subhedral. Patches of melt observed in thin sections suggest that melting was driven by biotite dehydration, as evidenced by the visible breakdown of most of the visible grains of biotite, giving rise to fluids in the pre-existing rock. The quartz shows signs of melting and later recrystallization, as relict grains of similarly oriented quartz are seen within larger quartz crystals.

North Sikkim 19-006: The thin section indicates quartz, K-feldspar, plagioclase feldspar, and biotite as the dominant mineral constituents with zircon and monazite occurring as accessory phases and melts present with plagioclase feldspar and deformed boundary of quartz (Figure 4c,d). The quartz is very coarse grained, as are the K-feldspar and plagioclase, which exhibit polysynthetic twinning. The biotite occurrence is limited, and all of the crystals are similarly oriented. A rare staurolite with inclusions of quartz is also observed. Grains are mainly subhedral to anhedral in many cases. Relict grains of similarly oriented quartz are seen within larger grains of both quartz and plagioclase, suggesting melting and recrystallization. In some of the plagioclase, patches of melt are also observed.

North Sikkim 19-009: The thin section shows quartz, K-feldspar, plagioclase feldspar, biotite, and muscovite, which are observed to be the dominant mineral constituents. Zircon and monazite occur as accessory phases. The quartz is very coarse grained and anhedral, and on occasion, it contains inclusions. The K-feldspar ranges from medium to coarse grained and is mostly subhedral. Plagioclase is coarse grained and anhedral and displays polysynthetic twinning. Biotite and muscovite occur as similarly oriented lath-shaped crystals, and signs of alteration along cleavage planes are evident in the muscovite. There are no signs of melting or other unique textures, the significance of which is discussed later on in the results.

West Sikkim 19-010: Under microscope, quartz, K-feldspar, plagioclase feldspar, biotite, and garnets are present as major constituents. Zircon and monazite occur as accessory phases. The garnet occurs as porphyroblasts and contains a variety of mineral inclusions such as biotite and feldspars along with minor amounts of monazite and zircon. Plagioclase displays polysynthetic twinning. A myrmekitic texture is seen in the K-feldspar at its boundary with the quartz crystals. Excluding the quartz and feldspars occurring in the myrmekite, they are present as coarse-grained, anhedral crystals, often containing large mineral inclusions of biotite, feldspar, or quartz.

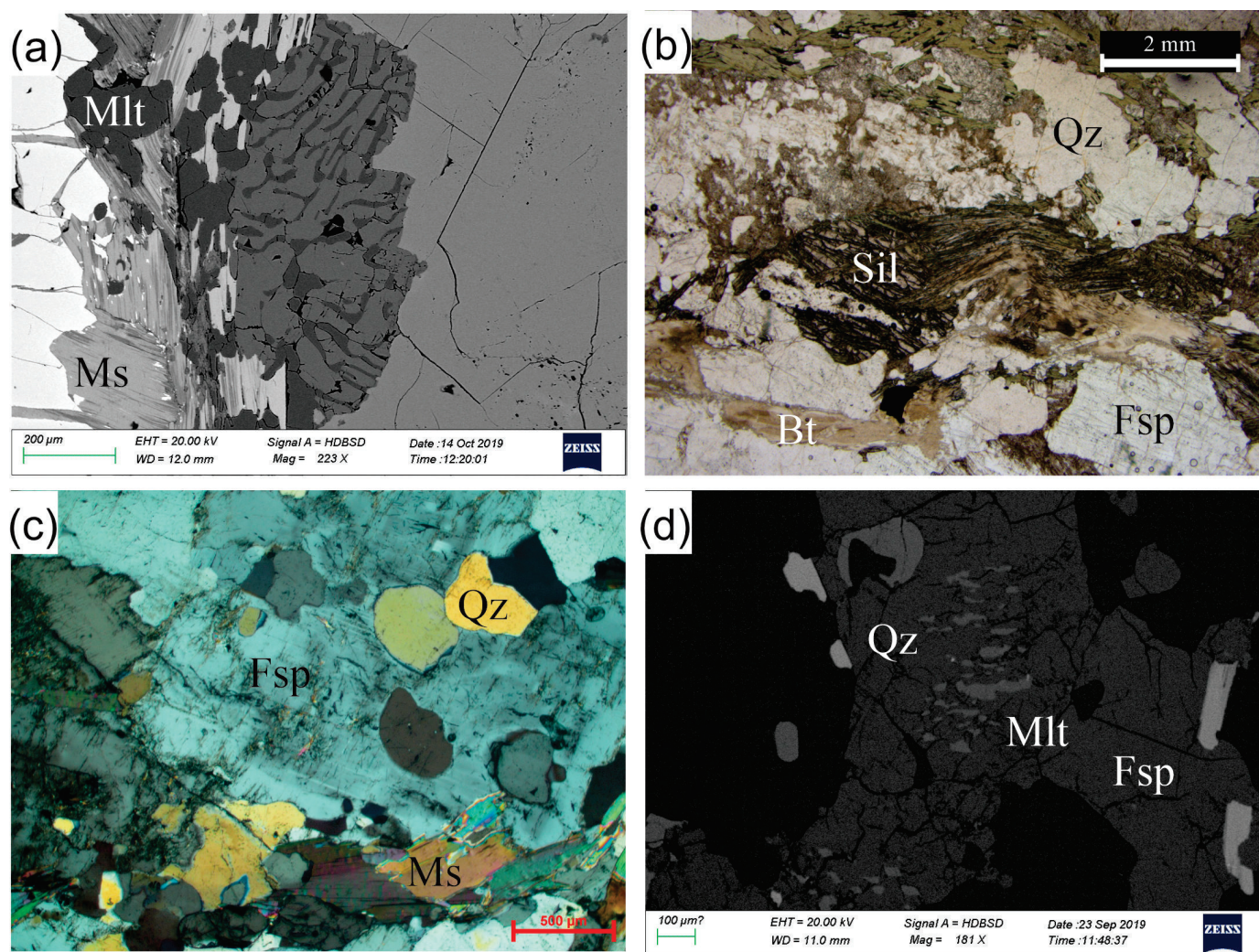


Figure 4. (a) Backscattered electrons (BSE) image of 19-005 showing the development of melt; (b) sample 19-005 contains quartz + K-feldspar + plagioclase feldspar + biotite + garnet + sillimanite (fibrolite) + (zircon + monazite) + melt; (c) sample 19-006 contains quartz + K-feldspar + plagioclase feldspar + muscovite + melt. (d) Melts are present within plagioclase feldspar and defused boundaries of quartz in sample 19-006.

Isotopic Studies: Zircon, monazite, and quartz were separated from four samples—19-005, 19-006, 19-009, and 19-010—at the Research School of Earth Sciences, Australian National University, using optimized techniques designed to avoid trace mineral cross-contamination. About 350 g of rock was chipped for each sample, and the chips were cleaned ultrasonically in water and then crushed to minus 250 μm in a ring mill. After the powder had been deslimed in running water, heavy minerals were concentrated using tetrabromoethane (2.96 g/cc) followed by methylene iodide (3.3 g/cc). Afterward, a handheld magnet was used to remove the magnetic portions followed by a Frantz magnetic barrier separator. Further, monazite and zircon concentrates were separated using a binocular microscope. Quartz was extracted from the low-density fraction.

The sample yielded a large number of zircon and monazite grains that were hand-picked for SHRIMP analysis. Over 300 grains of zircon per sample were selected at random and mounted in a 25 mm epoxy disc with zircon standards SL13 ($U = 238$ ppm), Temora 2 ($^{206}\text{Pb}/^{238}\text{U} = 0.06679$; [78]), and R33 ($\delta^{18}\text{O} = +5.55\text{‰}$; [64]). About 20 high-quality monazite grains (unbroken and free of large inclusions) were selected per sample and mounted in a 25 mm epoxy disc with monazite standard 44069 ($U \approx 2100$ ppm,

$^{206}\text{Pb}/^{238}\text{U} = 0.06813 \text{ Ma}$; [79], $\delta^{18}\text{O} = +7.67\text{‰}$; [80]). A variety of quartz grains were mounted in a 25 mm epoxy disc with quartz standard NBS 28 ($\delta^{18}\text{O} = +9.2\text{‰}$; [81]).

The mounts were first ground using 1200-grade SiC paper to expose the grains' centers, then they were polished using 3 and 1 μm diamond paste, respectively. They were then photographed at high magnification in transmitted and normal reflected light. The zircon mount was also imaged by cathodoluminescence (CL) using a JEOL JSM-6610A SEM fitted with a Robinson CL detector. Prior to the U-Th-Pb isotopic analysis, the zircon and monazite mounts were thoroughly cleaned using petroleum spirit, warm RBS35 detergent solution, and Millipore water. Using a Leica EM ACE600 coater, they were then cleaned by glow discharge and coated with $\sim 10 \text{ nm}$ of high-purity Au. Before O isotopic analysis, the Au was removed, and the mount was recleaned and coated with $\sim 12 \text{ nm}$ of high-purity Al. The quartz mount was also coated with high-purity Al.

The zircons were analyzed for U-Th-Pb isotopes using the SHRIMP IIe at Geoscience Australia, Canberra, and a procedure based on that described by [82]. In brief, a $\sim 2 \text{ nA}$, 10 kV primary beam of negative O_2 ions was focused on a probe with a $\sim 20 \mu\text{m}$ diameter. Positive secondary ions were extracted from the sample at 10 kV. The Zr, Pb, U, and Th atomic and molecular species of interest were analyzed at ~ 5000 mass resolution using a single ETP electron multiplier and magnetic peak switching. The Pb isotopic composition was measured directly, with no correction for mass-dependent isotopic mass fractionation required. Interelement fractionation was corrected using Temora 2 and a Pb/U-UO/U power law calibration equation [83]. Pb, U, and Th concentrations were measured relative to SL13. Common Pb corrections were made using ^{204}Pb or ^{207}Pb , depending on the zircon age, and a Pb isotopic composition commensurate with the age of each grain (Cumming and Richards, 1975 [84]). Uncertainties in the plots and data table are 1σ -precision estimates. Uncertainties in the calculated mean ages are 95% confidence limits (1σ). Ages were calculated using the constants recommended by the IUGS Subcommittee in [85].

The monazites were analyzed for U-Th-Pb isotopes using the SHRIMP II at the Research School of Earth Sciences, Australian National University, Canberra, and a similar procedure, except that moderate energy filtering was used to remove a molecular isobaric interference with ^{204}Pb , and Pb/U and Pb/Th were calibrated against 44069 independently using Pb/U-UO/U and Pb/Th-ThO/Th, respectively.

Prior to the O isotopic analysis, the zircon and monazite mounts were polished to remove any O implanted during the U-Th-Pb dating. The O analyses were then positioned as close as possible to the locations of the dated spots. The oxygen isotopic compositions of zircon, monazite, and quartz were measured using the ANU SHRIMP II and a procedure based on that described by [86]. In brief, a $\sim 3 \text{ nA}$, 15 kV beam of positive Cs ions was focused on a probe $\sim 25 \mu\text{m}$ diameter. Negative O secondary ions were extracted at 10 kV, mass separated at $\sim 3000 \text{ R}$, and measured in current mode using multiple collectors equipped with dual Faraday cups [resistors $10^{11} \Omega$ (^{16}O), $10^{12} \Omega$ (^{18}O)]. Charge on the sample surface was neutralized using a 1.2 kV focused electron beam. Each analysis consisted of 2 min preconditioning, during which electrometer baselines were measured, followed by optimization of the beam steering and $6 \times 20 \text{ s}$ measurements of $^{18}\text{O}/^{16}\text{O}$, resulting in a precision of $\sim 0.1\text{‰}$ s.e. (^{16}O 1.7–2.1 GHz). Corrections for electron-induced secondary ion emission (EISIE) were made based on EISIE measurements before and after each analysis. Isotopic fractionation was monitored, and corrections were made using analyses of matrix-matched standards (zircon R33, monazite 44069, and quartz NBS 28) throughout the analytical session.

4. Internal Structure of Zircon and Monazite

4.1. North Sikkim 19-005

The zircon grains are generally smaller than $100 \mu\text{m}$ and rounded (Figure 5a). Almost all of the zircons from this sample have detrital cores that are unzoned or exhibit banded, sector, or concentric zoning [87]. All zircon crystals have at least one layer that can be made out to be metamorphic overgrowth. Many have 2–3 discernible concentric layers with

varying shades of grey, with greyness decreasing with age (Figure 5a). The metamorphic overgrowths can be observed in many grains and seem to have caused deep embayment in the zircon and, in some cases, have affected the entire crystal leaving just a tiny remnant of the core. This suggests solid-state recrystallization.

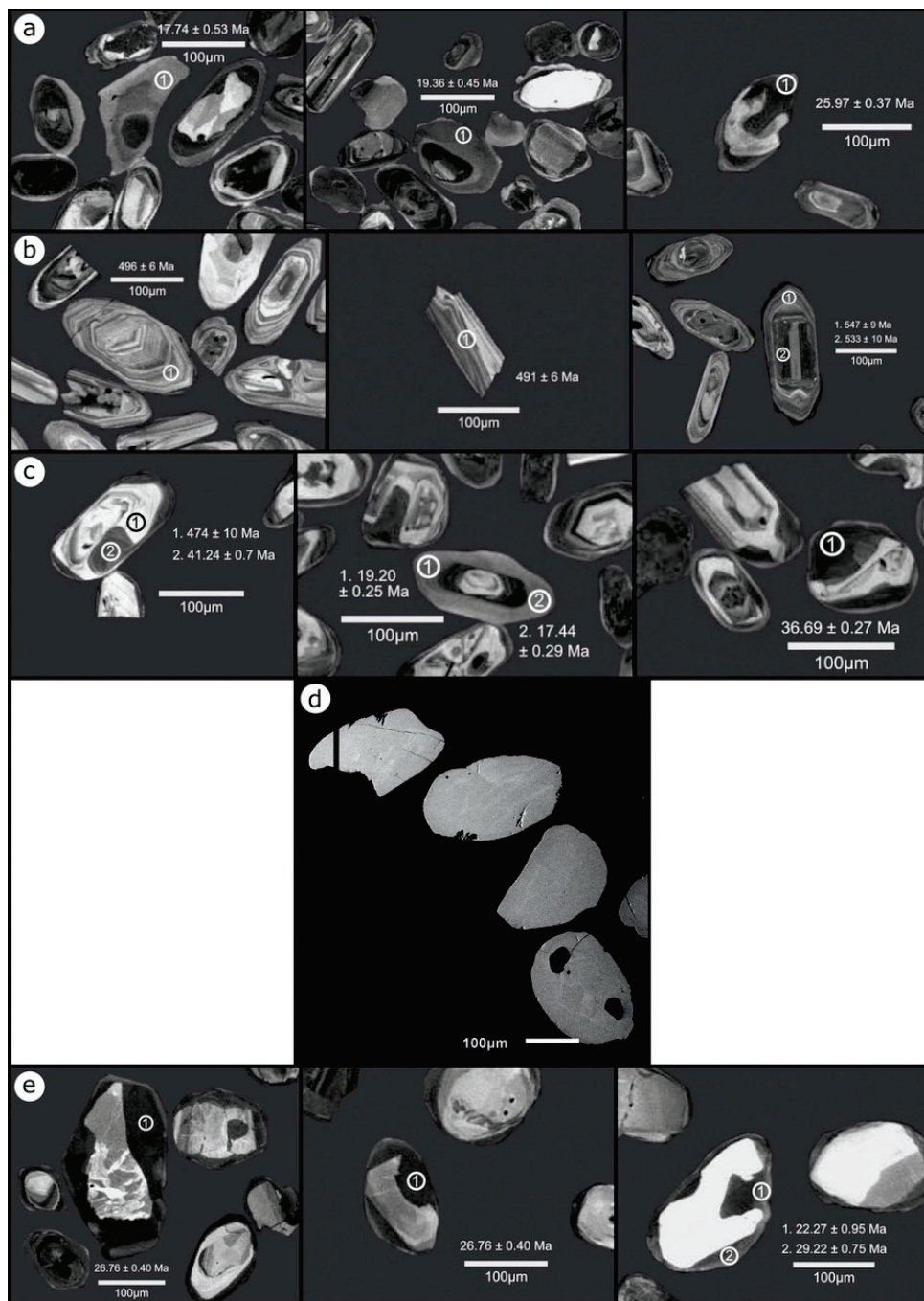


Figure 5. Cathodoluminescence images of selected zircon crystals representative of those dated and a BSE image of one of the monazite crystals dated. Circles indicate the location of SHRIMP analyses and are 20 μm in diameter. Numbers indicate dates with 1σ uncertainties. (a)—19-005 Zircon from North Sikkim, (b)—19-006 Zircon from North Sikkim, (c)—19-009 Zircon from North Sikkim, (d)—19-009 Monazite from North Sikkim, (e)—19-010 Zircon from West Sikkim.

The monazite grains are medium to coarse grained (50–250 μm), roughly equant, moderately angular, subhedral, pale yellowish-green crystals. About 20% of the crystals contain fine inclusions. The grains were uniform and displayed no zoning in BSE images.

4.2. North Sikkim 19-006

This sample was composed of entirely concentrically zoned igneous zircons with a very thin 1 to 2 μm overgrowth (assumed to be metamorphic) and detrital cores that are unzoned or exhibited banded, sector, or concentric zoning (Figure 5b). The grains are elongated and are 100 μm or more in length.

The monazite grains are medium grained (100–150 μm), roughly equant, mostly rounded, subhedral, brownish crystals, with fine- to medium-sized inclusions. The grains were uniform and displayed no zoning in BSE images.

4.3. North Sikkim 19-009

Zircon from this sample represents multiple zones (Figure 5c). It comprises the innermost unzoned detrital component followed by a concentric-zoned igneous component from the Cambro-Ordovician. This is then followed by at least two generations of thick, metamorphic overgrowths that are distinguished by a grey CL response. The younger overgrowths are a lighter grey as compared to the older overgrowths. Unlike sample 19-005, the zircon grains are not embayed by the younger metamorphic overgrowths, suggesting growth in the presence of a metamorphic fluid. The grains range in size from 30 μm up to 200 μm and vary in shape from round to elongated.

The monazite grains are medium to coarse grained (80–200 μm), equant, rounded, subhedral to euhedral, pale green crystals. About half of the crystals contain fine to rather large inclusions of what appears to be fluid in most cases and/or some opaque minerals observed with a transmitted light microscope. The grains are not uniform, and in the BSE images, faint zoning in some of the grains is evident (Figure 5d).

4.4. West Sikkim 19-010

Zircon from this sample consists of detrital zircon with at least two generations of concentric metamorphic overgrowths (Figure 5e). The detrital cores are unzoned or exhibit banded, sector, or concentric zoning. The younger growth is a lighter shade of grey as compared to the older ones. The grains range from about 50 μm up to 200 μm in size and are either rounded or slightly elongated (Figure 5e).

The monazite grains are medium to coarse grained (50–250 μm), approximately equant, moderately angular, anhedral, pale green crystals. Roughly 20% of the crystals contain fine- to medium-sized inclusions of fluid and/or transparent minerals, as observed with a transmitted light microscope. The grains appear to be fragments of larger crystals. In BSE images, the grains are uniform and display no zoning.

5. Results of the Zircon Dating

5.1. Protolith

The dates are based on radiogenic $^{206}\text{Pb}/^{238}\text{U}$ for cores < 1.2 Ga and on radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ for cores > 1.2 Ga or discordant analyses. The detrital component of zircon from the Sikkim Himalayas shows a similar result as that characterized in the NW Himalayas [26,62,88]. Zircon from the northern Sikkim samples marks the maximum age of deposition of the upper package to be up to 500 Ma. However, the zircon population (19-010) of the lower package lacks a zircon component lower than Neoproterozoic time (Figure 6). The data for all of the detrital measurements have been provided in the Supplementary Materials Tables S1–S4 and the concordia diagram presented in Supplementary Figure S1a–d.

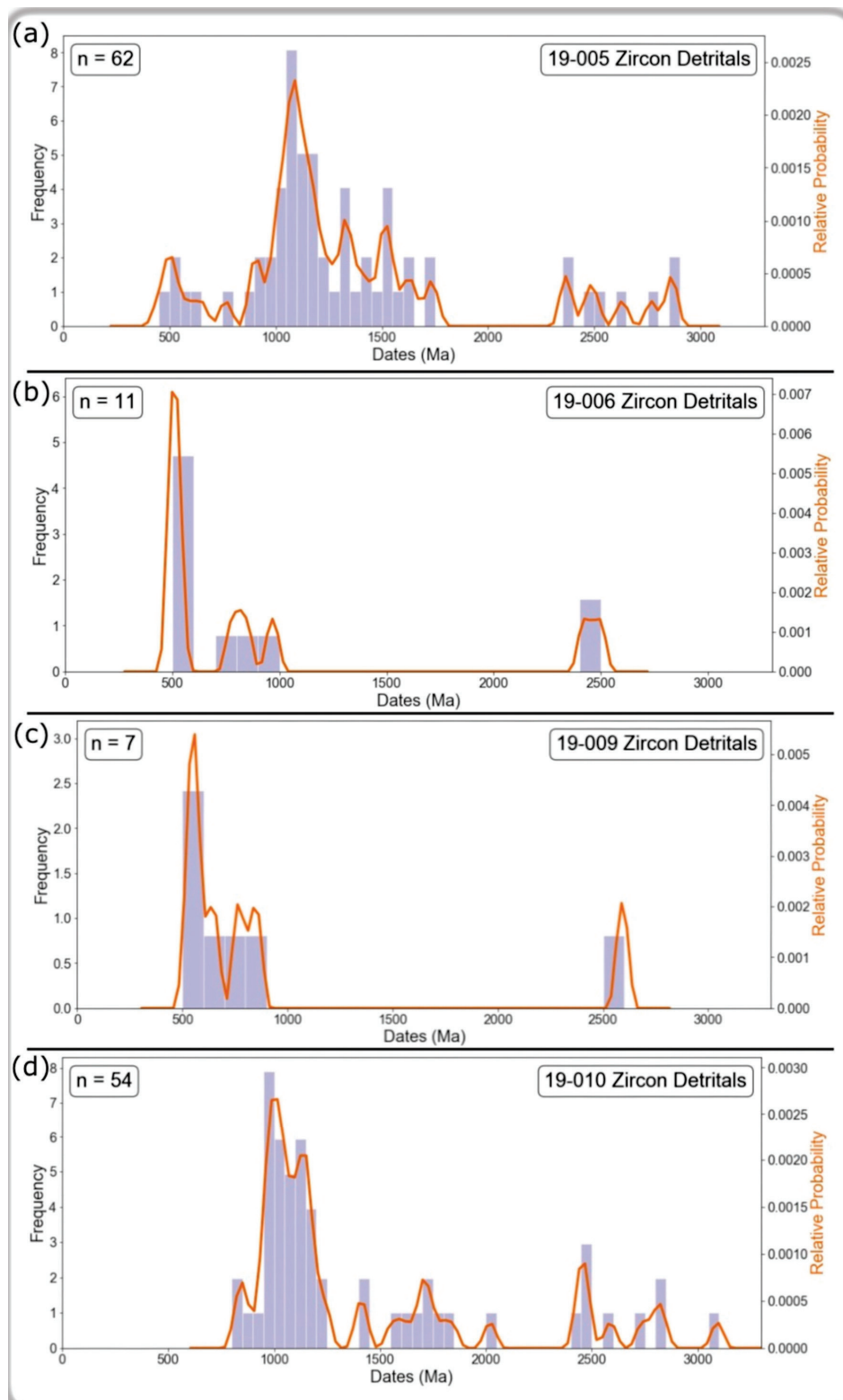


Figure 6. (a) Histogram and cumulative probability distribution curves of detrital zircon measurements (bin size 50 Ma) for the northernmost sample, WS 11/1 (19-006), part of the upper thrust package of the HHC. (b) Histogram and cumulative probability distribution curves of detrital zircon measurements (bin size 100 Ma) for the northernmost sample, WS 15/1 (19-006), part of the upper thrust package of the HHC. (c) Histogram and cumulative probability distribution curves of detrital zircon measurements (bin size 100 Ma) for the northernmost sample, WS 16/1 (19-009), part of the

upper thrust package of the HHC. (d) Histogram and cumulative probability distribution curves of detrital zircon measurements (bin size 50 Ma) for the northernmost sample, WS 1/1 (19-010), part of the lower thrust package of the HHC. Analyses are listed in Supplementary Materials Tables S1–S4 and the concordia diagram presented in Supplementary Figure S1a–d.

5.1.1. North Sikkim 19-005

A total of 62 analyses were carried out, with the youngest detrital age group measured to be c. 500 Ma (8% of all cores). Older prominent groups include some at c. 1200 Ma (23%) and c. 1600 Ma (13%), along with a few analyses that are as old as c. 2800 Ma (5%) (Figure 6a).

5.1.2. North Sikkim 19-006

Over 50% of the measurements on this sample indicate a c. 500 Ma group (6 out of 11 cores), consistent with the sample mentioned above. The oldest analyses are c. 2400 Ma (Figure 6b).

5.1.3. North Sikkim 19-009

Even with just seven measurements on this sample, we still get a clear indication that the youngest detrital components are around c. 500 Ma (3 out of 7 cores), with the oldest ones being c. 2500 Ma. This is consistent with all the other samples from North Sikkim and those of the NW Himalayas (Figure 6c), and marks the maximum age of deposition for the region at ~500 Ma.

5.1.4. West Sikkim 19-010

With a total of 54 measurements on this sample, most of the dates (57%) lie in the range 820–1240 Ma. The youngest detrital component is from c. 800 Ma. Also, clear evidence of groups is present at c. 1100 Ma (27% of all cores), c. 1700 Ma (9%), and c. 2500 Ma (7%). The oldest measurement on this sample is c. 3100 Ma (Figure 6d). The West Sikkim sample lacks the c. 500 Ma component in its detrital suite, suggesting its accretion from a different terrane during the Phanerozoic time. Assuming no significant lead loss, the maximum age of deposition of sediments from this sample is ~800 Ma.

5.2. Igneous Ages

Like the NW Himalayas, which display widespread Cambro-Ordovician magmatism marked by the emplacement of a chain of granitic plutons within the HHC [15,89], some of our samples display evidence of a Cambro-Ordovician magmatic event, with well-established outcrops of granite occurring near the MCT (Chungthang granite). Only two samples have igneous zircon populations of Cambro-Ordovician age (Figure 7).

North Sikkim 19-006: All 11 analyses carried out are concordant or within analytical uncertainty. The $^{206}\text{Pb}/^{238}\text{U}$ dates range from ~441 to 512 Ma. The analyses fall into one main group at 505.5 ± 4.7 Ma ($n = 10$) (Figure 7a—Supplementary Materials Table S2) with a Th/U of 0.0586 to 0.8209.

North Sikkim 19-009: All 11 analyses carried out are concordant or within analytical uncertainty. The $^{206}\text{Pb}/^{238}\text{U}$ dates range from ~451 to 506 Ma. The analyses fall into one main group at 491.6 ± 3.2 Ma ($n = 20$) (Figure 7c—Supplementary Materials Table S3) with Th/U values ranging from 0.01089 to 1.3869, indicative of primary magmatic origin.

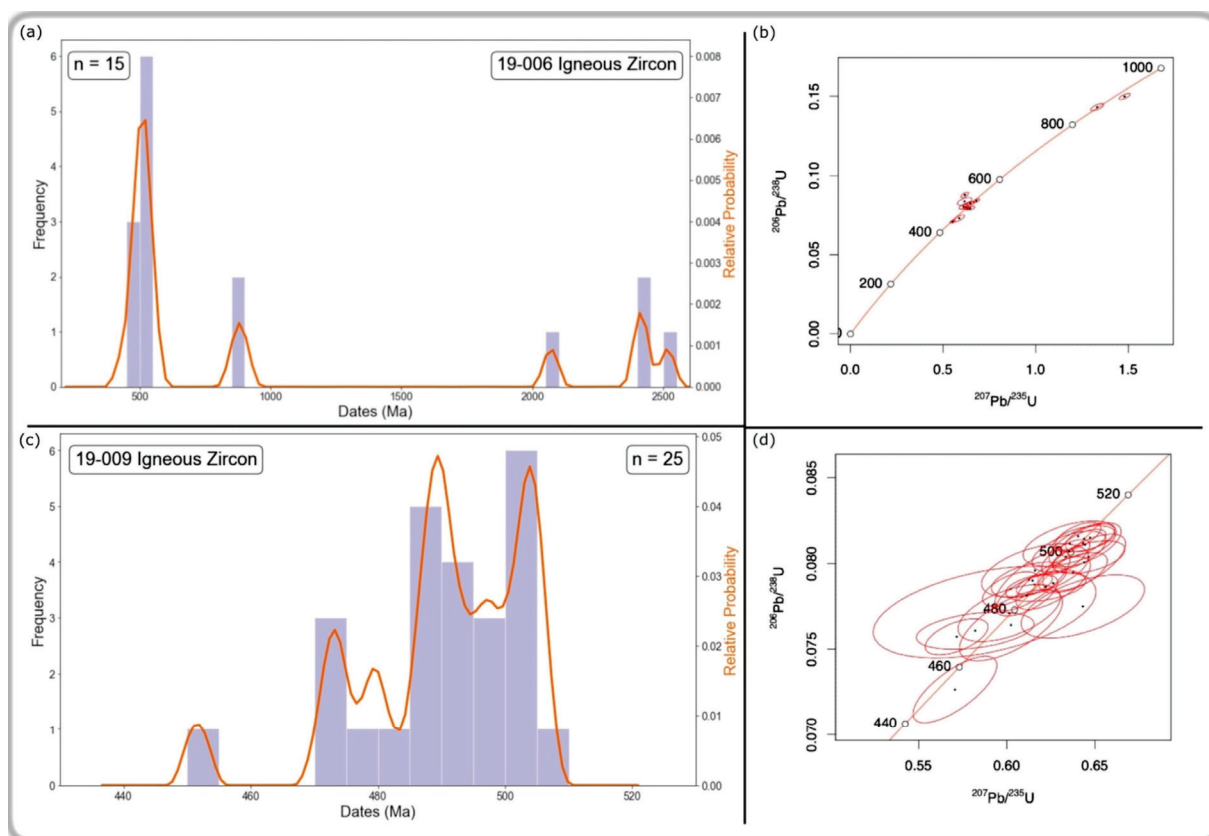


Figure 7. (a) Histogram and cumulative probability distribution curves of igneous zircon measurements of sample WS 15/1 (19-006). (b) Concordia diagram showing radiogenic U-Pb analyses of the zircon from sample WS 15/1 (19-006), uncertainties 1σ . (c) Histogram and cumulative probability distribution curves of igneous zircon measurements of sample WS 16/1 (19-009). (d) Concordia diagram showing radiogenic U-Pb analyses of the zircon from sample WS 16/1 (19-009), uncertainties 1σ . Analyses are listed in Supplementary Materials Tables S2 and S3.

5.3. Metamorphic Ages

The data for all the metamorphic measurements have been provided in the supplementary data tables. The zircons from sample 19-006 did not have large enough metamorphic rims that could be analyzed.

5.3.1. North Sikkim 19-005

The 84 analyses of overgrowths are all concordant with analytical uncertainty, even before correction for the very small amount of common Pb present. A significant range in the $^{206}\text{Pb}/^{238}\text{U}$ dates is observed, ~15–28 Ma, with an isolated analysis at c. 40 Ma. This large range, however, can be separated into two groups on the basis of the Th/U or U (ppm) values and dates. The first (and older) group indicates a $^{206}\text{Pb}/^{238}\text{U}$ age at 26.6 ± 0.17 Ma ($n = 24$) with a low and consistent value of Th/U between 0.00720 and 0.02068 (high values of U ranging from ~1100 to 2500 ppm). The second (and younger) group indicates trailing growth from about 22 Ma until 15 Ma ($n = 47$) (Figure 8a—Supplementary Materials Table S1). The Th/U values of this generation of overgrowth are more varied and range from 0.01863 to 0.05975 and possess lower U, ~270–1000 ppm (Figure 8b).

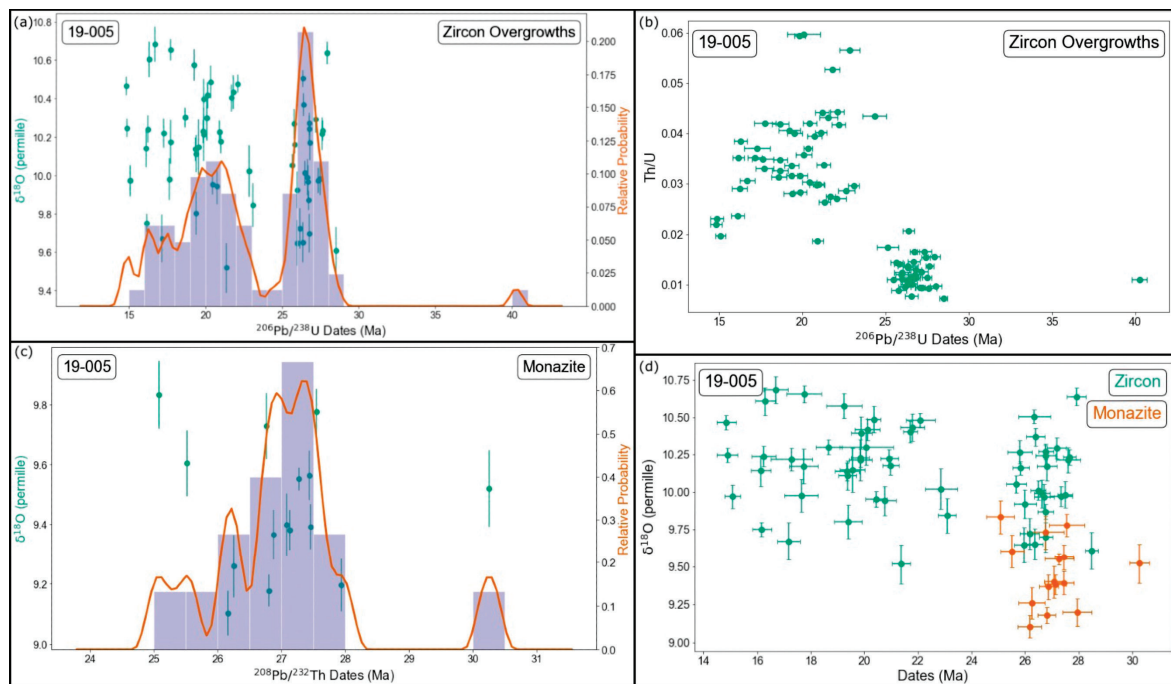


Figure 8. (a) Histogram and cumulative probability distribution curves of zircon overgrowths for sample WS 11/1 (19-005) combined with plots of $\delta^{18}\text{O}$ vs. dates. (b) Plot of Th/U vs. dates of zircon overgrowths. (c) Histogram and cumulative probability distribution curves of monazite for sample WS 11/1 (19-005) combined with plots of $\delta^{18}\text{O}$ vs. dates. (d) Plot of $\delta^{18}\text{O}$ vs. dates for both zircon and monazite. Analyses are listed in Supplementary Materials Tables S1, S5 and S9.

5.3.2. North Sikkim 19-009

The 45 analyses of overgrowths are all concordant with analytical uncertainty, even before correction for the very small amount of common Pb present. A considerable range in the $^{206}\text{Pb}/^{238}\text{U}$ dates is observed, ~15–55 Ma (Figure 9a—Supplementary Materials Table S3). This large range can be segregated into four episodes of metamorphic overgrowth. The older generations are embayments in the zircon crystals, and the younger ones are regular overgrowths. The $^{206}\text{Pb}/^{238}\text{U}$ age of the first event is 54.5 ± 3.0 Ma ($n = 2$) with a Th/U range of 0.01679–0.02362. The second event has a $^{206}\text{Pb}/^{238}\text{U}$ age of 36.4 ± 0.30 Ma ($n = 9$) with a Th/U of 0.0128–0.02011. The third event has a $^{206}\text{Pb}/^{238}\text{U}$ age of 29.2 ± 0.50 Ma ($n = 4$), possessing Th/U values in the range 0.01105–0.01963. These three metamorphic events are not particularly distinct, with a few zircons recording dates in between these values. The three events are followed by trailing growth from 22 Ma to 15 Ma ($n = 6$); these overgrowths have Th/U values ranging from 0.00583 to 0.01163 (Figure 9a,b—Supplementary Materials Table S3). A weak trend of decreasing values of Th/U with age can be observed in this sample; the U contents of the overgrowths too seem to follow this trend, suggesting extreme depletion of Th by the crystallization of other Th-rich minerals such as monazite, allanite, etc., occurring simultaneously (Figure 9b). This is the opposite of what is observed in sample 19-005.

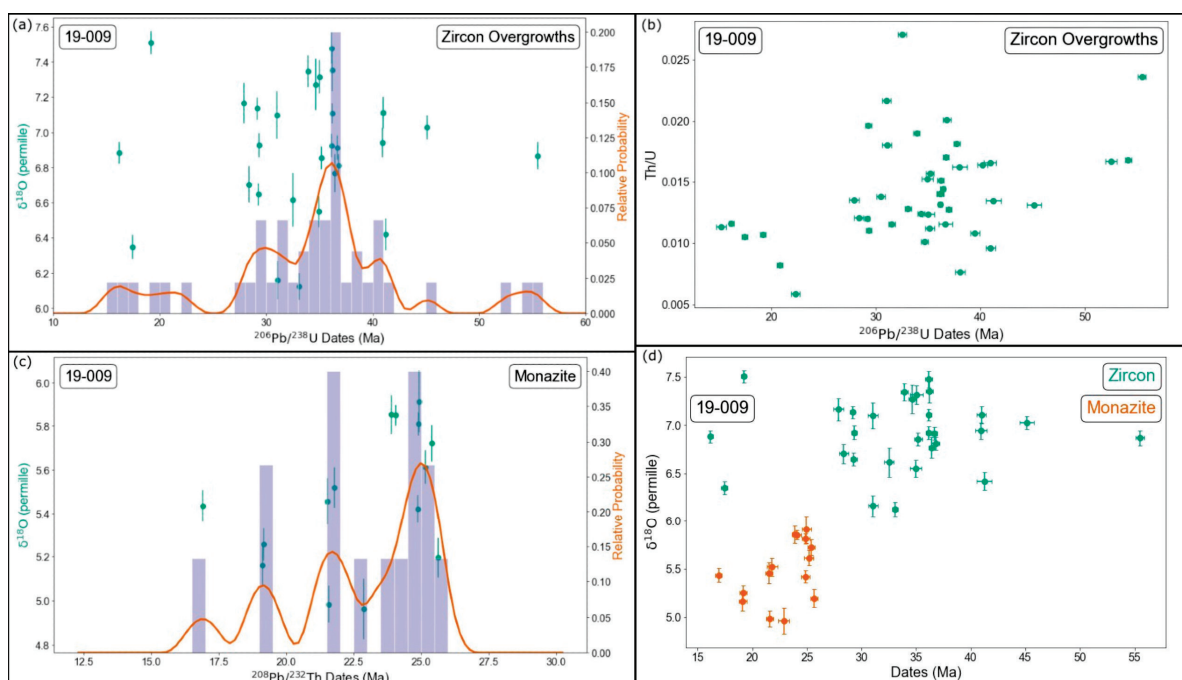


Figure 9. (a) Histogram and cumulative probability distribution curves of zircon overgrowths for sample WS 16/1 (19-009) combined with plots of $\delta^{18}\text{O}$ vs. dates. (b) Plot of Th/U vs. dates of zircon overgrowths. (c) Histogram and cumulative probability distribution curves of monazite for sample WS 16/1 (19-009) combined with plots of $\delta^{18}\text{O}$ vs. dates. (d) Plot of $\delta^{18}\text{O}$ vs. dates for both zircon and monazite. Analyses are listed in Supplementary Materials Tables S3, S7 and S11.

5.3.3. West Sikkim 19-010

All 22 analyses of overgrowths are concordant within analytical uncertainty, even before correcting for the very small amount of common Pb present. The $^{206}\text{Pb}/^{238}\text{U}$ dates range from ~20 to 30 Ma (Figure 10a—Supplementary Materials Table S4). This range can be split into three different episodes of metamorphic overgrowth. The older overgrowths occur as embayments in the crystals, while the younger ones occur as regular overgrowths. The first event has a $^{206}\text{Pb}/^{238}\text{U}$ age of 28.6 ± 1.0 Ma ($n = 4$) with a Th/U range of 0.0058–0.01161. The second event has a $^{206}\text{Pb}/^{238}\text{U}$ age of 26.4 ± 0.50 Ma ($n = 6$), possessing a slightly higher Th/U value ranging from 0.00809 to 0.01448. The third and final event has a $^{206}\text{Pb}/^{238}\text{U}$ age of 23.3 ± 0.5 Ma ($n = 6$) with a much higher Th/U range of 0.01442–0.02445 (Figure 10a,b—Supplementary Materials Table S4). A trend of increasing Th/U ratios of the overgrowths with decreasing age can be observed, and this effect can be attributed to concentrations of U decreasing with the dates of the metamorphic overgrowths (Figure 10b).

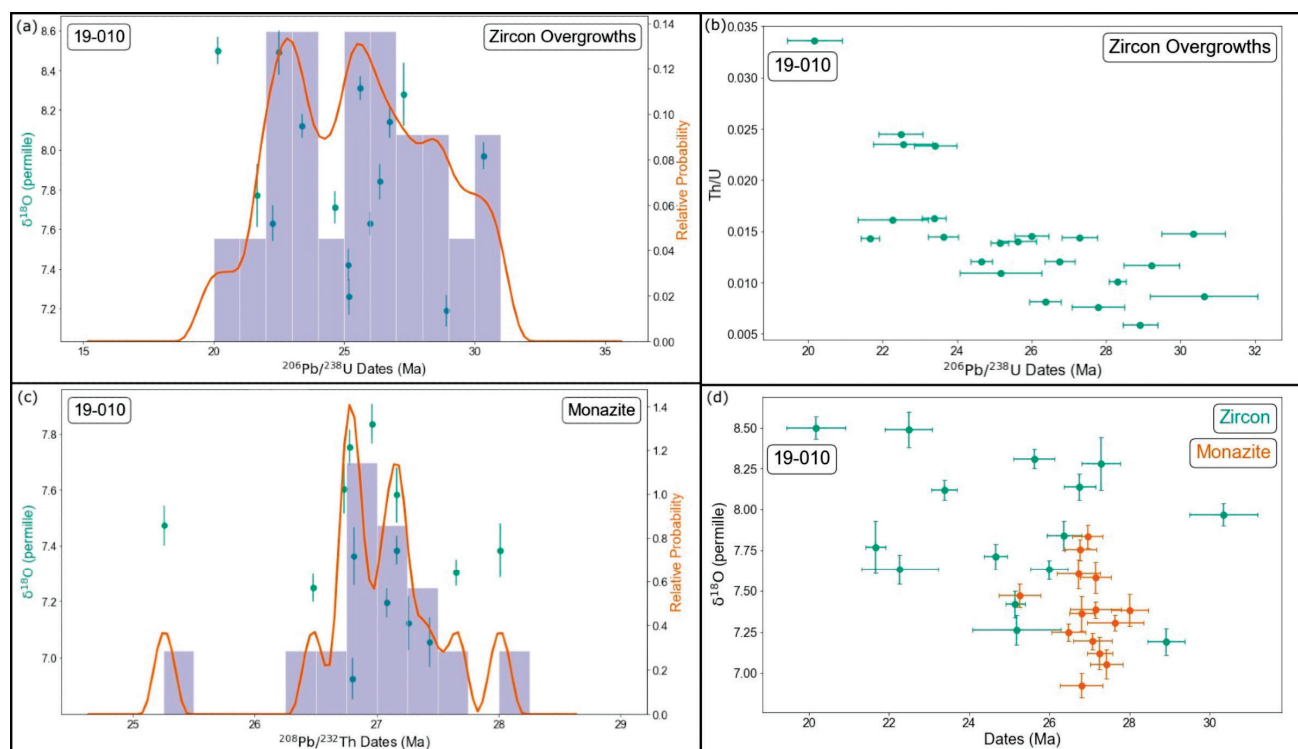


Figure 10. Histogram and cumulative probability distribution curves of sample WS 1/1 (19-010) combined with plots of $\delta^{18}\text{O}$ vs. dates for (a) zircon overgrowths and (b) monazite. (c) Plot of Th/U vs. dates. (d) Plot of $\delta^{18}\text{O}$ vs. dates for both zircon and monazite. Analyses are listed in Supplementary Materials Tables S4, S8 and S12.

6. Results of the Monazite Dating

6.1. North Sikkim 19-005

A total of 12 of the 15 grains of monazite were analyzed to have the same $^{208}\text{Pb}/^{232}\text{Th}$ within analytical uncertainty, giving a weighted mean age of 26.99 ± 0.32 Ma. The independently calibrated U-Pb isotopic compositions are also very internally consistent but provide a slightly higher weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 27.46 ± 0.54 Ma, even after a downward correction to account for the presence of initial ^{230}Th . Due to the higher precision of the mean $^{208}\text{Pb}/^{232}\text{Th}$ age and its independence from the need for a disequilibrium correction, 26.99 ± 0.32 Ma is the best estimate of the monazite age. This coincides well with the older metamorphic overgrowth on the zircon (Figure 8c—Supplementary Materials Table S5).

6.2. North Sikkim 19-006

A total of 13 out of 15 analyses of five grains of the monazite have the same $^{208}\text{Pb}/^{232}\text{Th}$ within analytical uncertainty, giving a weighted mean age of 24.29 ± 0.25 Ma (Figure 11—Supplementary Materials Table S6). The independently calibrated U-Pb isotopic compositions are also very internally consistent and provide a similar weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 24.34 ± 0.36 Ma post a correction to account for the presence of initial ^{230}Th . Though both the ages are very similar, the $^{208}\text{Pb}/^{232}\text{Th}$ age of 24.29 ± 0.25 Ma is the best estimate of monazite age. It has slightly higher precision and is independent of a disequilibrium correction.

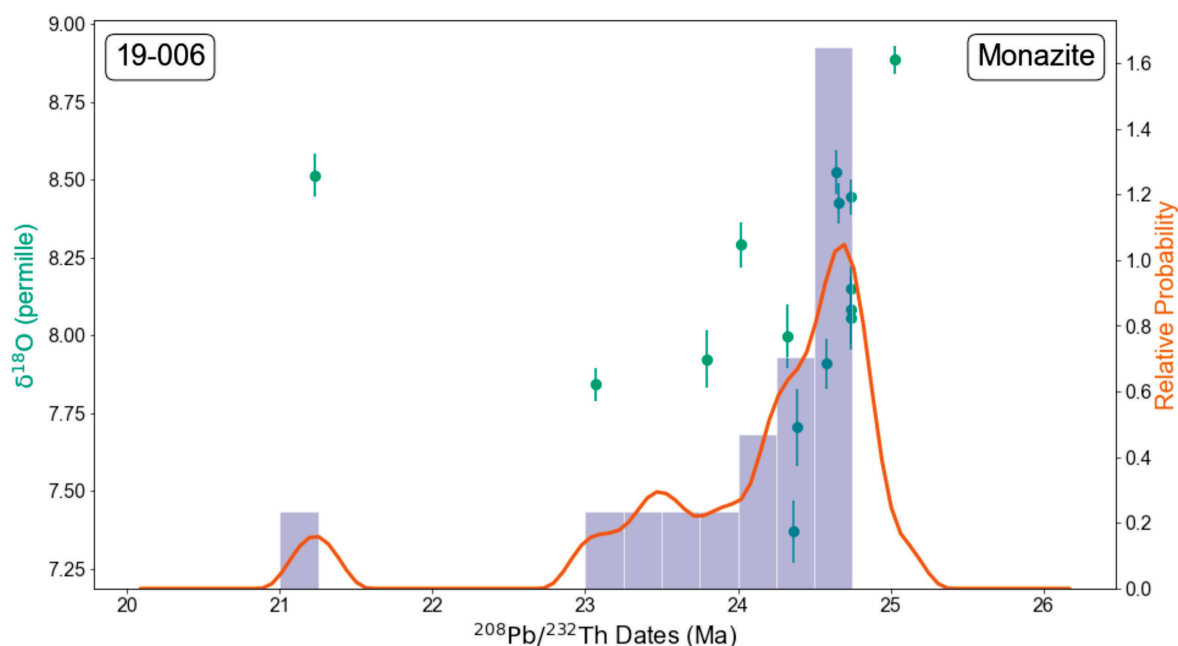


Figure 11. Histogram and cumulative probability distribution curves of sample WS 15/1 (19-006) combined with plots of $\delta^{18}\text{O}$ vs. dates for monazite. Analyses are listed in Supplementary Materials Tables S6 and S10.

6.3. North Sikkim 19-009

A total of 14 analyses of 12 grains of the monazite were made. They are separated into two groups of analyses, each possessing the same $^{208}\text{Pb}/^{232}\text{Th}$ within analytical uncertainty, giving us a weighted mean age of 24.99 ± 0.41 Ma ($n = 7$) for the older group and a weighted mean age of 21.65 ± 0.75 Ma ($n = 3$) for the younger group (Figure 9c—Supplementary Materials Table S7). Crystals accompany these ages with dates of ~ 19 Ma ($n = 2$) and ~ 16 Ma ($n = 1$). The independently calibrated U-Pb isotopic compositions are also very internally consistent but give a slightly higher weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age for 25.66 ± 0.46 Ma ($n = 6$) for the older group and 22.91 ± 0.73 Ma ($n = 4$) for the younger group. Considering the higher precision of the mean $^{208}\text{Pb}/^{232}\text{Th}$ age and its independence from the need for a disequilibrium correction, 24.99 ± 0.41 Ma and 21.65 ± 0.75 Ma are the best estimates of the monazite ages.

6.4. West Sikkim 19-010

The 14 monazite grains analyzed all have the same radiogenic $^{208}\text{Pb}/^{232}\text{Th}$ within analytical uncertainty, giving a weighted mean age of 27.03 ± 0.30 Ma (Figure 10c—Supplementary Materials Table S8). The independently calibrated U-Pb isotopic compositions are also very internally consistent and give a similar weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 26.92 ± 0.46 Ma post a downwards correction to account for the presence of initial ^{230}Th . Though both the ages are very similar, the $^{208}\text{Pb}/^{232}\text{Th}$ age of 27.03 ± 0.30 Ma is the best estimate of monazite age, as it has higher precision and is independent of a disequilibrium correction.

7. Results of the Oxygen Analyses

7.1. Zircon

All quoted values have standard deviations similar to those of the reference zircon measurements. The $\delta^{18}\text{O}$ value of mantle zircon has been measured to be $\sim 5.3\text{‰}$ by [64], and the $\delta^{18}\text{O}$ value of zircons from partial melts of mature sedimentary rocks was measured to be up to $\sim 12\text{‰}$ by [65,90]. These values have been referenced multiple times in the text below.

7.1.1. North Sikkim 19-005

The zircons for both age groups had roughly similar $\delta^{18}\text{O}$ values: $9.98 \pm 0.10\text{‰}$ for the ~26 Ma overgrowth and $10.24 \pm 0.05\text{‰}$ for the ~22–15 Ma overgrowths (Figure 8a,d—Supplementary Materials Table S9). These values are much higher than mantle zircon values and almost as high as those found in zircon from partial melts of mature sedimentary rocks. A mild increase in $\delta^{18}\text{O}$ values is noted with decreasing age. The $\delta^{18}\text{O}$ values are thereby indicative of derivation from an immature crustal/sediment-derived source.

7.1.2. North Sikkim 19-006

$\delta^{18}\text{O}$ measurements were carried out only on the igneous zircon. The $\delta^{18}\text{O}$ recorded for the ~500 Ma magmatic event is $9.62 \pm 0.20\text{‰}$ (Supplementary Materials Table S10). This value is significantly higher than that reported from other Cambro-Ordovician igneous zircons from the NW Himalayas (Prabha-Mohan et al., 2021 [62]). The $\delta^{18}\text{O}$ suggests a recycled/sediment-derived crustal magma source.

7.1.3. North Sikkim 19-009

The $\delta^{18}\text{O}$ for both the igneous zircon and metamorphic overgrowths were measured. The $\delta^{18}\text{O}$ recorded for the ~490 Ma magmatic event was $9.79 \pm 0.08\text{‰}$, similar to the sample above (19-006), characteristic of an immature, sediment-derived crustal magma source. Based on the $\delta^{18}\text{O}$ values, we can surmise that both samples' melt sources were most likely the same. The $\delta^{18}\text{O}$ values for each of the metamorphic generations identified, in decreasing order of age, are $6.90 \pm 0.10\text{‰}$ (~54 Ma), $7.34 \pm 0.31\text{‰}$ (~36 Ma), $6.85 \pm 0.10\text{‰}$ (~29 Ma), and $6.91 \pm 0.29\text{‰}$ (~22–15 Ma) (Figure 9a,d—Supplementary Materials Table S11). Even though there are slight variations in the $\delta^{18}\text{O}$, it has remained virtually constant at around 7 ‰ throughout the Cenozoic. These values are only slightly higher than values recorded in mantle zircon and are much lower than what has been recorded in zircon higher up in the valley. During the growth of the zircon rims, prior to 36 Ma and after 29 Ma, the growth seems to have occurred from a mixed source but with strong influence from certain undetermined, depleted fluids, as there is no evidence of mantle-derived fluids or melt within this timeframe in the Sikkim Himalayas. This is supported by the fact that only micaceous alteration was visible in the thin section, with no signs of parting melting.

7.1.4. West Sikkim 19-010

The $\delta^{18}\text{O}$ values were measured for each of the metamorphic generations identified. An increase in $\delta^{18}\text{O}$ values is noted with decreasing age: $7.21 \pm 0.28\text{‰}$ for the ~28 Ma overgrowth, $7.76 \pm 0.18\text{‰}$ for the ~26 Ma overgrowth, and $8.15 \pm 0.21\text{‰}$ for the ~23 Ma overgrowth (Figure 10a,d—Supplementary Materials Table S12). This is a clear indication that the metamorphic fluid from which the zircon had been crystallizing was getting heavier with time.

7.2. Monazite

The measured $\delta^{18}\text{O}$ needed to be corrected for the difference in chemical composition between the sample and standard. All corrections were applied, assuming mainly a cheralite substitution and a Th content the same as that of the dated spot [80].

7.2.1. North Sikkim 19-005

The correction applied raised the calculated $\delta^{18}\text{O}$ by 0.2–0.4‰. The $\delta^{18}\text{O}$ of 15 analyzed spots is the same within analytical uncertainty, giving a mean $\delta^{18}\text{O}$ of $9.73 \pm 0.05\text{‰}$ (Figure 8c,d—Supplementary Materials Table S9), marginally lower than that measured in the zircon of a similar age ($9.98 \pm 0.10\text{‰}$). This is inconsistent with the fractionation expected between zircon and monazite at any metamorphic temperature [69]. Hence, it can be inferred that the isotopic equilibrium between zircon and monazite had not been attained at the time of metamorphism.

7.2.2. North Sikkim 19-006

The correction applied raised the calculated $\delta^{18}\text{O}$ by 0.3–0.7‰. The $\delta^{18}\text{O}$ of 14 out of the 16 analyzed spots was the same within analytical uncertainty, giving a mean $\delta^{18}\text{O}$ of $8.56 \pm 0.09\text{‰}$, indicative of a mixed fluid source (Figure 11—Supplementary Materials Table S10). This value cannot be compared, as the zircon had no measurable metamorphic overgrowths.

7.2.3. North Sikkim 19-009

The correction applied raised the calculated $\delta^{18}\text{O}$ by 0.4–1.0‰. The $\delta^{18}\text{O}$ of 15 analyzed spots can be split into two groups within analytical uncertainty. The $\delta^{18}\text{O}$ of the group corresponding to the ~25 Ma metamorphic event recorded in the monazite is $6.32 \pm 0.08\text{‰}$, and the $\delta^{18}\text{O}$ of the < 22 Ma metamorphic event is $5.92 \pm 0.12\text{‰}$ (Figure 9c,d—Supplementary Materials Table S11). It can be observed that there is a slight downtrend of $\delta^{18}\text{O}$ with decreasing age, indicating that, during the growth of the monazite, the fluid it crystallized/grew must have been influenced strongly by the presence of surface waters. The values measured are also much lower than what was estimated on the corresponding zircon, opposite to the fractionation expected between the two minerals at any metamorphic temperature, confirming that the isotopic equilibrium had not been preserved at the time of metamorphism.

7.2.4. West Sikkim 19-010

The correction applied raised the calculated $\delta^{18}\text{O}$ by 0.2–0.7‰. With a single exception, the $\delta^{18}\text{O}$ of the 14 analyzed spots was the same within analytical uncertainty, $7.75 \pm 0.06\text{‰}$ (Figure 10c,d—Supplementary Materials Table S12), roughly the same as the zircon of a similar age; again, this is contrary to the fractionation expected between the two minerals at any metamorphic temperature (Vho et al., 2019 [69]), letting us know that the isotopic equilibrium between zircon and monazite had not been attained at the time of metamorphism.

7.3. Quartz

The quartz was homogenous within all the samples, providing confirmation that they were re-equilibrated simultaneously. While carrying out temperature estimations, the assumption was made (for all samples) that the quartz crystallized in oxygen isotopic equilibrium with the youngest zircon and/or monazite.

7.3.1. North Sikkim 19-005

Fourteen quartz grains were analyzed, all of which gave the same $\delta^{18}\text{O}$ ($12.32 \pm 0.10\text{‰}$, Supplementary Materials Table S9) within the expected analytical uncertainty. Given our assumption, the equilibration temperatures estimated from the size of isotopic fractionation with quartz are ~940 °C (zircon) and ~610°C (monazite). The temperature indicated by the zircon is large enough to produce partial melting during migmatization (>700 °C). This suggests that the zircon grew during the peak thermal conditions, as it can be assumed that the zircon O did not re-equilibrate following the last thermal event, given its resistance to O isotopic exchange at high temperatures (Valley, 2003 [64]). The monazite-derived temperature cannot be considered accurate, as the monazite pre-dates the youngest zircon, and therefore, there is a high probability that the quartz–monazite equilibrium was not preserved. According to our earlier assumption of zircon O not re-equilibrating after the last thermal event, the $\delta^{18}\text{O}$ of the quartz is about 1.2‰ lower than expected, and the $\delta^{18}\text{O}$ of the monazite is about 1‰ lower.

7.3.2. North Sikkim 19-006

Fourteen quartz grains were analyzed, all of which gave the same $\delta^{18}\text{O}$ ($11.53 \pm 0.08\text{‰}$, Supplementary Materials Table S10) within the expected analytical uncertainty. As per our assumption, the equilibration temperature estimated from the size of isotopic fractionation with quartz is ~530 °C (monazite). This is within the margin of error of the temperature at

which monazite begins to grow during the metamorphism of pelite (550–600 °C, [91,92]). This suggests that the quartz–monazite equilibrium has been maintained post the ~24 Ma metamorphic event recorded by the monazite in this sample.

7.3.3. North Sikkim 19-009

Twelve quartz grains were analyzed, all of which gave the same $\delta^{18}\text{O}$ ($9.87 \pm 0.14\text{‰}$, Supplementary Materials Table S11) within the expected analytical uncertainty. Given our assumption, the equilibration temperatures estimated from the size of isotopic fractionation with quartz are ~690 °C (zircon) and ~390 °C (monazite). The temperature indicated by the zircon is within the margin of error of the temperature required to produce partial melting during migmatization (>700 °C). This can be interpreted as the zircon recording the presence of partial melting conditions. As we suggested earlier, the monazite $\delta^{18}\text{O}$ seems to have been lowered noticeably by some external fluid; thus, the temperature estimated is relatively low and not reliable. If the zircon O did not re-equilibrate following the last thermal event, given its resistance to O isotopic exchange at high temperatures [64], then the $\delta^{18}\text{O}$ of the quartz is about 0.2‰ lower than expected, while the $\delta^{18}\text{O}$ of the monazite is 1.7‰ lower, providing us with a quantifiable measure of how much the external fluid has lowered the $\delta^{18}\text{O}$ of the monazite.

7.3.4. West Sikkim 19-010

Seven quartz grains were analyzed, all of which gave the same $\delta^{18}\text{O}$ ($10.39 \pm 0.15\text{‰}$, Supplementary Materials Table S12) within the expected analytical uncertainty. Accounting for our assumption, the equilibration temperatures estimated from the size of isotopic fractionation with quartz are ~880 °C (zircon) and ~600 °C (monazite). The temperature indicated by the zircon is higher than required to produce partial melting during migmatization (>700 °C), suggesting that the zircon grew during the peak thermal conditions. The monazite temperature is sufficiently high to enable growth during the metamorphism of pelites (550–600 °C, [91,92]). Assuming that the zircon O did not re-equilibrate following the last thermal event, given its resistance to O isotopic exchange at high temperatures [64], the $\delta^{18}\text{O}$ of the quartz is about 0.9‰ lower than expected, while the $\delta^{18}\text{O}$ of the monazite is 1.1‰ lower. This leaves us with the implication that the O in the quartz and monazite carried on re-equilibrating while the zircon O did not change as the temperature gradually dropped after the last thermal event.

8. Discussion

The Himalayan metamorphism having the same character indicates an inverted character along the mountain chain's entire strike. Migmatite is exposed in the highest metamorphic grade within the Higher Himalayan Crystallines (HHC) and forms most existing mixed igneous and metamorphic associations undergoing anataxis during the main Himalayan regional metamorphism. These migmatite zones are narrow in the NW Himalayas and in the middle of the HHC [16,17,24], whereas, in the Eastern Himalayas, they are exposed throughout the HHC, whether in Sikkim [16,17,31,32,70,74] or in the Bhutan Himalayas [93–95].

The HHC is a 15–20 km-thick package with two protolith packages of high-grade metamorphic rocks having a lower package with a zircon component older than the Neoproterozoic era; the upper package is characterized by the zircon component up to 500 Ma. These data are in agreement with other published data from the Himalayan orogeny ([26] and references therein).

Various earlier workers have provided age data using zircon [34], monazite [31,34,35], and garnet [32], which are presented in Table 1 from the Sikkim Himalayas. Catlos et al. [31] reported the first monazite ages from North Sikkim, identifying two age clusters of ~22 Ma and ~13 Ma. The data were clearly separated by the Chungthang Thrust, with an age of ~13 Ma even below the MCT. Monazite age clusters of ~22 Ma and ~13 Ma have also been discovered in Eastern Sikkim [31]. Rubatto et al. [34] reported zircon ages ranging from

31.4 Ma to 18.2 Ma and monazite ages ranging from ~37 Ma to ~20 Ma in samples above the Chungthang Thrust in North Sikkim, as well as monazite ages ranging from ~27 Ma to ~19 Ma in Eastern Sikkim. Motram et al. [35] found monazite ages of around 22 million years above the Chungthang Thrust in Eastern Sikkim. Harris et al. [32] determined the Sm-Nd garnet age from leucosomes to be around 23 Ma from the core and 16 Ma from the rim.

Table 1. Age data reported from Sikkim Himalayas.

Location	Sample Number	Age	References
North Sikkim			
Above Chungthang Thrust (Zircon ages)	CLN-8	31.4 Ma, 24.5 Ma	[34]
	LNT	20.5 Ma, 19.0 Ma, 18.5 Ma	[34]
	TG8	19.9 Ma, 18.2 Ma	[34]
	TG9	21.1 Ma, 22.0 Ma, 19.9 Ma	[34]
Above Chungthang Thrust (Monazite ages)	CLN-8 (migmatite metapelites)	22.7 ± 0.3 Ma	[31]
		21.9 ± 1.1 Ma	[31]
		31.4 Ma	[34]
	CLN-6	29.0 Ma, 25.3 Ma, 27.7 Ma, 23.8 Ma	[34]
		CLN-5	28.0 Ma, 26.8 Ma, 28.8 Ma, 25.6 Ma
	LNT-2	23.3–20.9 Ma, 23.5–20.7 Ma	[34]
	LNT-5	36.9–24.0–19.2 Ma	[34]
	TG-9 (migmatite and metapelite)	36.9–21.0 Ma, 36.4–35.6 Ma	[34]
	TG-9 (Leucosome)	24.5–22.5 Ma, 23.5–20.2 Ma	[34]
23.5–20.7 Ma, 24.5–22.5 Ma, 23.5–20.2 Ma, 21.4–16.9 Ma, 23.0–16.5 Ma		[34]	
TG-8 (migmatite metapelite)	25.5–20.6 Ma, 26.2 Ma	[34]	
Below Chungthang Thrust (Monazite ages)		13.8 ± 1.0 Ma	[31]
Below MCT (Monazite ages)		13.0 ± 0.2 Ma 12.3 ± 0.6 Ma	[31]
Eastern Sikkim			
Above Chungthang Thrust (Monazite ages)	141	22.0 ± 0.3 Ma	[31]
		24.0–18.9 Ma, 26.7–21.2 Ma, 26.5–18.8 Ma	[34]
		22.7 ± 0.3 Ma	[35]
		21.9 ± 1.1 Ma	
Below Chungthang Thrust (Monazite ages)		13.0 ± 0.4 Ma 12.7 ± 0.1 Ma	[31]
		15.9 ± 1.0 Ma	[35]
Around MCT (Monazite ages)		~21–12 Ma (Core and Rim of Gt)	[35]
		~21–16 Ma (Core and Rim of Gt)	
		12.8 ± 0.2 Ma (in Staurolite)	
		11.8 ± 0.2 Ma Matrix	
Western Sikkim			
Sm-Nd Gt from leucosome		16.1 ± 2.4 Ma RIM 23.0 ± 2.8 Ma CORE	[32]

The ages reported by earlier researchers from various sections of Sikkim are identical to those documented by us in this work. However, the age and oxygen isotopic data published in this article are primarily from the migmatitic rocks of the Sikkim Himalayas' northern and western sectors.

Zircon, being a robust mineral, has always been preferred to trace the magmatic process using oxygen isotopic analysis along with U-Pb geochronology [96]. The pressure, temperature, and fluid composition lead to recrystallization-caused metamorphism. Stable isotopic studies provide us with a unique opportunity to retrieve information about metamorphism (Sharp, 2017 [97]). The zircon $\delta^{18}\text{O}$ record is generally preserved, even though other minerals have been reset by high-grade metamorphism or intense hydrothermal alteration. A large number of studies have shown that non-metamict zircon kept its $\delta^{18}\text{O}$ value from the time of crystallization; hence, oxygen isotope ratios in zircons can be correlated with age or trace elemental composition [64].

Most analyzed zircon grains have $\delta^{18}\text{O}$ values ranging from 6.85 to 10.24‰, indicating that the fluids involved during the growth of the metamorphic zircon were derived from an extensive source region of higher $\delta^{18}\text{O}$ segments of the crust. The relationship of quartz and zircon with $\delta^{18}\text{O}$ values indicates that the fluids evolved from the host metasedimentary rock for the migmatites (Figure 12). However, the lower-elevation samples indicate interaction with surficial water. Quartz from migmatite samples shows homogenous oxygen isotopic values (9.87–12.32‰); however, zircon (6.85–10.24‰) displays oxygen isotopic heterogeneity (>2.0‰). The variation in oxygen isotopic ratio clearly indicates that it is a product of an open system, as a closed system produces only small differences [98–100]. This has also been narrated by Sharp [97] in that above greenschist facies, the system becomes open, and fluids and/or melt may escape through a fracture and network with the surroundings (Figure 12).

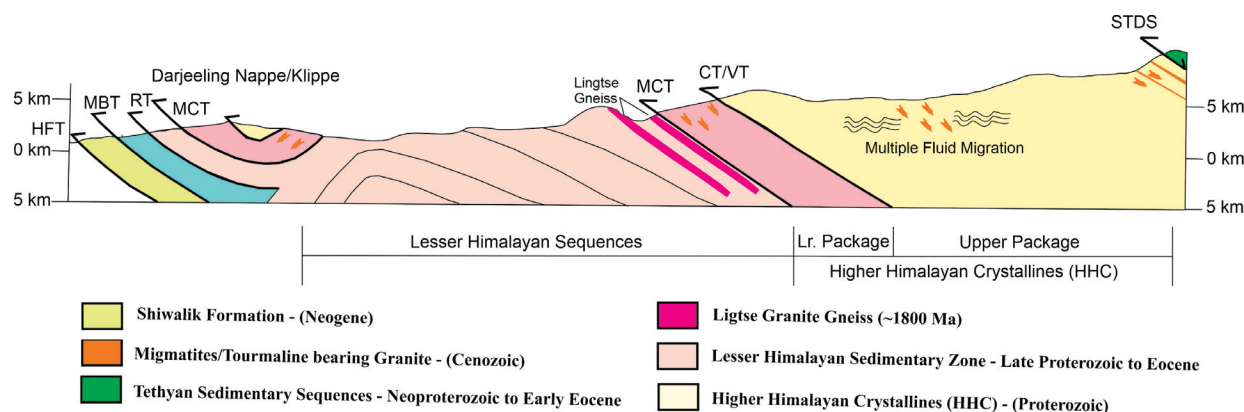


Figure 12. Cross-section of the Sikkim Himalayas showing migmatite zones and concordant sheets of leucogranite bodies in upper reaches along with multiple fluid migrations at mid-crustal levels around migmatite zones with distinct $\delta^{18}\text{O}$ values at different times.

The study's oxygen isotopic thermometric values generally agree with each other, except in cases when the last thermal event, as recorded by the zircon and monazite, differs in age considerably, such as in sample 19-005. In which case, we shall consider the temperature derived from the more recently equilibrated system to be the better and most likely answer. Temperatures derived for the sample 19-010 show the best agreement with each other.

9. Conclusions

The present work clearly indicates two packages of thrust sheets within the Higher Himalayan Crystallines (HHC) of the Sikkim Himalayas with clear detrital history and a strong Cambro-Ordovician magmatic activity followed by a Himalayan thermal event leading to the formation of metamorphic zircons in an episodic manner. However, monazite shows a single prominent metamorphic event. It also appears that the growth of zircon rims, before 29 Ma and after 22 Ma, came from a mixed source but was somewhat influenced by the depleted fluids. At the same time, monazite grains recorded a constant value irrespective of their dates, indicating that, during fluid crystallizing/growing, the monazite

must have been influenced strongly by the presence of surface waters at a lower elevation. The $\delta^{18}\text{O}$ values of quartz, zircon, and monazite also indicate that fluid involved during metamorphic zircon and monazite growth was derived from the metasedimentary host rock (Figure 12).

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14060572/s1>, Figure S1: Concordia diagram from Supplementary Data Tables S1–S4. (a) Concordia diagram showing radiogenic U–Pb analyses of the zircon from sample WS 11/1 (19-005). (b) Concordia diagram showing radiogenic U–Pb analyses of the zircon from sample WS 15/1 (19-006). (c) Concordia diagram showing radiogenic U–Pb analyses of the zircon from sample WS 16/1 (19-009). (d) Concordia diagram showing radiogenic U–Pb analyses of the zircon from sample WS 1/1 (19-010); Table S1: SHRIMP U–Pb Zircon Data of the Sikkim Sample—19-005 (WS11/1); Table S2: SHRIMP U–Pb Zircon Data of the Sikkim Sample—19-006 (WS15/1); Table S3: SHRIMP U–Pb Zircon Data of the Sikkim Sample—19-009 (WS16/1); Table S4: SHRIMP U–Pb Zircon Data of the Sikkim Sample—19-010 (WS1/1); Table S5: SHRIMP U–Th–Pb Monazite Data of the Sikkim Sample—19-005 (WS11/1); Table S6: SHRIMP U–Th–Pb Monazite Data of the Sikkim Sample—19-006 (WS15/1); Table S7: SHRIMP U–Th–Pb Monazite Data of the Sikkim Sample—19-009 (WS16/1); Table S8: SHRIMP U–Th–Pb Monazite Data of the Sikkim Sample—19-010 (WS1/1); Table S9: SHRIMP Oxygen Isotope Data of the Sample—19-005 (WS 11/1); Table S10: SHRIMP U–Pb Oxygen Isotope Data of the Sample—19-006 (WS 15/1); Table S11: SHRIMP Oxygen Isotope Data of the Sample—19-009 (WS 16/1); Table S12: SHRIMP Oxygen Isotope Data of the Sample—19-010 (WS 1/1).

Author Contributions: Conceptualization, S.S. and I.S.W. methodology, S.P.-M., S.S. and I.S.W.; software, S.P.-M., S.S. and I.S.W.; validation, S.P.-M., S.S. and I.S.W.; formal analysis, S.P.-M.; investigation, S.P.-M., S.S. and I.S.W.; resources, S.S. and I.S.W.; data curation, S.P.-M., S.S. and I.S.W.; writing—original draft preparation, S.P.-M., S.S. and I.S.W.; writing—review and editing, S.P.-M., S.S. and I.S.W.; visualization, S.S. and I.S.W.; supervision, S.S. and I.S.W.; project administration, S.S. and I.S.W.; funding acquisition, S.P.-M., S.S. and I.S.W. All authors have read and agreed to the published version of the manuscript.

Funding: Future Research Talent (FRT) Travel Award, Australian National University, Ministry of Earth Sciences, New Delhi, research project (grant no. MoES/P.O. (Geosci)/27/2014 & MOES/16/40/09-RDEAS).

Data Availability Statement: Data has been listed in Supplementary Materials.

Acknowledgments: S.P.-M. thanks the College of Science, Australian National University, for funding a visit to Canberra through the Future Research Talent (FRT) Travel Award. S.P.-M. also thanks the Australian Scientific Instruments (ASI), Ian S Williams, and the Research School of Earth Sciences, ANU, for providing him with valuable SHRIMP time. SS thanks Lukas Baumgartner of UNIL for the motivation to take up the $\delta^{18}\text{O}$ study. Financial support provided by a research project (grant no. MoES/P.O. (Geosci)/27/2014 & MOES/16/40/09-RDEAS) is thankfully acknowledged. The initial manuscript improved substantially after suggestions made by Robert Stern. We also thank guest editors for inviting us to contribute the manuscript. Comments from three anonymous reviewers improved the early version.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work presented in this paper.

References

1. Leech, M.L.; Singh, S.; Jain, A.K.; Klemperer, S.L.; Manickavasagam, R.M. The onset of India-Asia continental collision: Early, steep subduction required by the timing of UHP metamorphism in the western Himalaya. *Earth Planet. Sci. Lett.* **2005**, *234*, 83–97. [CrossRef]
2. Leech, M.L.; Singh, S.; Jain, A.K. Continuous Metamorphic Zircon Growth and Interpretation of U–Pb SHRIMP Dating: An Example from the Western Himalaya. *Int. Geol. Rev.* **2007**, *49*, 313–328. [CrossRef]
3. Parsons, A.J.; Hosseini, K.; Palin, R.M.; Sigloch, K. Geological, geophysical and plate kinematic constraints for models of the India-Asia collision and the post-Triassic central Tethys oceans. *Earth Sci. Rev.* **2020**, *208*, 103084. [CrossRef]
4. Singh, S.; Barley, M.E.; Jain, A.K. Tale of two migmatites and leucogranite generation within the Himalayan Collisional Zone: Evidences from SHRIMP U–Pb zircon ages from Higher Himalayan Metamorphic Belt and Trans-Himalayan Karakoram Metamorphic Belt, India. *Himal. J. Sci.* **2004**, *2*, 251–252. [CrossRef]

5. Le Fort, P. Metamorphism and magmatism during the Himalayan Collision. In *Collision Tectonics*; Coward, M.P., Ries, A., Eds.; Special Publication; Geological Society: London, UK, 1986; Volume 19, pp. 159–172.
6. Kohn, M.J. Himalayan metamorphism and its tectonic implications. *Annu. Rev. Earth Planet. Sci.* **2014**, *42*, 381–419. [CrossRef]
7. Jain, A.K.; Singh, S.; Manickavasagam, R.M. Himalayan Collision Tectonics. *Gondwana Res. Group Mem.* **2002**, *7*, 114.
8. Jain, A.K.; Manickavasagam, R.M. Inverted metamorphism in the intracontinental ductile shear zone during Himalayan collision tectonics. *Geology* **1993**, *21*, 407–410. [CrossRef]
9. Yin, A. Cenozoic tectonic evolution of the Himalayan orogen as constrained by along-strike variation of structural geometry, exhumation history, and foreland sedimentation. *Earth-Sci. Rev.* **2006**, *76*, 1–131. [CrossRef]
10. Goscombe, B.; Gray, D.; Foster, D.A. Metamorphic response to collision in the Central Himalayan Orogen. *Gondwana Res.* **2018**, *57*, 191–265. [CrossRef]
11. Singh, S. Collision Tectonics: Metamorphic and Geochronological Constraints from Parts of Himachal Pradesh, NW-Himalaya. Ph.D. Thesis, University of Roorkee, Roorkee, India, 1993.
12. Singh, S.; Jain, A.K. Deformation and strain pattern in parts of the Jutogh Nappe along the Sutlej valley in Jeori-Wangtu region, Himachal Pradesh, India. *J. Himal. Geol.* **1993**, *4*, 41–55.
13. Singh, S.; Jain, A.K. Himalayan Granitoids. *J. Virtual Explor.* **2003**, *11*, 1–20. [CrossRef]
14. Searle, M.P.; Cottle, J.M.; Streule, M.J.; Waters, D.J. Crustal melt granites and migmatites along the Himalaya: Melt source, segregation, transport and granite emplacement mechanisms. *Earth Environ. Sci. Trans. R. Soc. Edinb.* **2009**, *100*, 219–233. [CrossRef]
15. Singh, S. Himalayan magmatism through space and time. *Episodes* **2020**, *43*, 358–368. [CrossRef]
16. Singh, S.; Rit, B.; Prabha Mohan, S.; Kushwaha, A. Crustal melting evidence in migmatites of Higher Himalayan Crystallines (HHC) along Bhagirathi, Dhauliganga valleys, and Sikkim Himalayas, India. *J. Geol. Soc. India* **2022**, *98*, 69–73. [CrossRef]
17. Singh, S.; Kushwaha, A. Melt Enhanced Deformation in Migmatites of Higher Himalayan Crystallines (HHC), India. *J. Geol. Soc. India* **2023**, *99*, 9–12. [CrossRef]
18. Najman, Y.M.R.; Pringle, M.S.; Johnson, M.R.W.; Robertson, A.H.F.; Wijbrans, J.R. Laser $^{40}\text{Ar}/^{39}\text{Ar}$ dating of single detrital muscovite grains from early foreland basin sediments in India: Implications for early Himalayan evolution. *Geology* **1997**, *25*, 535–538. [CrossRef]
19. Najman, Y.; Johnson, C.; White, N.M.; Oliver, G. Constraints on foreland basin and orogenic evolution from detrital mineral fission track analyses and sediment facies of the Himalayan foreland basin, NW India. *Basin Res.* **2004**, *16*, 1–24. [CrossRef]
20. Najman, Y.; Carter, A.; Oliver, G.; Garzanti, E. Provenance of early foreland basin sediments, Nepal: Constraints to the timing and diachroneity of early Himalayan orogenesis. *Geology* **2005**, *33*, 309–312. [CrossRef]
21. DeCelles, P.G.; Gehrels, G.E.; Quade, J.; Ojha, T.P. Eocene-early Miocene foreland basin development and the history of Himalayan thrusting, western and central Nepal. *Tectonics* **1988**, *17*, 741–765. [CrossRef]
22. Najman, Y.; Garzanti, E. Reconstructing early Himalayan tectonic evolution and paleogeography from Tertiary foreland basin sedimentary rocks, northern India. *Geol. Soc. Am. Bull.* **2000**, *112*, 435–449. [CrossRef]
23. White, N.M.; Pringle, M.; Garzanti, E.; Bickle, M.; Najman, Y.; Chapman, H.; Friend, P. Constraints on the exhumation and erosion of the High Himalayan Slab, NW India, from foreland basin deposits. *Earth Planet. Sci. Lett.* **2002**, *195*, 29–44. [CrossRef]
24. Singh, S. Protracted zircon growth in migmatites and in situ melt of Higher Himalayan Crystallines: U–Pb ages from Bhagirathi valley, NW Himalaya, India. *Geosci. Front.* **2019**, *10*, 793–809. [CrossRef]
25. Singh, S.; Jain, A.K.; Barley, M.E. SHRIMP U–Pb c. 1860 Ma anorogenic magmatic signatures from the NW Himalaya: Implications for Palaeoproterozoic assembly of the Columbia Supercontinent. *Geol. Soc. Lond. Spec. Publ.* **2009**, *323*, 283–300. [CrossRef]
26. Mukherjee, P.K.; Jain, A.K.; Singhal, S.; Singha, N.B.; Singh, S.; Kumud, K.; Seth, P.; Patel, R.C. U–Pb zircon ages and Sm–Nd isotopic characteristics of the Lesser and Great Himalayan sequences, Uttarakhand Himalaya, and their regional tectonic implications. *Gondwana Res.* **2019**, *75*, 282–297. [CrossRef]
27. Brown, M. Orogeny, migmatites and leucogranites: A review. *J. Earth Syst. Sci.* **2001**, *110*, 313–336. [CrossRef]
28. Grujic, D.; Hollister, L.S.; Parrish, R.R. Himalayan metamorphic sequence as an orogenic channel: Insight from Bhutan. *Earth Planet. Sci. Lett.* **2002**, *198*, 177–191. [CrossRef]
29. Neogi, S.; Dasgupta, S.; Fukuoka, M. High P–T polymetamorphism, dehydration melting and generation of migmatites and granites in the Higher Himalayan Crystalline complex, Sikkim, India. *J. Petrol.* **1998**, *39*, 61–99. [CrossRef]
30. Chakraborty, S.; Dasgupta, S.; Neogi, S. Generation of migmatites and the nature of partial melting in a continental collision zone setting: An example from the Sikkim Himalaya. *Indian J. Geol. Aniruddha De Meml.* **2003**, *75*, 38–53.
31. Catlos, E.J.; Dubey, C.S.; Harrison, T.M.; Edwards, M.A. Late Miocene movement within the Himalayan Main Central Thrust shear zone, Sikkim, Northeast India. *J. Metamorph. Geol.* **2004**, *22*, 207–226. [CrossRef]
32. Harris, N.B.W.; Caddick, M.; Kosler, J.; Goswami, S. The pressure-temperature-time path of migmatites from the Sikkim Himalaya. *J. Metamorph. Geol.* **2004**, *22*, 249–264. [CrossRef]
33. Imayama, T.; Takeshita, T.; Yi, K.; Cho, D.L.; Kitajima, K.; Tsutsumi, Y.; Kayama, M.; Nishido, H.; Okumura, T.; Yagi, K.; et al. Two-stage partial melting and contrasting cooling history within the higher Himalayan crystalline sequence in the far-eastern Nepal Himalaya. *Lithos* **2012**, *134–135*, 1–22. [CrossRef]

34. Rubatto, D.; Chakraborty, S.; Dasgupta, S. Timescales of crustal melting in the Higher Himalayan Crystallines (Sikkim, Eastern Himalaya) inferred from trace element-constrained monazite and zircon chronology. *Contrib. Mineral. Petrol.* **2013**, *165*, 349–372. [CrossRef]
35. Mottram, C.M.; Argles, T.W.; Harris, N.B.; Parrish, R.R.; Horstwood, M.S.; Warren, C.J.; Gupta, S. Tectonic interleaving along the Main Central Thrust, Sikkim Himalaya. *J. Geol. Soc. Lond.* **2014**, *171*, 255–286. [CrossRef]
36. Smith, H.A.; Chamberlain, C.P.; Zeitler, P.K. Timing and duration of Himalayan metamorphism within the India plate, northwest Himalaya, Pakistan. *J. Geol.* **1994**, *102*, 493–508. [CrossRef]
37. DeCelles, P.G. Tectonic Implications of U–Pb Zircon Ages of the Himalayan Orogenic Belt in Nepal. *Science* **2000**, *288*, 497–499. [CrossRef] [PubMed]
38. White, N.M.; Parrish, R.R.; Bickle, M.J.; Najman, Y.M.R.; Burbank, D.; Maithani, A. Metamorphism and exhumation of the NW Himalaya constrained by U–Th–Pb analyses of detrital monazite grains from early foreland basin sediments. *J. Geol. Soc.* **2001**, *158*, 625–635. [CrossRef]
39. Catlos, E.J.; Harrison, T.M.; Manning, C.E.; Grove, M.; Rai, S.M.; Hubbard, M.S.; Upreti, B.N. Records of the evolution of the Himalayan orogen from in situ Th–Pb ion microprobe dating of monazite: Eastern Nepal and western Garhwal. *J. Asian Earth Sci.* **2002**, *20*, 459–479. [CrossRef]
40. Lee, J.; Whitehouse, M.J. Onset of mid-crustal extensional flow in southern Tibet: Evidence from U/Pb zircon ages. *Geology* **2007**, *35*, 45–48. [CrossRef]
41. Martin, A.J.; Gehrels, G.E.; DeCelles, P.G. The tectonic significance of (U, Th)/Pb ages of monazite inclusions in garnet from the Himalaya of central Nepal. *Chem. Geol.* **2007**, *244*, 1–24. [CrossRef]
42. Booth, A.L.; Chamberlain, C.P.; Kidd, W.S.F.; Zeitler, P.K. Constraints on the metamorphic evolution of the eastern Himalayan Syntaxis from geochronologic and petrologic studies of Namche Barwa. *Geol. Soc. Am. Bull.* **2009**, *121*, 385–407. [CrossRef]
43. Larson, K.P.; Cottle, J.M.; Godin, L. Petrochronologic record of metamorphism and melting in the upper Greater Himalayan sequence, Manaslu-Himal Chuli Himalaya, west-central Nepal. *Lithosphere* **2011**, *3*, 379–392. [CrossRef]
44. Lederer, G.W.; Cottle, J.M.; Jessup, M.J.; Langille, J.M.; Ahmad, T. Time-scales of partial melting in the Himalayan middle crust: Insight from the Leo Pargil dome, northwest India. *Contrib. Mineral. Petrol.* **2013**, *166*, 1415–1441. [CrossRef]
45. Rehman, H.U.; Kobayashi, K.; Tsujimori, T.; Ota, T.; Yamamoto, H.; Nakamura, E.; Hirajima, T. Ion microprobe U–Th–Pb geochronology and study of micro-inclusions in zircon from the Himalayan high- and ultrahigh-pressure eclogites, Kaghan Valley of Pakistan. *J. Asian Earth Sci.* **2013**, *63*, 179–196. [CrossRef]
46. Kellett, D.A.; Grujic, D.; Coutand, I.; Cottle, J.; Mukul, M. The South Tibetan detachment system facilitates ultra rapid cooling of granulite-facies rocks in Sikkim Himalaya. *Tectonics* **2013**, *32*, 252–270. [CrossRef]
47. Montomoli, C.; Iaccarino, S.; Carosi, R.; Langone, A.; Visonà, D. Tectonometamorphic discontinuities within the Greater Himalayan Sequence in Western Nepal (Central Himalaya): Insights on the exhumation of crystalline rocks. *Tectonophysics* **2013**, *608*, 1349–1370. [CrossRef]
48. Larson, K.P.; Cottle, J.M. Initiation of Crustal Shortening in Himalaya. *Terra Nova* **2015**, *27*, 169–174. [CrossRef]
49. Wang, J.M.; Rubatto, D.; Zhang, J.J. Timing of Partial Melting and Cooling across the Greater Himalayan Crystalline Complex (Nyalam, Central Himalaya): In-sequence Thrusting and its Implications. *J. Petrol.* **2015**, *56*, 1677–1702. [CrossRef]
50. Palin, R.M.; Treloar, P.J.; Searle, M.P.; Wald, T.; White, R.W.; Mertz-Kraus, R. U–Pb monazite ages from the Pakistan Himalaya record pre-Himalayan Ordovician orogeny and Permian continental breakup. *Geol. Soc. Am. Bull.* **2018**, *130*, 2047–2061. [CrossRef]
51. Copeland, P.; Parrish, R.R.; Harrison, T.M. Identification of inherited radiogenic Pb in monazite and its implications for U–Pb systematics. *Nature* **1988**, *333*, 760–763. [CrossRef]
52. Parrish, R.P.; Tirrul, R. U–Pb ages of the Baltoro granite, northwest Himalaya, and implications for zircon inheritance and monazite U–Pb systematics. *Geology* **1989**, *17*, 1076–1079. [CrossRef]
53. Parrish, R.R. U–Pb dating of monazite and its application to geological problems. *Can. J. Earth Sci.* **1990**, *7*, 1431–1450. [CrossRef]
54. Weinberg, R.F.; Wolfram, L.C.; Nebel, O.; Hasalová, P.; Závada, P.; Kylander-Clark, A.R.C.; Becchio, R. Decoupled U–Pb date and chemical zonation of monazite in migmatites: The case for disturbance of isotopic systematics by coupled dissolution-reprecipitation. *Geochim. Cosmochim. Acta* **2020**, *269*, 398–412. [CrossRef]
55. Montel, J.M. Experimental determination of the solubility of Ce-monazite in SiO₂–Al₂O₃–K₂O–Na₂O melts at 800 °C, 2 kbar, under H₂O-saturated conditions. *Geology* **1986**, *14*, 659–662. [CrossRef]
56. Rapp, R.P.; Ryerson, F.J.; Miller, C.F. Experimental evidence bearing on the stability of monazite during crustal anatexis. *Geophys. Res. Lett.* **1987**, *14*, 307–310. [CrossRef]
57. Kelsey, D.E.; Clark, C.; Hand, M. Thermobarometric modelling of zircon and monazite growth in melt-bearing systems: Examples using model metapelitic and metapsammitic granulites. *J. Metamorph. Geol.* **2008**, *26*, 199–212. [CrossRef]
58. Yakymchuk, C.; Brown, M. Consequences of open-system melting in tectonics. *J. Geol. Soc. Lond.* **2014**, *171*, 21–40. [CrossRef]
59. Kohn, M.J.; Malloy, M.A. Formation of monazite via prograde metamorphic reactions among common silicates: Implications for age determinations. *Geochim. Cosmochim. Acta* **2004**, *68*, 101–113. [CrossRef]
60. Skipton, D.R.; Schneider, D.A.; McFarlane, C.R.M.; St-Onge, M.R.; Jackson, S.E. Multi-stage zircon and monazite growth revealed by depth profiling and in situ U–Pb geochronology: Resolving the Paleoproterozoic tectonics of the Trans-Hudson Orogen on southeastern Baffin Island, Canada. *Precambrian Res.* **2016**, *285*, 272–298. [CrossRef]

61. Košler, J.; Fonneland, H.; Sylvester, P.; Tubrett, M.; Pedersen, R.-B. U–Pb dating of detrital zircons for sediment provenance studies—A comparison of laser ablation ICPMS and SIMS techniques. *Chem. Geol.* **2002**, *182*, 605–618. [CrossRef]
62. Prabha-Mohan, S.; Williams, I.S.; Singh, S. Direct zircon U–Pb evidence for pre-Himalayan HT metamorphism in the Higher Himalayan Crystallines, eastern Garhwal Himalaya, India. *Geol. J.* **2021**, *57*, 133–149. [CrossRef]
63. Valley, J.W.; Kinny, P.D.; Schulze, D.J.; Spicuzza, M.J. Zircon megacrysts from kimberlite: Oxygen isotope variability among mantle melts. *Contrib. Mineral. Petrol.* **1998**, *133*, 1–11. [CrossRef]
64. Valley, J.W. Oxygen Isotopes in Zircon. *Rev. Mineral. Geochem.* **2003**, *53*, 343–385. [CrossRef]
65. Valley, J.W.; Lackey, J.S.; Cavoie, A.J.; Clechenko, C.; Spicuzza, M.J.; Basei, M.A.S.; Bindeman, I.N.; Ferreira, V.P.; Sial, A.N.; King, E.M.; et al. 4.4 billion years of crustal maturation: Oxygen isotope ratios of magmatic zircon. *Contrib. Mineral. Petrol.* **2005**, *150*, 561–580. [CrossRef]
66. Claesson, S.; Bibikova, E.V.; Shumlyanskyy, L.; Whitehouse, M.J.; Billström, K. Can oxygen isotopes in magmatic zircon be modified by metamorphism? A case study from the Eoarchean Dniester-Bug Series, Ukrainian Shield. *Precambrian Res.* **2016**, *273*, 1–11. [CrossRef]
67. Ayers, J.C.; Loflin, M.; Miller, C.F.; Barton, M.D.; Coath, C.D. In situ oxygen isotope analysis of monazite as a monitor of fluid infiltration during contact metamorphism: Birch Creek Pluton aureole, White Mountains, eastern California. *Geology* **2006**, *34*, 653–656. [CrossRef]
68. Gauthiez-Putallaz, L.; Rubatto, D.; Hermann, J. Dating prograde fluid pulses during subduction by in situ U–Pb and oxygen isotope analysis. *Contrib. Mineral. Petrol.* **2016**, *171*, 15. [CrossRef]
69. Vho, A.; Lanari, P.; Rubatto, D. An Internally-Consistent Database for Oxygen Isotope Fractionation Between Minerals. *J. Petrol.* **2019**, *60*, 2101–2130. [CrossRef]
70. Gupta, S.; Das, A.; Goswami, S. Evidence for structural discordance in the inverted metamorphic sequence of Sikkim Himalaya: Towards resolving the Main Central Thrust controversy. *J. Geol. Soc. India* **2010**, *75*, 313–322. [CrossRef]
71. GSI Miscellaneous Publication. Geology and Mineral Resources of Sikkim. *Geol. Surv. India Misc. Publ.* **2012**, *30*, 54.
72. Mukhopadhyay, D.K.; Chakraborty, S.; Treppmann, C.; Rubatto, D.; Anczkiewicz, R.; Gaidies, F.; Dasgupta, S.; Chowdhury, P. The nature and evolution of the Main Central Thrust: Structural and geochronological constraints from the Sikkim Himalaya, NE India. *Lithos* **2017**, *282–283*, 447–463. [CrossRef]
73. Jain, A.K.; Banerjee, D.M.; Kale, V.S. *Tectonics of the Indian Subcontinent*; Society of Earth Scientists Series; Springer Publication: Cham, Switzerland, 2020; 576p. [CrossRef]
74. Dasgupta, S.; Ganguly, J.; Neogi, S. Inverted metamorphic sequence in the Sikkim Himalayas: Crystallization history, P–T gradient and implications. *J. Metamorph. Geol.* **2004**, *22*, 395–412. [CrossRef]
75. Ganguly, J.; Dasgupta, S.; Cheng, W.; Neogi, S. Exhumation history of a section of the Sikkim Himalayas, India: Records in the metamorphic mineral equilibria and compositional zoning of garnet. *Earth Planet. Sci. Lett.* **2000**, *183*, 471–486. [CrossRef]
76. Sorcar, N.; Hoffe, U.; Dasgupta, S.; Chakraborty, S. High temperature cooling histories of migmatites from the High Himalayan Crystallines in Sikkim, India-rapid cooling unrelated to exhumation. *Contrib. Mineral. Petrol.* **2014**, *167*, 957. [CrossRef]
77. Anczkiewicz, R.; Chakraborty, S.; Dasgupta, S.; Mukhopadhyay, D.; Kołtonik, K. Timing, duration, and inversion of prograde Barrovian metamorphism constrained by high-resolution Lu–Hf garnet dating: A case study from the Sikkim Himalaya, NE India. *Earth Planet. Sci. Lett.* **2014**, *407*, 70–81. [CrossRef]
78. Black, L.P.; Kamo, S.L.; Allen, C.M.; Davis, D.W.; Aleinikoff, J.N.; Valley, J.W.; Mundil, R.; Campbell, I.H.; Korsch, R.J.; Williams, I.S.; et al. Improved $^{206}\text{Pb}/^{238}\text{U}$ microprobe geochronology by the monitoring of a trace-element-related matrix effect; SHRIMP, ID-TIMS, ELA-ICP-MS and oxygen isotope documentation for a series of zircon standards. *Chem. Geol.* **2004**, *205*, 115–140. [CrossRef]
79. Aleinikoff, J.N.; Schenck, W.S.; Plank, M.O.; Srogi, L.; Fanning, C.M.; Kamo, S.L.; Bosbyshell, H. Deciphering igneous and metamorphic events in high-grade rocks of the Wilmington Complex, Delaware: Morphology, cathodoluminescence and backscattered electron zoning, and SHRIMP U–Pb geochronology of zircon and monazite. *Geol. Soc. Am. Bull.* **2006**, *118*, 39–64. [CrossRef]
80. Rubatto, D.; Putlitz, B.; Gauthiez-Putallaz, L.; Crépeisson, C.; Buick, I.S.; Zheng, Y.F. Measurement of in-situ oxygen isotope ratios in monazite by SHRIMP ion microprobe: Standards, protocols and implications. *Chem. Geol.* **2014**, *380*, 84–96. [CrossRef]
81. Kusakabe, M.; Matsuhisa, A. Oxygen three-isotope ratios of silicate reference materials determined by direct comparison with VSMOW-oxygen. *Geochem. J.* **2008**, *42*, 309–317. [CrossRef]
82. Williams, I.S. U–Th–Pb Geochronology by Ion Microprobe. In *Applications of Microanalytical Techniques to Understanding Mineralizing Processes: Reviews in Economic Geology*; McKibben, M.A., Shanks, W.C., III, Ridley, W.I., Eds.; Society of Economic Geologists: Littleton, CO, USA, 1998; Volume 7, pp. 1–35.
83. Claoué-Long, J.C.; Compston, W.; Roberts, J.; Fanning, C.M. Two Carboniferous ages: A comparison of SHRIMP zircon dating with conventional zircon ages and $^{40}\text{Ar}/^{39}\text{Ar}$ analysis. In *Geochronology, Timescales and Global Stratigraphic Correlation*; Berggren, W.A., Kent, D.V., Aubry, M.-P., Hardenbol, J., Eds.; SEPM Special Publication; SEPM Society for Sedimentary Geology: Claremore, OK USA, 1995; Volume 54, pp. 3–21.
84. Cumming, G.L.; Richards, J.R. Ore lead isotope ratios in a continuously changing earth. *Earth Planet. Sci. Lett.* **1975**, *28*, 155–171. [CrossRef]

85. Steiger, R.H.; Jäger, E. Subcommission on geochronology: Convention on the use of decay constants in geo- and cosmo-chronology. *Earth Planet. Sci. Lett.* **1977**, *36*, 359–362. [CrossRef]
86. Ickert, R.B.; Hiess, J.; Williams, I.S.; Holden, P.; Ireland, T.R.; Lanc, P.; Schram, N.; Foster, J.J.; Clement, S.W. Determining high precision, in situ, oxygen isotope ratios with a SHRIMP II: Analyses of MPI-DING silicate-glass reference materials and zircon from contrasting granites. *Chem. Geol.* **2008**, *257*, 114–128. [CrossRef]
87. Corfu, F.; Hanchar, J.M.; Hoskin, P.W.O.; Kinny, P. Atlas Zircon Textures. *Rev. Mineral. Geochem.* **2003**, *53*, 469–500. [CrossRef]
88. Spencer, C.J.; Harris, R.A.; Dorais, M.J. Depositional provenance of the Himalayan metamorphic core of Garhwal region, India: Constrained by U-Pb and Hf isotopes in zircons. *Gondwana Res.* **2012**, *22*, 26–35. [CrossRef]
89. Dhiman, R.; Singh, S. Neoproterozoic and Cambro-Ordovician magmatism: Episodic growth and reworking of continental crust, Himachal Himalaya, India. *Int. Geol. Rev.* **2021**, *63*, 422–436. [CrossRef]
90. Jeon, H.; Williams, I.S.; Chappell, B.W. Magma to mud to magma: Rapid crustal recycling by Permian granite magmatism near the eastern Gondwana margin. *Earth Planet. Sci. Lett.* **2012**, *319*, 104–117. [CrossRef]
91. Williams, I.S. Response of detrital zircon and monazite, and their U-Pb isotopic systems, to regional metamorphism and host-rock partial melting, Cooma Complex, southeastern Australia. *Aust. J. Earth Sci.* **2001**, *48*, 557–580. [CrossRef]
92. Rubatto, D.; Williams, I.S.; Buick, I.S. Zircon and monazite response to prograde metamorphism in the Reynolds Range, central Australia. *Contrib. Mineral. Petrol.* **2001**, *140*, 458–468. [CrossRef]
93. Long, S.; McQuarrie, N.; Tobgay, T. Tectonostratigraphy of the Lesser Himalaya of Bhutan: Implications for the along strike stratigraphic continuity of the northern Indian margin. *Geol. Soc. Am. Bull.* **2011**, *123*, 1406–1426. [CrossRef]
94. Jain, A.K.; Sushmita Singh, S.; Mukherjee, P.K. Migmatization, granite generation and melt accumulation in the Himalayan Orogenic Channel, Central and Eastern Bhutan. *Curr. Sci.* **2018**, *114*, 1903–1912. Available online: <http://www.jstor.org/stable/26495339> (accessed on 14 May 2018). [CrossRef]
95. Phillips, S.E.; Argles, T.W.; Warren, C.J.; Harris, N.B.W.; Kunz, B.E. Kyanite petrogenesis in migmatites: Resolving melting and metamorphic signatures. *Contrib. Mineral. Petrol.* **2023**, *178*, 10. [CrossRef]
96. Wotzlaw, J.-F.; Bindeman, I.N.; Watts, K.E.; Schmitt, A.K.; Caricchi, L.; Schaltegger, U. Linking rapid magma reservoir assembly and eruption trigger mechanisms at evolved Yellowstone-type supervolcanoes. *Geology* **2014**, *42*, 807–810. [CrossRef]
97. Sharp, Z. *Principles of Stable Isotope Geochemistry*, 2nd ed.; Prentice Hall: Hoboken, NJ, USA, 2017. [CrossRef]
98. Taylor, H.P.; Sheppard, S.M.F. Igneous rocks: I. Processes of isotopic fractionation and isotope systematics. In *Stable Isotopes in High Temperature Geological Processes. Reviews in Mineralogy*; Valley, J.W., Taylor, H.P., O’Neil, J.R., Eds.; Mineralogical Society of America: Washington, DC, USA, 1986; pp. 227–271.
99. Chappell, B.W.; White, A.J.R. I- and S-Type Granites in the Lachlan Fold Belt. *Trans. R. Soc. Edinb. Earth Sci.* **1992**, *83*, 1–26. [CrossRef]
100. King, E.M.; Valley, J.W. The source, magmatic contamination, and alteration of the Idaho batholith. *Contrib. Mineral. Petrol.* **2001**, *142*, 72–88. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

A Geochemical and Isotopic Investigation of Carbonatites from Huangshui, Central China: Implications for Petrogenesis and Mantle Sources

Hao Zhao ^{1,2,*}, Antonio Simonetti ³, Stefanie Simonetti ³, Xiaopeng Cao ⁴ and Yushan Du ¹

¹ Research Institute of Petroleum Exploration and Development, Shengli Oilfield Sinopec, Dongying 257015, China; duyushan817.slyt@sinopec.com

² Working Stations for Postdoctors of Shengli Oilfield, Dongying 257015, China

³ Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, South Bend, IN 46556, USA; antonio.simonetti.3@nd.edu (A.S.); simonetti.4@nd.edu (S.S.)

⁴ Xianhe Oil Production Plant of Sinopec Shengli Oilfield Company, Dongying 257068, China; caoxiaopeng.slyt@sinopec.com

* Correspondence: zhaohao716.slyt@sinopec.com

Abstract: The exact geological processes involved in the formation of subduction zone-related carbonatites remain ambiguous, along with their implications for crustal/carbon recycling in carbonatite melt generation. This study provides new geochemical and stable (C, O) and radiogenic (Sr, Nd, Pb) isotope data for Huangshui carbonatite, located within the Lesser Qinling Orogen, with the aim to decipher its complex petrogenetic history. The carbonatites display elevated CaO, low MgO and alkali contents, and significant enrichments of Pb, Mo, and HREEs compared to typical carbonatites. The $\delta^{13}\text{C}_{\text{PDB}}$ (−4.6 to −4.9‰) and $\delta^{18}\text{O}_{\text{SMOW}}$ (+6.6 to +7.8‰) values plot within the field of primary igneous carbonatites. The carbonatites are characterized by consistent radiogenic isotopic compositions [$(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.70599\text{--}0.70603$; $\epsilon_{\text{Nd}} = -10.4$ to -12.8 ; $^{206}\text{Pb}/^{204}\text{Pb} = 16.24\text{--}17.74$]. These combined results suggest that the carbonatites represent late-stage differentiation products of a parental, mantle-derived carbonatite melt. Their corresponding Sr-Nd-Pb isotopic compositions support the hypothesis that the Lesser Qinling carbonatites originate from a heterogeneous upper mantle source involving an EMI-like mantle component coupled with minor assimilation of the basement rocks. The parental carbonatite melt was derived by the melting of carbonate-bearing subcontinental lithospheric mantle metasomatized as the result of Early Triassic subduction of the Mianlue Ocean.

Keywords: carbonatite; Lesser Qinling Orogen; Huangshui; C-O-Sr-Nd-Pb isotope; mantle source

1. Introduction

Carbonatites are considered unique mantle-derived igneous rocks [1–3], which consist of >50% carbonate minerals [4] and are most notably enriched in rare earth elements (REEs), and other incompatible trace elements, such as Sr and Ba. Carbonatitic melts are extremely mobile as their low viscosities facilitate their rapid ascent, transport, and emplacement [5–7]. Their low viscosity reduces the likelihood of host rock–melt interaction/contamination during their ascent through the subcontinental lithospheric mantle and overlying crust; consequently, carbonatitic melts can preserve their inherited primary radiogenic isotope compositions from their upper mantle sources [8]. Additionally, their elevated Sr (>>1000 ppm) and Nd (100 s of ppm) contents buffer their mantle-inherited radiogenic isotope signatures against crustal contamination processes [1,9]. Hence, these combined chemical and physical properties render carbonatites as insightful probes into deciphering the chemical nature, metasomatic history, temporal evolution, and carbon cycle of Earth's upper mantle [1,10–14].

Carbonatites occur in different tectonic environments [4], but predominantly within anorogenic settings related to intracontinental rifts (e.g., East African Rift) [11,15], and rarely hosted within oceanic plates (e.g., Cape Verde Islands) [13,16] and orogenic domains (e.g., Qinglin) [3,17]. Moreover, there remains much debate as to whether carbonatitic melts are derived exclusively within the lithosphere [10], the subcontinental lithosphere [18–20], or asthenosphere (or deeper levels of the mantle) [1,21,22]. Bell and Simonetti [1] hypothesized a heterogeneous (mixed) mantle source for most carbonatites [23,24] based primarily on the critical stable (C, O) and radiogenic (Nd, Sr, and Pb) signatures of young (<200 Ma) carbonatites worldwide. In brief, carbonatite melts are derived from a heterogeneous mantle source that may involve HIMU (high- μ ; $^{238}\text{U}/^{204}\text{Pb}$ ratio) [25], EM I (enriched mantle I) [26], and FOZO (FOcal ZOne) [26], and have been linked to a volatile-rich, asthenospheric/plume mantle interacting with overlying lithosphere.

The Lesser Qinling carbonatite occurrences within the Qinling orogenic belt are situated in central China (Figure 1). Subsequent to the recognition of carbonatite-related mineralization, multiple commodities have been exploited, including REE, Mo, Nb, and U ores [3,27–29]. Numerous previous studies have investigated the chronology, mineralization, petrological evolution, mantle source, and tectonic setting of the carbonatite complexes within the Lesser Qinling [3,17,27,28,30–33]. The timing of generation and ore mineralization associated with these carbonatites occurred between 197 Ma and 225 Ma [31,32,34–37]. Huang [31] and Cao [35] reported Re–Os ages for molybdenite from Huangshuiian (HSA) carbonatite and their record ages of 209.5 ± 4.2 Ma and 208.4 ± 3.6 Ma. A new and similar LA-ICP-MS U–Th–Pb age of 207 ± 4 Ma was obtained for bastnäsite from this deposit [36]. The Lesser Qinling carbonatites are unique and important mineral resources, and host economic deposits of molybdenite with total reserves of approximately 80×10^4 t Mo metal [27,35,38,39]. These carbonatites are associated with quartz and are characterized by relatively flat REE patterns with enrichment in HREEs, which is a distinct feature compared to most carbonatites worldwide [3,17,28,40]. The enrichment in HREEs and Mo for these carbonatites is attributed to significant crystal fractionation involving calcite and non-silicate minerals (e.g., oxides and apatite) coupled with precipitation of a C–H–O supercritical fluid enriched in HREE, Mo, Si, and sulfate [17,32,33]. In an alternative hypothesis, the carbonatite magmas metasomatized the thickened eclogitic lower crust that produced high levels of Mo and HREE [3]. Moreover, the late-stage alteration with non-LREE-selective ligands (e.g., Cl^- , CO_3^{2-} , SO_4^{2-}) was suggested to account for the preferential HREE addition in the carbonatites [28].

Several previous investigations proposed that the Late Triassic Lesser Qinling carbonatites formed in a post-collisional extensional setting that occurred between the North and South China Blocks [30,33,41]. It is postulated that they are the result of fractional crystallization of primary alkaline silicate–carbonate melt derived from the partial melting of lithospheric mantle characterized by Sr–Nd–Pb isotopic compositions of EM I-like mantle [17,29–32]. Notably, it is postulated that their mantle sources contain recycled crustal materials [42] and are chemically enriched by subducted sedimentary carbonates [3,29]. Carbonate magmatism metasomatized the thickened eclogitic lower crust, which in turn may produce an enriched subcontinental lithospheric source [3,30]. Experimental petrology provides support for this latter hypothesis that involves the melting of carbonated eclogites at pressures > 2.5 GPa [43,44]. Alternatively, Xu [45] argued that 15%–20% of lower crustal granulites were incorporated into the subcratonic mantle beneath the Qinling region. Çimen et al. [46] argue that the Miaoya carbonatite complex in South Qinling was derived from an isotopically heterogeneous mantle source containing recycled crustal carbon. Direct evidence for this interpretation is provided by the occurrence of a slab-derived eclogite xenolith identified within the Paleoproterozoic Fengzhen carbonatite in the North China craton [47].

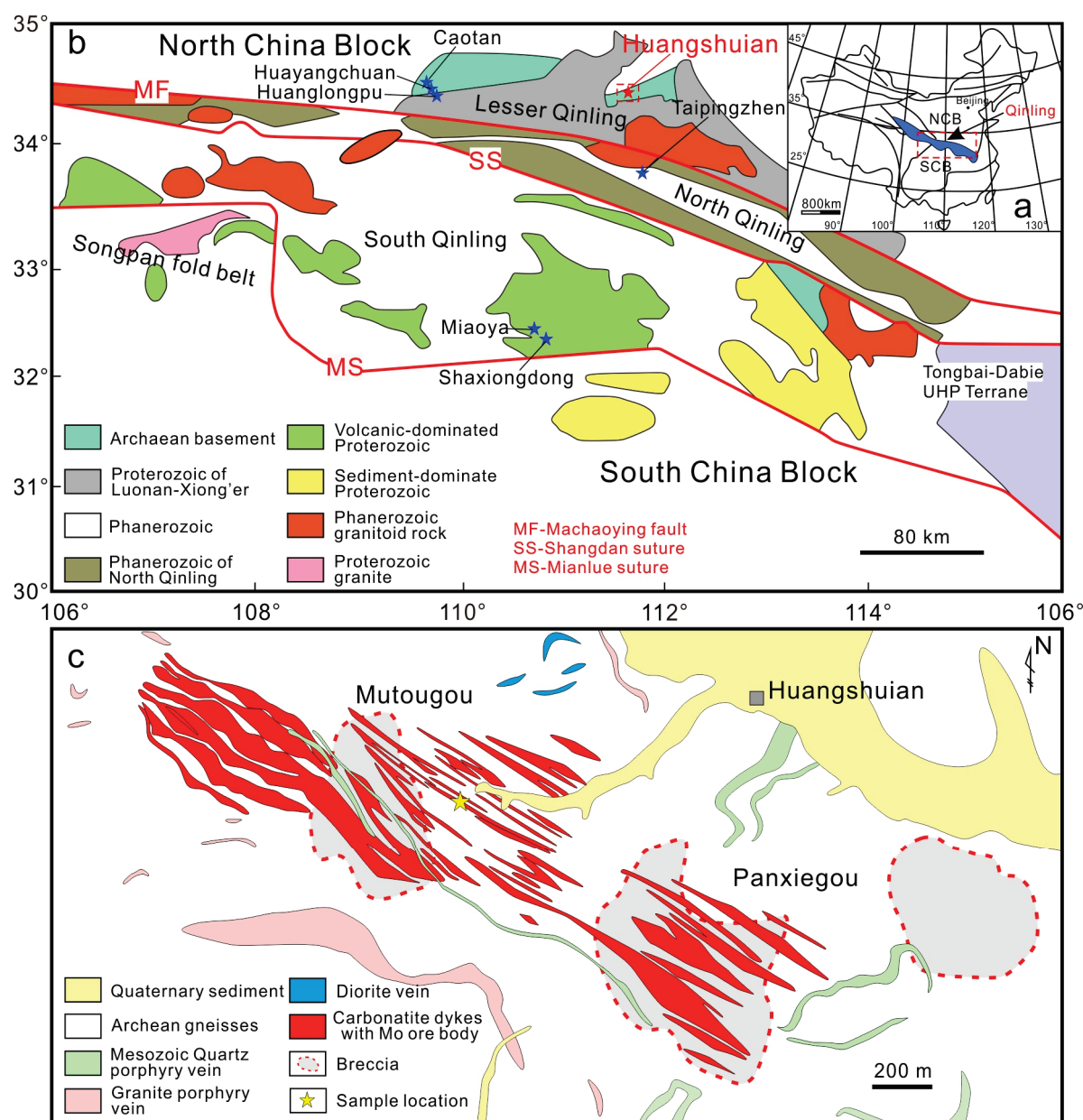


Figure 1. (a) Tectonic regions of China [30]. NCB—North China Block; SCB—South China Block. (b) Geological sketch map illustrating the locations of carbonatite complexes within the Qinling orogenic belt, including the HSA complex [30]. (c) Simplified geological maps of the HSA carbonatite complex [35].

To date, most previous investigations have focused on carbonatites located within anorogenic settings, whereas those related or found within collision/subduction zones have received relatively less attention [48]. In particular, there remains a lack of clear understanding of the geological processes involved, and systematic investigation of their genesis, source, and impact of crustal recycling on carbonatite melt generation. Thus, this study reports new stable (C, O) and radiogenic (Sr, Nd, Pb) isotope data, combined with major and trace elements signatures from the collision-related HSA carbonatite complex, in Lesser Qinling Orogen, central China (Figure 1). The geochemical and remaining isotope signatures will be used to decipher the complex petrogenetic history of the carbonatite and provide valuable insights into the chemical nature of its upper mantle source.

2. Geological Setting and Sample Descriptions

The Qinling orogenic belt, located in central China, separates the South China Block from the North China Block. It is regarded as a multistage orogenic belt recording the closure of the northernmost Paleo-Tethys Sea, the final continental collision between the North China Craton and Yangtze Craton [49]. It can be tectonically divided into four sections from north to south and delineated by main sutures, namely the Lesser Qinling orogenic belt, the North Qinling orogenic belt, the South Qinling orogenic belt, and the Songpan fold belt at the northern margin of the Yangtze Craton (Figure 1a,b) [49]. The Lesser Qinling orogenic belt lies within the Huaxiong Block, which forms part of the southern margin of the North China Block and comprises a crystalline basement, i.e., Mesoproterozoic Taihua Group of amphibolite-to-granulite facies suite and Neoproterozoic Dengfeng Group of granite–greenstone affinity [50]. The basement is unconformably overlain by the ~1780 Ma Mesoproterozoic intermediate to felsic volcanic rocks of the Xiong'er Group [51]. In turn, the Xiong'er Group volcanics are overlain by the Mesoproterozoic littoral clastic and carbonate rocks of the Guandaokou Group, the Neoproterozoic shallow marine clastic and carbonate rocks of the Luanchuan Group, and the Cambrian to Ordovician passive marginal sediments [52]. The Mesozoic magmatic intrusions are widely distributed within the Lesser Qinling region and were emplaced mainly at 220–190 and 160–110 Ma. The former stage is dominated by alkaline granites, which are inferred to form in a post-collisional extensional environment [53]. The latter stage is characterized by Late Jurassic–Early Cretaceous granites and porphyries, commonly associated with Mo mineralization [54,55].

The carbonatite complexes in Lesser Qinling Orogen include Caotan (CT), Huayangchuan (HYC), Huanglongpu (HLP), and Huangshui (HSA) from west to east (Figure 1b). Compared to the HLP carbonatite, which was discovered earlier, the HSA carbonatite complex also contains a similar, significant economic value. It is in Songxian county within the western Henan Province (Figure 1c). HSA carbonatite typically occurs as dykes or veins and intrudes into the Neoproterozoic Taihua Group gneiss, and these extend from <1 m to >1 km in length and follow a main NW-trending fault [31]. The carbonatite dykes and gneiss are locally crushed and occur as breccia, and silicification, feldspathization, sulfuration, and carbonatization are generally common at their contact margins. Of note, carbonatite is associated with Mo-(REE) mineralization with an estimated Mo reserve of 19.86×10^4 t with an average grade of 0.082 wt. % [35]. Huang [31] and Bai [33] detail and summarize the geology, petrography, geochemistry, and mineralization of the carbonatites, and their relationship to the molybdenum deposits at HSA and HLP. These previous studies postulated that these rocks were derived from extensive fractional crystallization of a common carbonated silicate parental melt generated from an EM1-like mantle based on their REE patterns and radiogenic isotope compositions.

The Lesser Qinling carbonatite has a complex mineral paragenetic sequence that involves three mineralization stages for the carbonatite veins: 1—an early quartz K-feldspar stage; 2—a middle sulfide–REE mineral stage, and a 3—late sulfate–biotite stage [33]. The HSA carbonatites are generally dominated by calcite, quartz, and K-feldspar, which show extremely uneven mineral distribution in a single dyke (Figure 2). The calcite is pink or white in color, medium- or coarse-grained euhedral. The quartz and K-feldspar are coarse-grained anhedral and crystallized earlier than calcite (Figure 2j,k). The mineralized carbonatite veins commonly contain variable amounts of accessory mineral phases including pyrite, galena, molybdenite, barite, and celestite with minor REE minerals (monazite, bastnäsite, and parisite). Molybdenite is closely associated with REE minerals and usually disseminated within the calcite and quartz microfractures in the form of disseminated and veined (Figure 2l). Lastly, other accessory minerals include aegirine (Figure 2e,j), augite, and magnetite.

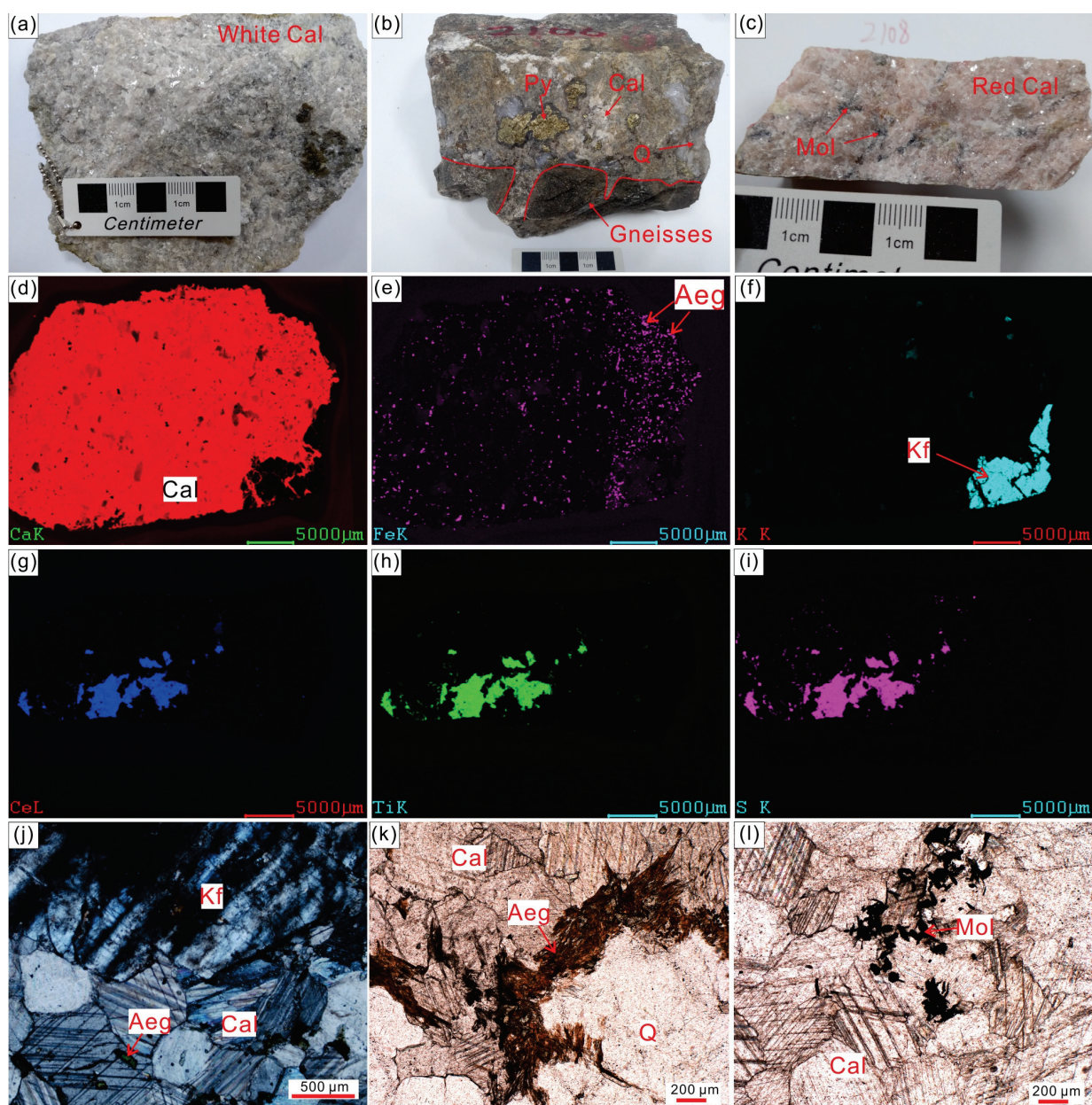


Figure 2. Photographs illustrating the textures and mineralogy of HSA carbonatite rocks investigated here. (a) Sample 2106 showing the white carbonatite with medium-grained calcite (Cal). (b) Sample 2106 exhibiting the contact margin between carbonatite and wall rock with silicification (Q: quartz) and sulfuration (Py: pyrite). (c) Sample 2108 representing pink carbonatite with sparsely disseminated molybdenite. Micro-XRF images illustrating distribution of Ca (d), Fe (e), and K (f) for sample 2104; Ce (g), Ti (h), and S (i) for sample 2108 showing the presence of calcite (Cal), fine-grained aegirine (Aeg), and K-feldspar (Kf). Photomicrographs for samples 2104 (j), 2105 (k), and 2108 (l) displaying the domination medium-grained calcite with early coarse-grained anhedral quartz and K-feldspar, and late interstitial aegirine and molybdenite (Mol).

3. Analytical Methods

Semi-quantitative major element compositional maps (Si, Al, Mg, Ca, Fe, Ti, K, P, S) for samples investigated here were produced with ~100 µm thick petrographic sections using an Edax Orbis micro-XRF instrument (AMETEK, Inc., Berwyn, PA, USA) housed at the Center for Environmental Science and Technology (CEST), University of Notre Dame (UND). The chemical maps were generated using a 30 µm beam overnight (~12 h) with

an amplification time of 12.8 μ s and a fluorescent energy of 32 kV. The major element concentrations for whole-rock sample powders were determined by ICP-OES (Inductively Coupled Plasma–Optical Emission Spectrometry, PerkinElmer, Inc., Waltham, MA, USA) within CEST (UND) using an external calibration technique, whereas trace element abundances were obtained by ICP-MS (Inductively Coupled Plasma–Mass Spectrometry) at the Midwest Isotope and Trace Element Research Analytical Center (MITERAC, UND). Trace element abundances were obtained using a Nu Plasma atom High-Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS, Nu Instruments Ltd., Wrexham, UK) in medium-resolution mode ($M/\Delta M \approx 3000$) housed within MITERAC. At the start of each analytical session, the instrument was tuned and calibrated with a multi-element 1 ppb standard solution. The concentrations of the trace elements were determined by a standard/spike addition method [56], which includes corrections for matrix effects and instrumental drift.

The carbon and oxygen isotope analyses for calcite separates were conducted by reacting carbonate powder with concentrated H_3PO_4 (100%) at 100 °C [57], using a Delta V Advantage isotope ratio mass spectrometer housed at CEST. Results are reported in per mil notation (‰) using standard delta notation relative to Peedee belemnite (PDB) and standard mean ocean water (SMOW). The accuracy of the $\delta^{13}C$ and $\delta^{18}O$ values reported here was validated by using three standards: NBS 19, YWCC, and ROYCC.

The bulk-rock Sr, Nd, and Pb isotope measurements reported here were analyzed using a NuPlasma II MC-ICP-MS instrument at MITERAC. Sr isotope measurements were determined using the protocols described in [58], with further details of ion exchange separation and collection for Sr outlined in [46]. Strontium isotope ratios were measured using 5 Faraday collectors in static, multi-collection mode and in dry plasma mode utilizing a DSN-100 desolating system (Nu Instruments, Wales, UK). The accuracy and reproducibility of the Sr isotope results were verified using a 100 ppb solution of the NIST SRM 987 strontium isotope standard, and the average value obtained for $^{87}Sr/^{86}Sr$ ratio was 0.710153 ± 0.000027 (2σ standard deviation; $n = 6$); the Sr isotope ratios for the samples were therefore normalized to the accepted value for the NIST SRM 987 standard ($^{87}Sr/^{86}Sr = 0.710245$). The Nd isotope ratios were determined using the same MC-ICP-MS instrument and following the analytical protocol described in [46]. REEs and Nd were sequentially separated using ion exchange columns containing AG50W-X8 and Eichrom Ln-Spec resins, respectively. The mass bias and drift for the instrument were calibrated using the repeated analysis of a 100 ppb solution of the JNdi-1 standard, which yielded an average $^{143}Nd/^{144}Nd$ value of 0.512090 ± 0.000010 (2σ standard deviation; $n = 4$); the accepted $^{143}Nd/^{144}Nd$ is 0.512115 [59].

The procedure for analyzing Pb isotope compositions via solution-mode MC-ICP-MS is described in [60]. The chemical separation and purification procedure involving ion exchange chromatography followed the procedures described by [61]. The purified Pb aliquot is spiked with a NIST SRM 997 Thallium standard solution (2.5 ppb) prior to analysis in dry plasma mode for instrumental mass bias correction based on the measured $^{205}Tl/^{203}Tl$ ($=2.3871$) for the NIST SRM 997 Tl isotope standard using the exponential fractionation law. Prior to sample introduction, a baseline (“on-peak-zero”) measurement consisting of the gas and acid blank was conducted for 30 s. Throughout the two analytical sessions, a 25 ppb solution of the standard NIST SRM 981 Pb (spiked with 6 ppb NIST SRM 997 Tl standard) was also analyzed periodically. Repeated measurements ($n = 9$) of the NIST SRM 981 + Tl standard solution yielded average values and associated (2σ) standard deviations as follows: $^{206}Pb/^{204}Pb = 16.936 \pm 0.021$, $^{207}Pb/^{204}Pb = 15.491 \pm 0.009$, $^{208}Pb/^{204}Pb = 36.697 \pm 0.009$, which are within analytical uncertainty of the accepted values for this standard given the associated uncertainties [62].

4. Results

4.1. Whole-Rock Geochemistry

The major and trace element results for HSA carbonatite samples investigated here are listed in Table S1 and trace element abundances illustrated in Figure 3. All carbonatite samples define low MgO and alkali abundances, and high and variable CaO (41.48–51.04 wt. %) contents, which are typical for calciocarbonatite [4] with CaO/(CaO + MgO + FeO + MnO) ratios of 96.0–96.8. The trace element signatures for HSA carbonatite reported here are similar in general, and completely overlap those previously reported for Lesser Qinling carbonatite except for the abundances of Mo (4.38–950 ppm), which are significantly higher than the average calcite carbonatite value of 12 ppm (Figure 3) [33]. The HSA carbonatite samples exhibit relatively consistent primitive mantle-normalized trace element patterns (Figure 3a), and are characterized by the enrichment of Ba, U, Pb, and Sr and strong depletion of the high-field-strength elements (HFSEs: Nb, Ta, Zr and Hf). They also display lower Rb and higher Pb and Y abundances relative to those for typical calciocarbonatite [4]. Of particular interest is the fact that these samples contain substantially higher HREE abundances compared to average carbonatite worldwide ([63] and references therein). The total REE abundances range from 895 to 4760 ppm for the HAS carbonatite samples, and chondrite normalized REE patterns display negative slopes with variable (La/Yb)_N ratios that range from 9.28 to 62.16, and lack Eu anomalies (Figure 3b).

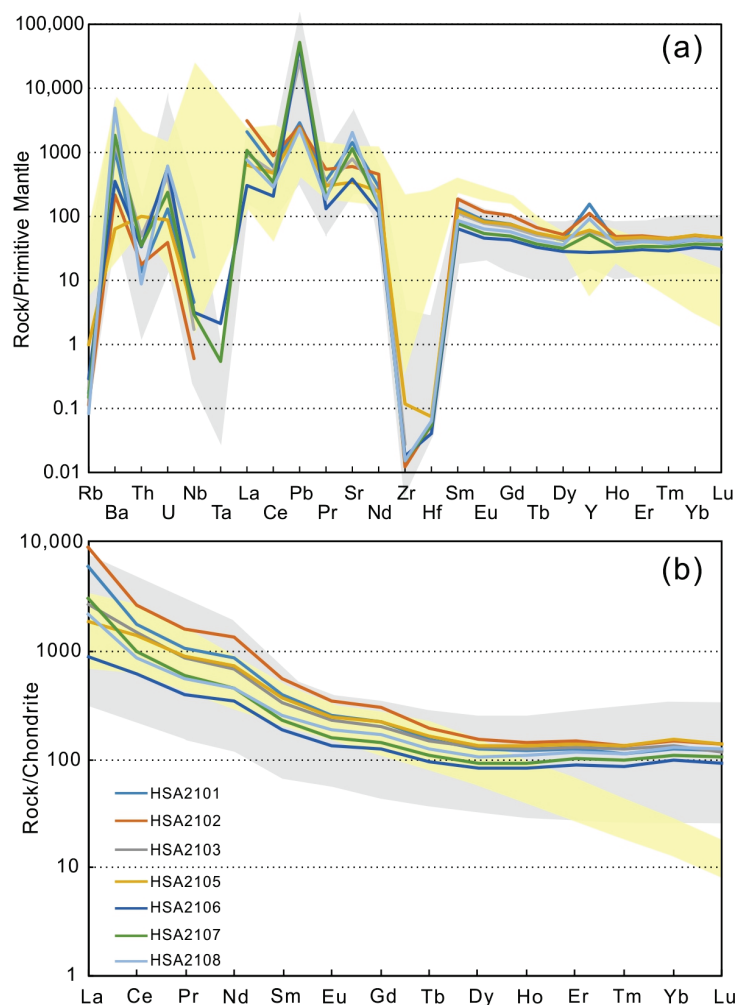


Figure 3. (a) Primitive mantle-normalized trace element spidergrams. (b) Chondrite-normalized REE patterns for samples of HSA carbonatite. Primitive mantle values and chondrite values are from [64]. The gray field represents the chondrite-normalized REE data for bulk carbonatites from Lesser Qinling [33], whereas the light yellow field represents compositions for average calciocarbonatite [4].

4.2. C and O Isotope Compositions

The C and O isotope data obtained here for calcite separates from samples of HSA carbonatite and are summarized in Table S2 and illustrated in Figure 4. A majority of the calcite separates from carbonatite within the HSA complex record a remarkably uniform range of $\delta^{13}\text{C}_{\text{PDB}}$ (−4.6 to −4.9‰) and $\delta^{18}\text{O}_{\text{SMOW}}$ (+6.6 to +7.8‰) values, respectively, and plot within the field defined for “primary igneous carbonatites” (PIC). In addition, one sample (HSA2106) exhibits lower $\delta^{13}\text{C}_{\text{PDB}}$ (−5.1‰) but significantly lower $\delta^{18}\text{O}_{\text{SMOW}}$ (+5.1‰) values (Figure 4), and plots slightly to the left of the PIC box (Figure 4). The carbonate investigated here from HSA carbonatite displays similar C and O isotope compositions compared to those reported in [31,33], but has higher $\delta^{13}\text{C}_{\text{PDB}}$ values relative to those recorded for carbonatite from the HLP complex [27,65].

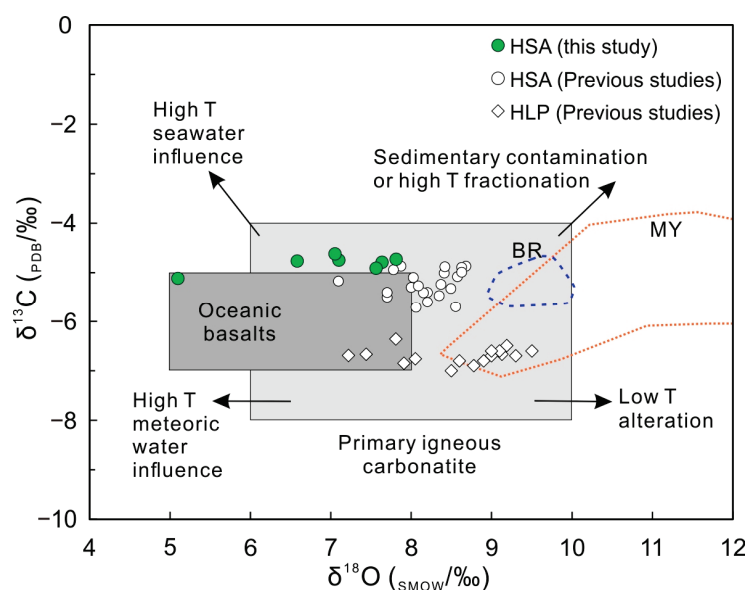


Figure 4. Illustrates carbon and oxygen isotopic compositions for carbonate separated from the HSA carbonatite samples investigated here. The white-colored points represent analyses for samples from HSA reported previously by [31,33]. These are compared to those carbonatites from HLP [27,65], South Qinling (MY) [45,46] and Blue River, Canada (BR) [66]. Primary igneous carbonatite field and oceanic basalts box as defined by [67]. Illustrated are the major processes responsible for changes in C–O isotopic composition of carbonatites [68].

4.3. Sr, Nd, and Pb Isotope Compositions

The new Sr, Nd, and Pb isotopic data for samples of HSA carbonatite are listed in Tables S3 and S4 and displayed in Figures 5 and 6. The age of 208 Ma (molybdenite Re–Os) [35] for the HSA carbonatite has been adopted for the age corrections of measured isotope ratios.

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios for HSA carbonatites investigated here display a limited range with values between 0.70599 and 0.70603, which are slightly higher compared to the HLP carbonatites (Figure 5). The initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios range between 0.51171 and 0.51184, which correspond to $\epsilon_{\text{Nd}(t)}$ values of −10.4 to −12.8, similar to the range of values previously reported for HSA carbonatites [31], and lower than those for HLP carbonatites [30]. The T_{DM} Nd model ages for the carbonatites range from 1.38 to 1.80 Ga (Table S3). The initial Sr isotope ratios are relatively close to the values expected for melts derived from an EM I (enriched mantle I) mantle component, but are more radiogenic in nature (i.e., higher Sr and lower Nd ratios).

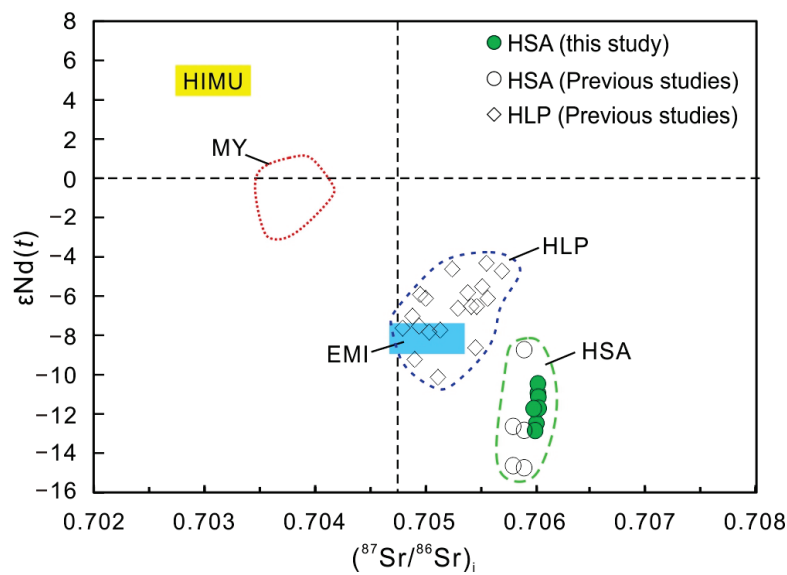


Figure 5. Diagrams of initial $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $\epsilon_{\text{Nd}(t)}$ values for samples of HSA carbonatite. These are compared to initial Sr and Nd isotope data reported for those carbonatites from Lesser Qinling [30,31], and South Qinling (MY) [45,46]. The fields for HIMU and EM I (enriched mantle I) mantle components are from [69].

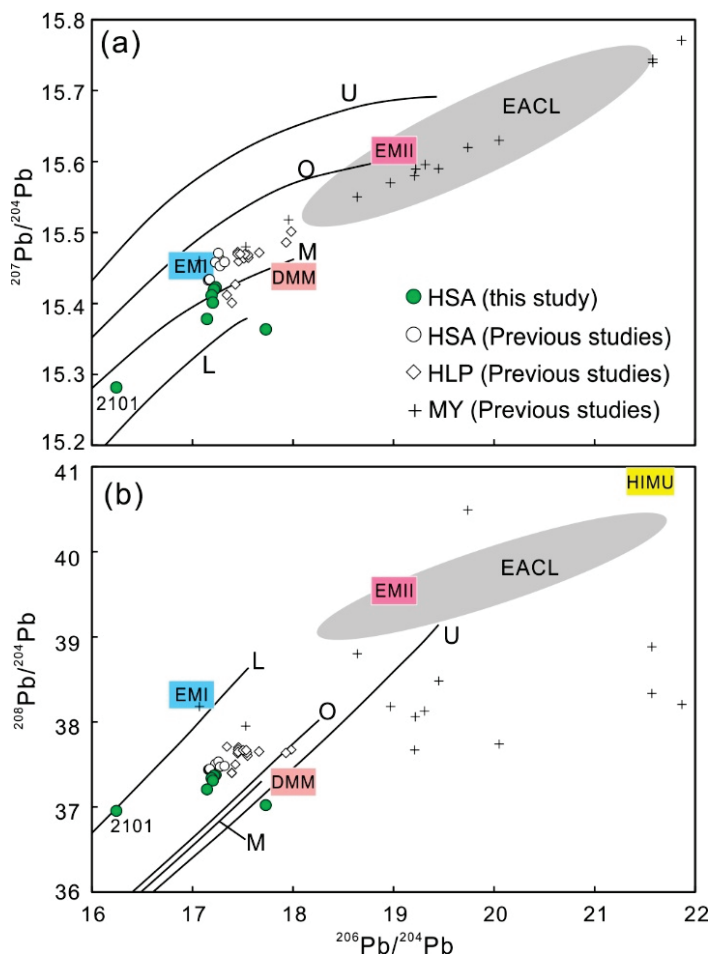


Figure 6. Diagrams of initial $^{207}\text{Pb}/^{204}\text{Pb}$ (a) and initial $^{208}\text{Pb}/^{204}\text{Pb}$ (b) vs. $^{206}\text{Pb}/^{204}\text{Pb}$ values for samples of HSA carbonatite. These are compared to initial Pb isotope data reported for those

carbonatites from Lesser Qinling (HSA and HLP) [30,31] and South Qinling (MY) [45,46]. These Pb isotopic features for EACL carbonatites are from [20]. The fields for HIMU, EM I, EM II, and DMM (depleted MORB mantle) mantle components are from [69]. The trends for U (upper crust), O (orogenic belt), M (mantle) and L (lower crust) are from [70].

The initial Pb isotope values for samples of HSA carbonatite define the following ranges: $^{206}\text{Pb}/^{204}\text{Pb}$ (16.24–17.73), $^{207}\text{Pb}/^{204}\text{Pb}$ (15.28–15.42), and $^{208}\text{Pb}/^{204}\text{Pb}$ (36.95–37.38), respectively. In general, the five samples investigated here show similar Pb isotope values compared to those previously reported for HSA and HLP carbonatites from Lesser Qinling [30,31]. Moreover, they have similar $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ but lower $^{208}\text{Pb}/^{204}\text{Pb}$ ratios compared to those for the EM I mantle component (Figure 6). Of note, sample HSA2106 is characterized by relatively low initial Pb isotope ratios (Table S4, Figure 7) and associated with a lighter $\delta^{18}\text{O}_{\text{SMOW}}$ composition (Figure 5).

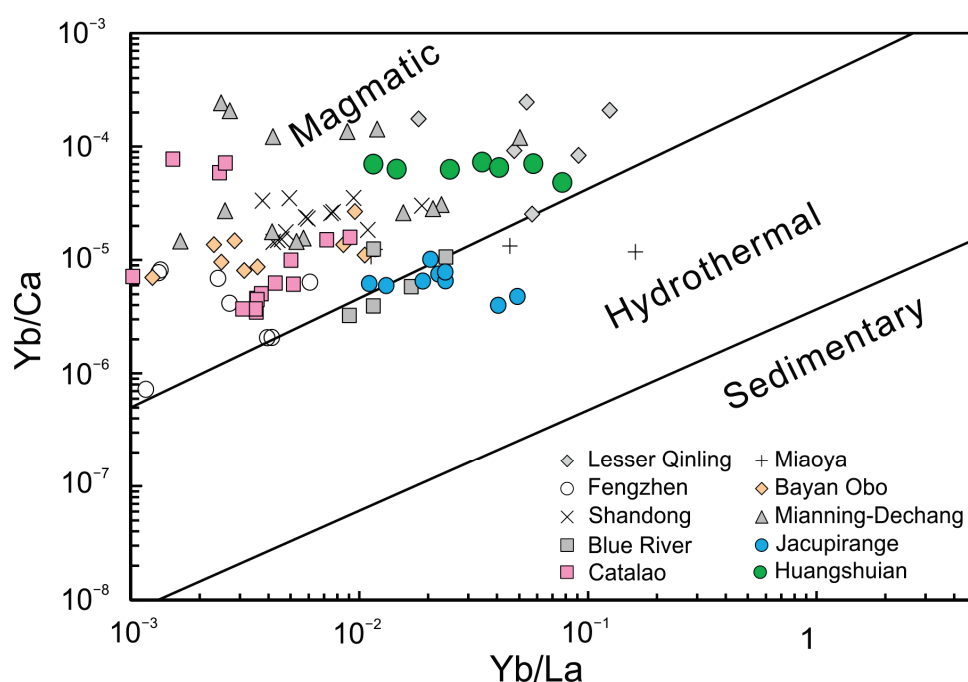


Figure 7. Yb/La vs. Yb/Ca diagram for HSA carbonatites [71]. These are compared to those carbonatites from Lesser Qinling reported previously by [31,33]; Miaoya [46], Fengzhen [47], Bayan Obo [72], Shandong [73], Mianning-Dechang [48], Blue River, Canada [66], Jacupiranga, Brazil [74], and Catalao, Brazil [75].

5. Discussion

5.1. Petrogenesis of the HSA Carbonatites

The stable carbon and oxygen isotopic values for these Lesser Qinling carbonatites plot mainly within the primary igneous carbonatite field (Figure 4), which is indicative of their pristine nature and derivation from mantle sources. Moreover, due to their low viscosity and high contents of both Sr and Nd, the feasibility of contamination of carbonatite magma is negligible [1]. Compared to the primitive mantle, HSA carbonatites exhibit enrichment in Sr, Ba, U, and Pb and depletion in HFSEs such as Nb, Ta, Zr, Hf and Ti. They also display higher total REE abundances without evident chondrite-normalized, negative Ce and Eu anomalies. They are characterized by negatively sloped chondrite-normalized REE patterns with enrichment of LREE and more pronounced fractionation between LREE and HREE compared to the average calciocarbonatite. Overall, these geochemical features are generally consistent with the characteristics of typical carbonatite worldwide. HSA carbonatites plot within the magmatic field in the Yb/La vs. Yb/Ca diagram (Figure 7).

The exact petrogenetic origin of carbonatites is still uncertain and has been attributed to three principal hypotheses: (1) low-degree, direct partial melting of a carbonate-bearing mantle [76–80]; (2) extensive fractional crystallization of a carbonated silicate magma [81–84]; and (3) liquid immiscibility between silicate and carbonate melts [81,82,85–90].

The Lesser Qinling carbonatites have abundant K-feldspar, quartz, and sulfate minerals, and are closely associated and co-crystallized with mafic minerals that suggest a common magmatic origin (Figure 2) [32,91]; this petrographic mineral assemblage is not common in typical carbonatite. HSA carbonatites record high CaO and low MgO and alkali contents ($\text{Na}_2\text{O} + \text{K}_2\text{O}$), which contrasts with primary carbonatite melt [87,92,93]. Hence, it is difficult to interpret the combined geochemical characteristics of the HSA carbonatites, as well as those from HYC and Bayan Obo [29]. For example, experimental results indicate that carbonatites formed by immiscibility are typically poor in alkali and abundant in silicate [93]. However, the HSA carbonatites contain much higher silicate contents, and are therefore not consistent with these experimental findings. Furthermore, elements such as Mo and W tend to preferentially enter the silicate phase during the liquid immiscibility process between carbonatite and silicate, leading to a lack of potential Mo mineralization associated with carbonatite [32]. Additionally, typical primary igneous carbonatites originating from metasomatized upper mantle source regions, such as the Spitskop carbonates in South Africa [92], are commonly associated with mafic silicate rocks and contain some specific, high-temperature/pressure minerals derived solely from the mantle, such as Cr-rich minerals and diamonds [22]. The HAS carbonatites lack such specific, mantle-derived minerals and contemporaneous related silicic rocks. Therefore, given these features, liquid immiscibility most likely cannot account for the formation of the HAS carbonatites.

Melting experiments conducted on carbonated peridotite produced low-degree partial melts (<1%) that contained relatively high MgO and alkali contents but very low SiO_2 abundances in equilibrium with mantle peridotite [94,95]. This carbonatite melt is converted from magnesium to calcium by segregated crystallization and CO_2 release [87,96]. The crystallization differentiation of carbonate, oxides, apatite, olivine, clinopyroxene, and other accessory minerals was interpreted to be critical in transforming primary Mg-rich carbonatite to Ca-rich carbonatite and significantly higher Si and Mo abundances in the Lesser Qinling carbonatitic magmas [17,29,32]. Carbonate minerals commonly present within carbonatites do not readily host incompatible elements such as Mo, REE, Sr, and Ba [3], which are enriched in residual melt. HAS carbonatites are characterized by extremely high Mo, Sr, and Ba contents, which indicates that these carbonatites do not represent the original magma, but likely represent residual melt fractions present in the late stages of carbonatite magma differentiation [17]. Moreover, the differentiated magnesiocarbonatite melt is characterized by low viscosity and is therefore capable of rapid ascent. When the pressure is <2 GPa, the melt composition changes by reacting with the surrounding rock at mantle depth, leading to an increase in CaO/MgO value and forming a calcite-rich composition. Wei [42] suggested that the calcite carbonatites from Caotan, which are also located within Lesser Qinling, are the product of metasomatic interaction between primary dolomitic melts and felsic wall rocks.

The carbonatite magmas resulting from low-degree partial melting of carbonated mantle peridotites and subsequent liquid immiscibility are usually enriched with LREE relative to HREE [97,98]. However, the HAS carbonatites contain higher HREE contents compared to typical carbonatites. The HREE enrichment of the Lesser Qinling carbonatites results in the uncommonly observed flat chondrite normalized REE pattern, and is believed to be the result of a combination of factors. Smith [28] proposed an HREE-enrichment model in which magmatic, HREE-enriched calcite with a relatively flat REE pattern provided a baseline source of secondary REE mineralization. Late-stage alteration with non-LREE-selective ligands may play an important role in forming HREE-enriched carbonatites [28]. Moreover, fractional crystallization of calcite assisted by high Si and alkaline activities will most likely yield primary HREE enrichment in the residual melts [99–101]. Sulfate

complexation may be a preferential ligand for the transport of REE, while the lack of free F-greatly reduces the precipitation of LREE [28,33,101].

In summary, it is hypothesized that HSA carbonatites most likely represent residual melts formed at the late stage of melt differentiation of the original carbonatite magma.

5.2. Source of the Carbonatite and Deep Tectonic Processes

Most young (<200 Ma) carbonatites worldwide show variable Sr, Nd, and Pb isotopic compositions overlapping with those for oceanic island basalts (OIBs), which indicate derivation from a heterogeneous mantle source involving HIMU, EMI, and FOZO mantle components [1,15,17,20]. The EMI-type mantle end members are characterized by high $^{87}\text{Sr}/^{86}\text{Sr}$, low $^{143}\text{Nd}/^{144}\text{Nd}$, and moderate Pb isotope values [26], which may include the component of recycled subducted oceanic crust/continental lower crust, or old continental lithospheric mantle. The HIMU-type mantle component (characterized by a high $^{238}\text{U}/^{204}\text{Pb}$ ratio) [25] is associated with recirculating ancient altered oceanic crust, or old carbonate–metasomatic lithospheric mantle [102–104]. The FOZO-type mantle component, with depleted Sr and Nd but fairly radiogenic Pb isotope values, is a mixed end member representing the average components of the lower mantle [26].

All the stable C and O isotopic values reported for the Lesser Qinling carbonatites indicate their pristine nature and origin from the mantle. The oxygen isotopes of quartz in HLP carbonatites ($\delta^{18}\text{O}_{\text{H}_2\text{O}} = 8.1\text{--}10.2$) [32] and quartz in HSA Mo deposits ($\delta^{18}\text{O}_{\text{H}_2\text{O}} = 7.4\text{--}10.1$) [55] indicate a magmatic origin, while sulfur isotopes exhibit characteristics consistent with sulfur from the mantle. The Sr–Nd–Pb isotopic diagrams in Figures 6 and 8 display data for the Lesser Qinling (HAS and HLP) carbonatites and are compared to those for carbonatites worldwide (e.g., East African, North America, Brazil, Bayan Obo, Miaoya, Fengzhen and Shandong from China). The Sr, Nd, and Pb isotopic compositions for the HSA carbonatites are slightly more radiogenic compared to those for the HLP carbonatites. However, isotope compositions from both complexes show characteristics similar to that of EMI-type mantle, far removed from the depleted DMM end member (Figure 5), indicating significant involvement of an enriched end member, possibly such as continental crust. The Pb isotopic characteristics of these carbonatites are significantly distinct compared to those from the Precambrian rocks in the North China Block, but similar to those of basement rocks in the South Qinling [30]. The ratios of $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ for the Lesser Qinling carbonatites differ from those of carbonatites from the East African Rift, but plot between the average Pb isotope evolution curves for orogenic terranes and mantle (Figure 6a). In Figure 6b, the carbonatites mainly plot between the Pb isotope evolution curves for the lower crust and orogenic terranes [70], which may reflect the orogenic event associated with the subduction of the Mianlue Ocean beneath the South Qinling orogenic belt. Overall, the Lesser Qinling carbonatites display enriched radiogenic Sr–Nd–Pb isotopic compositions (negative ϵ_{Nd} values and high, relatively constant initial $^{87}\text{Sr}/^{86}\text{Sr}$ and Pb isotopic ratios) compared to typical carbonatites globally, with the exception of the Shandong carbonatites (Figure 8). The latter carbonatites display isotopic signatures that represent a mixture between an EMI-like mantle source and the basement rocks (Taihua and Xiong'er Groups). Here, the Sr–Nd–Pb isotopic compositions of Lesser Qinling carbonatites are best explained as melts derived from an EMI-like mantle source that have subsequently experienced minor contamination of Xiong'er and Taihua basement (Figure 8). Alternatively, the Lesser Qinling carbonatites may have originated as low-degree partial melts from a volumetrically small (distinct), metasomatized, and isotopically heterogeneous section of the upper mantle within this region of the North China Block.

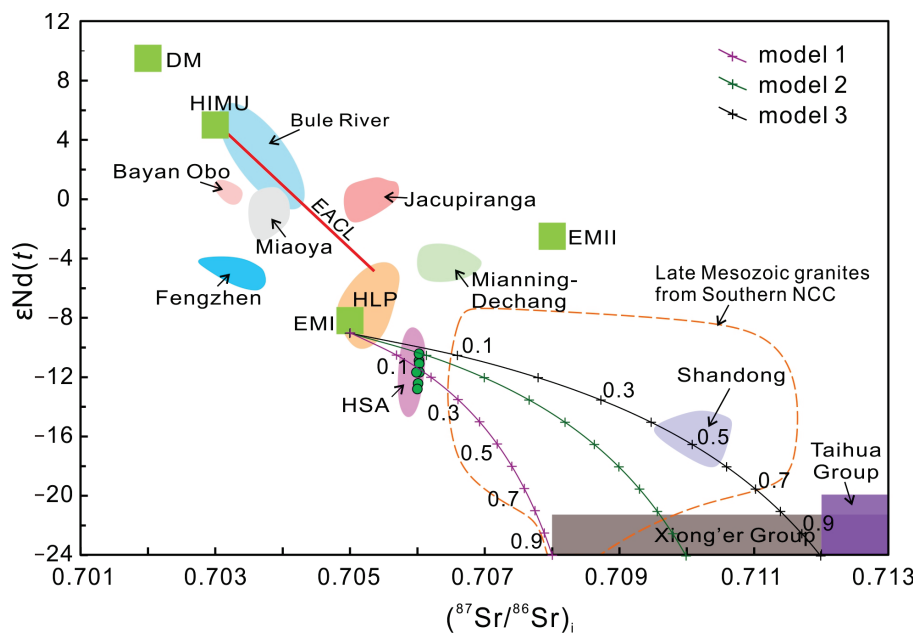


Figure 8. Diagrams of initial $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $\epsilon_{\text{Nd}(t)}$ values for samples of those carbonatites from China [30,31,45–48,72,73,105]. These are compared to initial Sr and Nd isotope data reported for EACL carbonatites [20], Blue River carbonatites from Canada [66], and Jacupiranga carbonatites from Brazil [65]. The fields for Late Mesozoic granites, Taihua Group, and Xiong'er Group are from [33,106]. The fields for DM, HIMU, EM I and EMII mantle components are from [69]. Binary mixing model curves between the assumed EM I and Xiong'er Group. The $\epsilon_{\text{Nd}(t)}$ is assumed to be -9 in the EM I and -24 in the Xiong'er Group in the models. The $(^{87}\text{Sr}/^{86}\text{Sr})_i$ of 0.705 is adopted for EM I in 3 models. The $(^{87}\text{Sr}/^{86}\text{Sr})_i$ of the Xiong'er Group is taken to be 0.708, 0.709, and 0.710 in models 1, 2, and 3, respectively. A mixture of 10% Xiong'er Group and 90% EM I is represented by 0.1.

Previous studies have proposed that most of the world's carbonatites derive from carbonated lithospheric mantle, and are triggered by either asthenospheric upwelling or plume activity [1,22]. However, this tectonic model is less plausible for the generation of carbonatite magma within orogenic belts. Recently, several studies have focused on the genesis of carbonatite magmas within an orogenic regime and how these relate to the subduction process [3,30,47,48,107–110]. Xu [110] proposed that the carbonatite complexes located within orogenic belts may result from the low-degree melting of subcontinental lithospheric mantle metasomatized by melts/fluids derived from the subduction of terrigenous carbon-rich sediments. The trace element-enriched nature of Chinese carbonatites found within orogenic belts indicates a contribution of recycled crustal material to their mantle source through subduction fluid metasomatism (Figure 9). The subduction of surface carbon into the deep mantle not only provides oxygen-rich components for a more reduced mantle source region, but also facilitates REE enrichment in parent carbonatite magma and formation of REE deposits [3,111–113]. Recent investigations of the B and Ca isotope compositions for carbonatite complexes worldwide are consistent with the hypothesis that the source of the younger (<300 Ma) carbonatites records the input of recycled crustal carbonates [3,14,114,115]. The low-Mg isotopic compositions ($\delta^{26}\text{Mg} = -1.89\sim-1.07\text{‰}$) [3] of the HYC carbonatites overlap those of Mesozoic marine dolomites ($<-1.0\text{‰}$) [116], which also suggests a recycled sedimentary contribution in their mantle sources [3]. A recent study of an Afghanistan carbonatite occurrence proposed that magmas can efficiently recycle sedimentary carbon from subducting slabs into the overlying lithospheric mantle [117].

During the Early Triassic, the oceanic crust of the Mianlue Ocean subducted beneath the South Qinling Orogen Belt, resulting in a significant influx of carbonate sediments into the mantle peridotite [3,29,45]. The subcontinental lithospheric mantle could be

metasomatically reworked by carbonate-rich melts derived from EMI-type recycled crust components [30]. Subsequently, in the Middle Triassic, the collision between the QOB and the North China Block led to the formation of a series of NW- and NWW-trending fault zones [118–122]. In the Late Triassic period following ocean closure, post-collisional extension induced upwelling of asthenosphere material. This led to low-degree partial melting of carbonated mantle peridotite and subsequent formation of carbonatite magmas. These magmas ascended along trans-lithospheric faults at craton edges resulting in the emplacement of Lesser Qingling carbonatites including HSA, HLP, and HYC [33,36,37].

Overall, the combined Sr-Nd-Pb isotopic compositions for the HSA carbonatites support the hypotheses that the Lesser Qingling carbonatites originate from a heterogeneous upper mantle source involving an EMI-like mantle component and minor assimilation of the basement rocks. The Lesser Qingling carbonatite magmas were derived from the direct melting of the carbonated subcontinental lithospheric mantle, which metasomatized the early subduction of the Mianlue oceanic crust during the incipient stages of the regional orogenic regime.

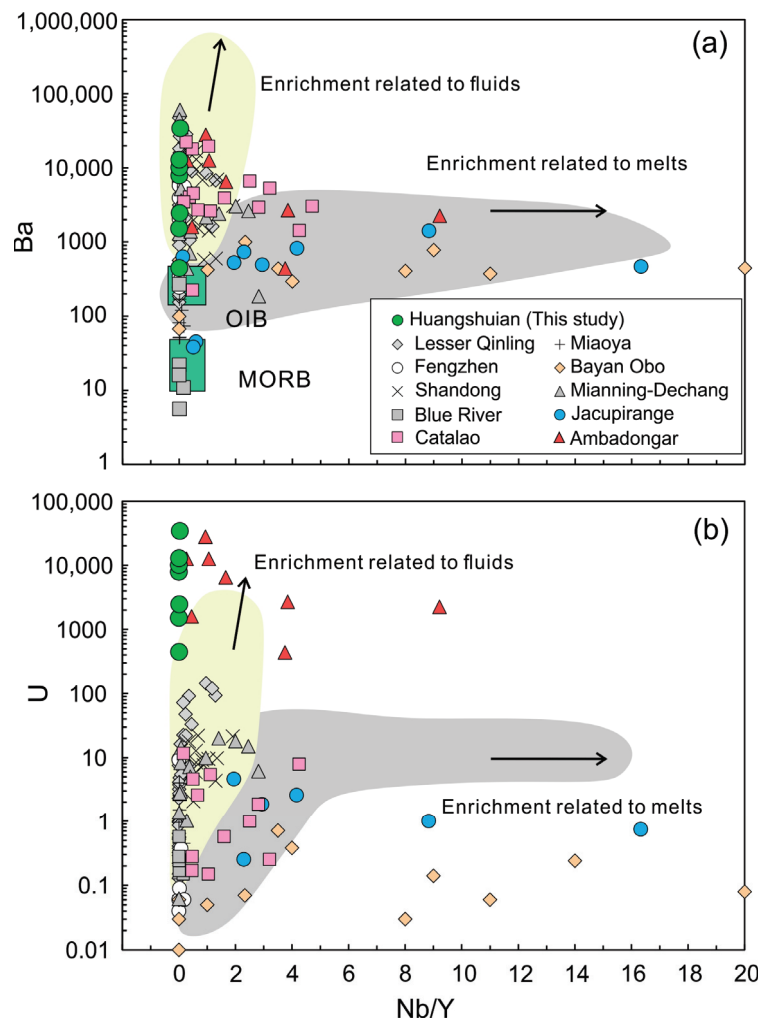


Figure 9. Diagrams of Ba (ppm) vs. Nb/Y (a) and U (ppm) vs. Nb/Y (b) for HSA carbonatite and other carbonatites worldwide (references after Figure 7 and Ambadongar, India [123]).

6. Conclusions

- (1) The Huangshuiian carbonatites in Lesser Qingling Orogen display elevated CaO and low MgO and alkali contents, as well as significant enrichments of Pb, Mo, and HREE, compared to typical carbonatites. The stable C and O isotope compositions suggest

their pristine nature and derivation from mantle source(s). It is postulated that Huangshuian carbonatites represent residual melts of late-stage magmatic differentiation from the parental carbonatite magma.

- (2) The combined Sr-Nd-Pb isotopic compositions for the carbonatites support the hypothesis that the Lesser Qinling carbonatites were derived from a heterogeneous upper mantle source involving an EMI-like mantle component and minor assimilation of the basement rocks.
- (3) We propose that the Lesser Qinling carbonatite magmas were derived directly from the melting of the carbonate-bearing subcontinental lithospheric mantle metasomatized by the subduction of the Mianlue Ocean during the early phase of the regional orogenic tectonism during the Early Triassic.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/min14090953/s1>. Table S1: Major and trace elements compositions of the Huangshuian carbonatites in Lesser Qinling; Table S2: C–O isotopic compositions of the Huangshuian carbonatites in Lesser Qinling; Table S3: Sr–Nd isotopic compositions of the Huangshuian carbonatites in Lesser Qinling; Table S4: Pb isotopic compositions of the Huangshuian carbonatites in Lesser Qinling.

Author Contributions: Methodology, A.S., S.S. and Y.D.; formal analysis, H.Z. and S.S.; investigation, H.Z.; data curation, S.S.; writing—original draft, H.Z.; writing—review and editing, H.Z., A.S., X.C. and Y.D.; visualization, H.Z.; supervision, A.S.; funding acquisition, X.C. and Y.D. All authors have read and agreed to the published version of the manuscript.

Funding: This study was financially supported by Projects of Shengli Oilfield Sinopec (YKY2401, YKB2312).

Data Availability Statement: All data generated or analyses are included within this study and its Supplementary Materials.

Acknowledgments: We thank three reviewers for their constructive comments and detailed suggestions, which greatly improved the manuscript. We are grateful to Loretta Corcoran and Corinne Kuebler for their assistance with sample preparation, processing, and analyses within the MITERAC clean room laboratories.

Conflicts of Interest: Hao Zhao, Xiaopeng Cao and Yushan Du are employees of Shengli Oilfield Sinopec. The authors declare no conflicts of interest.

References

1. Bell, K.; Simonetti, A. Source of parental melts to carbonatites—critical isotopic constraints. *Mineral. Petrol.* **2010**, *98*, 77–89. [CrossRef]
2. Woolley, A.R.; Kjarsgaard, B.A. Carbonatite occurrences of the world: Map and database; geological survey of Canada. *Open File* **2008**, 5796. [CrossRef]
3. Song, W.L.; Xu, C.; Smith, M.P.; Kynicky, J.; Huang, K.J.; Wei, C.W.; Zhou, L.; Shu, Q.H. Origin of unusual HREE-Mo-rich carbonatites in the Qinling orogen, China. *Sci. Rep.* **2016**, *6*, 37377. [CrossRef] [PubMed]
4. Woolley, A.R. Carbonatites: Nomenclature, average chemical compositions, and element distribution. In *Carbonatites: Genesis and Evolution*; Unwin Hyman: London, UK, 1989; pp. 1–13.
5. Treiman, A.H.; Schedl, A. Properties of Carbonatite Magma and Processes in Carbonatite Magma Chambers. *J. Geol.* **1983**, *91*, 437–447. [CrossRef]
6. Krafft, M.; Keller, J. Temperature Measurements in Carbonatite Lava Lakes and Flows from Oldoinyo Lengai, Tanzania. *Science* **1989**, *245*, 168–170. [CrossRef]
7. Dawson, J.B.; Pinkerton, H.; Norton, G.E.; Pyle, D.M. Physicochemical properties of alkali carbonatite lavas; data from the 1988 eruption of Oldoinyo Lengai, Tanzania. *Geology* **1990**, *18*, 260–263. [CrossRef]
8. Jones, A.P.; Genge, M.; Carmody, L. Carbonate Melts and Carbonatites. *Rev. Mineral. Geochem.* **2013**, *75*, 289–322. [CrossRef]
9. Bell, K.; Blenkinsop, J. Neodymium and strontium isotope geochemistry of carbonatites. In *Carbonatites—Genesis and Evolution*; Bell, K., Ed.; Unwin Hyman: London, UK, 1989; pp. 278–300.
10. Bell, K.; Blenkinsop, J.; Cole, T.J.S.; Menagh, D.P. Evidence from Sr isotopes for long-lived heterogeneities in the upper mantle. *Nature* **1982**, *298*, 251–253. [CrossRef]
11. Bell, K.; Blenkinsop, J. Nd and Sr isotopic compositions of East African carbonatites; implications for mantle heterogeneity. *Geology* **1987**, *15*, 99–102. [CrossRef]

12. Tilton, G.R.; Bell, K. Sr-Nd-Pb isotope relationships in Late Archean carbonatites and alkaline complexes, Applications to the geochemical evolution of Archean mantle. *Geochim. Cosmochim. Acta* **1994**, *58*, 3145–3154. [CrossRef]
13. Hoernle, K.; Tilton, G.; Le Bas, M.J.; Duggen, S.; Garbe-Schönberg, D. Geochemistry of oceanic carbonatites compared with continental carbonatites, mantle recycling of oceanic crustal carbonate. *Contrib. Mineral. Petrol.* **2002**, *142*, 520–542. [CrossRef]
14. Hulett, S.R.W.; Simonetti, A.; Rasbury, E.T.; Hemming, N.G. Recycling of subducted crustal components into carbonatite melts revealed by boron isotopes. *Nat. Geosci.* **2016**, *9*, 904–908. [CrossRef]
15. Bell, K.; Simonetti, A. Carbonatite Magmatism and Plume Activity, Implications from the Nd, Pb and Sr Isotope Systematics of Oldoinyo Lengai. *J. Petrol.* **1996**, *37*, 1321–1339. [CrossRef]
16. Doucelance, R.; Hammouda, T.; Moreira, M.; Martins, J.C. Geochemical constraints on depth of origin of oceanic carbonatites: The Cape Verde case. *Geochim. Cosmochim. Acta* **2010**, *74*, 7261–7282. [CrossRef]
17. Xu, C.; Campbell, I.H.; Allen, C.M.; Huang, Z.L.; Qi, L.; Zhang, H.; Zhang, G.S. Flat rare earth element patterns as an indicator of cumulate processes in the Lesser Qinling carbonatites, China. *Lithos* **2007**, *95*, 267–278. [CrossRef]
18. Nelson, D.R.; Chivas, A.R.; Chappell, B.W.; McCulloch, M.T. Geochemical and isotopic systematics in carbonatites and implications for the evolution of ocean-island sources. *Geochim. Cosmochim. Acta* **1988**, *52*, 1–17. [CrossRef]
19. Bailey, D.K. Carbonate magmas. *J. Geol. Soc. Lond.* **1993**, *150*, 637–651. [CrossRef]
20. Bell, K.; Tilton, G.R. Probing the mantle: The story from carbonatites. *Eos Trans. Am. Geophys. Union* **2002**, *83*, 273–277. [CrossRef]
21. Bell, K. Carbonatites: Relationships to mantle-plume activity. *Geol. Soc. Am. Spec. Pap.* **2001**, *352*, 267–290.
22. Bell, K.; Rukhlov, A.S. Carbonatites from the Kola Alkaline Province, origin, evolution and source characteristics. In *Phoscorites and Carbonatites from Mantle to Mine, the Key Example of the Kola Alkaline Province*; Mineralogical Society of Great Britain & Ireland: London, UK, 2004; Volume 10, pp. 421–455.
23. Gerlach, D.C.; Cliff, R.A.; Davies, G.R.; Norry, M.; Hodgson, N. Magma sources of the Cape Verdes archipelago, Isotopic and trace element constraints. *Geochim. Cosmochim. Acta* **1988**, *52*, 2979–2992. [CrossRef]
24. Simonetti, A.; Goldstein, S.L.; Schmidberger, S.S.; Viladkar, S.G. Geochemical and Nd, Pb, and Sr Isotope Data from Deccan Alkaline Complexes—Inferences for Mantle Sources and Plume-Lithosphere Interaction. *J. Petrol.* **1998**, *39*, 1847–1864. [CrossRef]
25. Hart, S.R. Heterogeneous mantle domains, signatures, genesis and mixing chronologies. *Earth Planet. Sci. Lett.* **1988**, *90*, 273–296. [CrossRef]
26. Hart, S.R.; Hauri, E.H.; Oschmann, L.A.; Whitehead, J.A. Mantle Plumes and Entrainment, Isotopic Evidence. *Science* **1992**, *256*, 517–520. [CrossRef]
27. Xu, C.; Kynicky, J.; Chakhmouradian, A.R.; Qi, L.; Song, W.L. A unique Mo deposit associated with carbonatites in the Qinling orogenic belt, central China. *Lithos* **2010**, *118*, 50–60. [CrossRef]
28. Smith, M.; Kynicky, J.; Xu, C.; Song, W.L.; Spratt, J.; Jeffries, T.; Brtnicky, M.; Kopriva, A.; Cangelosi, D. The origin of secondary heavy rare earth element enrichment in carbonatites: Constraints from the evolution of the Huanglongpu district, China. *Lithos* **2018**, *308*, 65–82. [CrossRef]
29. Xue, S.; Ling, M.X.; Liu, Y.L.; Kang, Q.Q.; Huang, R.F.; Zhang, Z.K.; Sun, W.D. The formation of the giant Huayangchuan U-Nb deposit associated with carbonatite in the Qingling Orogenic Belt. *Ore Geol. Rev.* **2020**, *122*, 103498. [CrossRef]
30. Xu, C.; Taylor, R.N.; Kynicky, J.; Chakhmouradian, A.R.; Song, W.L.; Wang, L.J. The origin of enriched mantle beneath North China block, Evidence from young carbonatites. *Lithos* **2011**, *127*, 1–9. [CrossRef]
31. Hou, Z.Q.; Yang, Z.M.; Li, Z.Q.; Xu, D.X. Geological and geochemical characteristics, metallogenetic mechanism and tectonic setting of carbonatite vein type Mo (Pb) deposits in the East Qinling molybdenum ore belt. *Acta Geol. Sin.* **2009**, *83*, 1968–1984. (In Chinese with English Abstract)
32. Song, W.L.; Xu, C.; Qi, L.; Zhou, L.; Wang, L.J.; Kynicky, J. Genesis of Si-rich carbonatites in Huanglongpu Mo deposit, Lesser Qinling orogen, China and significance for Mo mineralization. *Ore Geol. Rev.* **2015**, *64*, 756–765. [CrossRef]
33. Bai, T.; Chen, W.; Jiang, S.Y. Evolution of the carbonatite Mo-HREE deposits in the Lesser Qinling Orogen: Insights from in situ geochemical investigation of calcite and sulfate. *Ore Geol. Rev.* **2019**, *113*, 103069. [CrossRef]
34. Stein, H.J.; Markey, R.J.; Morgan, J.W.; Du, A.; Sun, Y. Highly precise and accurate Re-Os ages for molybdenite from the East Qinling molybdenum belt, Shaanxi Province, China. *Econ. Geol.* **1997**, *92*, 827–835. [CrossRef]
35. Cao, J.; Ye, H.S.; Li, H.Y.; Li, Z.Y.; Zhang, X.K.; He, W.; Li, C. Geological characteristics and molybdenite Re-Os isotopic dating of Huangshui carbonatite vein-type Mo(Pb) deposit in Songxian County, Henan Province. *Miner. Depos.* **2014**, *33*, 53–69. (In Chinese with English Abstract)
36. Zhang, W.; Chen, W.T.; Gao, J.F.; Chen, H.K.; Li, J.H. Two episodes of REE mineralization in the Qinling Orogenic Belt, Central China, in-situ U-Th-Pb dating of bastnäsite and monazite. *Miner. Depos.* **2019**, *54*, 1265–1280. [CrossRef]
37. Chen, H.Y.; Wu, C.; Jiang, H.J.; Gao, C.; Kang, Q.Q.; Yang, C.S.; Wang, D.E.; Lai, C. Genesis of the supergiant Huayangchuan carbonatite-hosted uranium-polymetallic deposit in the Qinling Orogen, Central China. *Gondwana Res.* **2020**, *86*, 250–265.
38. Mao, J.W.; Xie, G.Q.; Bierlein, F.; Qü, W.J.; Du, A.D.; Ye, H.S.; Pirajno, F.; Li, H.M.; Guo, B.J.; Li, Y.F.; et al. Tectonic implications from Re-Os dating of Mesozoic molybdenum deposits in the East Qinling–Dabie orogenic belt. *Geochim. Cosmochim. Acta* **2008**, *72*, 4607–4626. [CrossRef]
39. Li, N.; Pirajno, F. Early Mesozoic Mo mineralization in the Qinling Orogen, An overview. *Ore Geol. Rev.* **2017**, *81*, 431–450. [CrossRef]
40. Kynicky, J.; Smith, M.P.; Xu, C. Diversity of Rare Earth Deposits: The Key Example of China. *Elements* **2012**, *8*, 361–367. [CrossRef]

41. Huang, G.W.; Pan, C.R.; Pan, J.Y.; Zhong, F.J.; Chen, Z.L.; Xia, F.; Yan, J.; Wu, D.H.; Min, Z. REE mineralization age and geodynamic setting of the Huanglongpu deposit in the East Qinling orogen, China: Evidence from mineralogy, U–Pb geochronology, and in-situ Nd isotope. *Ore Geol. Rev.* **2023**, *152*, 105255. [CrossRef]
42. Wei, C.W.; Xu, C.; Chakhmouradian, A.R.; Brenna, M.; Kynicky, J.; Song, W.L. Carbon–Strontium Isotope Decoupling in Carbonatites from Caotan (Qinling, China): Implications for the Origin of Calcite Carbonatite in Orogenic Settings. *J. Petrol.* **2020**, *61*, ega024. [CrossRef]
43. Yaxley, G.M.; Brey, G.P. Phase relations of carbonate-bearing eclogite assemblages from 2.5 to 5.5 GPa: Implications for petrogenesis of carbonatites. *Contrib. Mineral. Petrol.* **2004**, *146*, 606–619. [CrossRef]
44. Thomson, A.R.; Walter, M.J.; Kohn, S.C.; Brooker, R.A. Slab melting as a barrier to deep carbon subduction. *Nature* **2016**, *529*, 76–79. [CrossRef] [PubMed]
45. Xu, C.; Chakhmouradian, A.R.; Taylor, R.N.; Kynicky, J.; Li, W.B.; Song, W.L.; Fletcher, I.R. Origin of carbonatites in the South Qinling orogen, Implications for crustal recycling and timing of collision between the South and North China Blocks. *Geochim. Cosmochim. Acta* **2014**, *143*, 189–206. [CrossRef]
46. Çimen, O.; Kuebler, C.; Monaco, B.; Simonetti, S.S.; Corcoran, L.; Chen, W.; Simonetti, A. Boron, carbon, oxygen and radiogenic isotope investigation of carbonatite from the Miaoya complex, central China, Evidences for late-stage REE hydrothermal event and mantle source heterogeneity. *Lithos* **2018**, *322*, 225–237. [CrossRef]
47. Xu, C.; Kynický, J.; Song, W.L.; Tao, R.B.; Lü, Z.; Li, Y.X.; Yang, Y.H.; Pohanka, M.; Galiova, M.V.; Zhang, L.F.; et al. Cold deep subduction recorded by remnants of a Paleoproterozoic carbonated slab. *Nat. Commun.* **2018**, *9*, 2790. [CrossRef]
48. Hou, Z.Q.; Tian, S.H.; Yuan, Z.X.; Xie, Y.L.; Yin, S.P.; Yi, L.S.; Fei, H.C.; Yang, Z.M. The Himalayan collision zone carbonatites in western Sichuan, SW China, Petrogenesis, mantle source and tectonic implication. *Earth Planet. Sci. Lett.* **2006**, *244*, 234–250. [CrossRef]
49. Zhang, G.W.; Meng, Q.G.; Lai, S.C. Tectonics and structure of Qinling Orogenic Belt. *Sci. China Ser. B* **1995**, *38*, 1379–1394.
50. Kröner, A.; Compston, W.; Zhang, G.W.; Guo, A.L.; Todt, W. Age and tectonic setting of Late Archean greenstone-gneiss terrain in Henan Province, China, as revealed by single-grain zircon dating. *Geology* **1988**, *16*, 211–215. [CrossRef]
51. Peng, P.; Zhai, M.G.; Ernst, R.E.; Guo, J.H.; Liu, F.; Hu, B. A 1.78 Ga large igneous province in the North China craton, The Xiong'er Volcanic Province and the North China dyke swarm. *Lithos* **2008**, *101*, 260–280. [CrossRef]
52. Zhao, G.C.; He, Y.H.; Sun, M. The Xiong'er volcanic belt at the southern margin of the North China Craton: Petrographic and geochemical evidence for its outboard position in the Paleo-Mesoproterozoic Columbia Supercontinent. *Gondwana Res.* **2009**, *16*, 170–181. [CrossRef]
53. Zhang, C.L.; Wang, T.; Wang, X.X. Origin and tectonic setting of the Early Mesozoic granitoids in Qinling orogenic belt. *Geol. J. China Univ.* **2008**, *14*, 304–316.
54. Mao, J.W.; Xie, G.Q.; Pirajno, F.; Ye, H.S.; Wang, Y.B.; Li, Y.F.; Xiang, J.F.; Zhao, H.J. Late Jurassic–Early Cretaceous granitoid magmatism in Eastern Qinling, central-eastern China: SHRIMP zircon U–Pb ages and tectonic implications. *Aust. J. Earth Sci.* **2010**, *57*, 51–78. [CrossRef]
55. Cao, J.; Ye, H.S.; Chen, X.D.; He, W.; Wang, P. Geochemistry, Zircon U–Pb Age, and Lu–Hf Isotope of the Granite Porphyry in Leimengou Mo Deposit in the East Qinling Molybdenum Ore Belt, China. *Minerals* **2018**, *8*, 293. [CrossRef]
56. Jenner, G.A.; Longerich, H.P.; Jackson, S.E.; Fryer, B.J. ICP–MS—A powerful tool for high-precision trace-element analysis in Earth sciences: Evidence from analysis of selected U.S.G.S. reference samples. *Chem. Geol.* **1990**, *83*, 133–148. [CrossRef]
57. McCrea, J.M. On the Isotopic Chemistry of Carbonates and a Paleotemperature Scale. *J. Chem. Phys.* **1950**, *18*, 849–857. [CrossRef]
58. Balboni, E.; Jones, N.; Spano, T.; Simonetti, A.; Burns, P.C. Chemical and Sr isotopic characterization of North America uranium ores, Nuclear forensic applications. *Appl. Geochem.* **2016**, *74*, 24–32. [CrossRef]
59. Tanaka, T.; Togashi, S.; Kamioka, H.; Amakawa, H.; Kagami, H.; Hamamoto, T.; Yuhara, M.; Orihashi, Y.; Yoneda, S.; Shimizu, H.; et al. JNd-1, a neodymium isotopic reference in consistency with LaJolla neodymium. *Chem. Geol.* **2000**, *168*, 279–281. [CrossRef]
60. Simonetti, A.; Gariépy, C.; Banic, C.M.; Tanabe, R.; Wong, H.K. Pb isotopic investigation of aircraft-sampled emissions from the Horne smelter (Rouyn, Québec), Implications for atmospheric pollution in northeastern North America. *Geochim. Cosmochim. Acta* **2004**, *68*, 3285–3294. [CrossRef]
61. Manhès, G.; Minster, J.F.; Allègre, C.J. Comparative uranium–thorium–lead and rubidium–strontium study of the Saint Séverin amphibolite, consequences for early solar system chronology. *Earth Planet. Sci. Lett.* **1978**, *39*, 14–24. [CrossRef]
62. Baker, J.; Peate, D.; Waight, T.; Meyzen, C. Pb isotopic analysis of standards and samples using a 207Pb–204Pb double spike and thallium to correct for mass bias with a double-focusing MC–ICP–MS. *Chem. Geol.* **2004**, *211*, 275–303. [CrossRef]
63. Kjarsgaard, B.A. The genesis of carbonatites by immiscibility. In *Carbonatites: Genesis and Evolution*; Unwin Hyman: London, UK, 1989; pp. 388–404.
64. Sun, S.S.; McDonough, W.F. Chemical and isotopic systematics of oceanic basalts, implications for mantle composition and processes. *Geol. Soc. Spec. Publ.* **1989**, *42*, 313–345. [CrossRef]
65. Huang, Y.M.; Hawkesworth, C.J.; van Calsteren, P.; McDermott, F. Geochemical characteristics and origin of the Jacupiranga carbonatites, Brazil. *Chem. Geol.* **1995**, *119*, 79–99. [CrossRef]
66. Çimen, O.; Kuebler, C.; Simonetti, S.S.; Corcoran, L.; Mitchell, R.; Simonetti, A. Combined boron, radiogenic (Nd, Pb, Sr), stable (C, O) isotopic and geochemical investigations of carbonatites from the Blue River Region, British Columbia (Canada), Implications for mantle sources and recycling of crustal carbon. *Chem. Geol.* **2019**, *529*, 119240. [CrossRef]

67. Keller, J.; Hoefs, J. Stable Isotope Characteristics of Recent Natrocarbonatites from Oldoinyo Lengai. In *Carbonatite Volcanism*; Springer: Berlin/Heidelberg, Germany, 1995; pp. 113–123.
68. Demény, A.; Ahijado, A.; Casillas, R.; Vennemann, T.W. Crustal contamination and fluid/rock interaction in the carbonatites of Fuerteventura (Canary Islands, Spain), a C, O, H isotope study. *Lithos* **1998**, *44*, 101–115. [CrossRef]
69. Zindler, A.; Hart, S.R. Chemical geodynamics. *Annu. Rev. Earth Planet. Sci.* **1986**, *14*, 493–571. [CrossRef]
70. Zartman, R.E.; Doe, B.R. Plumbotectonics—The model. *Tectonophysics* **1981**, *75*, 135–162. [CrossRef]
71. Möller, P.; Parekh, P.P.; Schneider, H.J. The application of Tb/Ca-Tb/La abundance ratios to problems of fluorspar genesis. *Miner. Depos.* **1976**, *11*, 111–116. [CrossRef]
72. Kuebler, C.; Simonetti, A.; Chen, W.; Simonetti, S.S. Boron isotopic investigation of the Bayan Obo carbonatite complex, Insights into the source of mantle carbon and hydrothermal alteration. *Chem. Geol.* **2020**, *557*, 119859. [CrossRef]
73. Ying, Y.F.; Zhou, X.H.; Zhang, H.F. Geochemical and isotopic investigation of the Laiwu-Zibo carbonatites from western Shandong Province, China, and implications for their petrogenesis and enriched mantle source. *Lithos* **2004**, *75*, 413–426. [CrossRef]
74. Chmyz, L.; Arnaud, N.; Biondi, J.C.; Azzone, R.G.; Bosch, D.; Ruberti, E. Ar-Ar ages, Sr-Nd isotope geochemistry, and implications for the origin of the silicate rocks of the Jacupiranga ultramafic-alkaline complex (Brazil). *J. S. Am. Earth Sci.* **2017**, *77*, 286–309. [CrossRef]
75. Guarino, V.; Wu, F.; Melluso, L.; de Barros Gomes, C.; Tassinari, C.C.G.; Ruberti, E.; Brilli, M. U–Pb ages, geochemistry, C–O–Nd–Sr–Hf isotopes and petrogenesis of the Catalão II carbonatitic complex (Alto Paranaíba Igneous Province, Brazil): Implications for regional-scale heterogeneities in the Brazilian carbonatite associations. *Int. J. Earth Sci.* **2017**, *106*, 1963–1989. [CrossRef]
76. Wyllie, P.J.; Huang, W. Influence of mantle CO₂ in the generation of carbonatites and kimberlites. *Nature* **1975**, *257*, 297–299. [CrossRef]
77. Green, D.H.; Wallace, M.E. Mantle metasomatism by ephemeral carbonatite melts. *Nature* **1988**, *336*, 459–462. [CrossRef]
78. Moore, K.R.; Wood, B.J. The Transition from Carbonate to Silicate Melts in the CaO–MgO–SiO₂–CO₂ System. *J. Petrol.* **1998**, *39*, 1943–1951. [CrossRef]
79. Wyllie, P.J.; Lee, W.J. Model System Controls on Conditions for Formation of Magnesiocarbonatite and Calciocarbonatite Magmas from the Mantle. *J. Petrol.* **1998**, *39*, 1885–1893. [CrossRef]
80. Grassi, D.; Schmidt, M.W. Melting of carbonated pelites at 8–13 GPa, generating K-rich carbonatites for mantle metasomatism. *Contrib. Mineral. Petrol.* **2011**, *162*, 169–191. [CrossRef]
81. Lee, W.J.; Wyllie, P.J. Experimental Data Bearing on Liquid Immiscibility, Crystal Fractionation, and the Origin of Calciocarbonatites and Natrocarbonatites. *Int. Geol. Rev.* **1994**, *36*, 797–819. [CrossRef]
82. Lee, W.J.; Wyllie, P.J. Processes of Crustal Carbonatite Formation by Liquid Immiscibility and Differentiation, Elucidated by Model Systems. *J. Petrol.* **1998**, *39*, 2005–2013. [CrossRef]
83. Veksler, I.V.; Petibon, C.; Jenner, G.A.; Dorfman, A.M.; Dingwell, D.B. Trace Element Partitioning in Immiscible Silicate–Carbonate Liquid Systems: An Initial Experimental Study Using a Centrifuge Autoclave. *J. Petrol.* **1998**, *39*, 2095–2104. [CrossRef]
84. Doroshkevich, A.G.; Veksler, I.V.; Klemm, R.; Khromova, E.A.; Izbrodin, I.A. Trace-element composition of minerals and rocks in the Belaya Zima carbonatite complex (Russia): Implications for the mechanisms of magma evolution and carbonatite formation. *Lithos* **2017**, *284–285*, 91–108. [CrossRef]
85. Lee, W.J.; Wyllie, P.J. Liquid immiscibility between nephelinite and carbonatite from 1.0 to 2.5 GPa compared with mantle melt compositions. *Contrib. Mineral. Petrol.* **1997**, *127*, 1–16. [CrossRef]
86. Veksler, I.V.; Nielsen, T.F.D.; Sokolov, S.V. Mineralogy of Crystallized Melt Inclusions from Gardiner and Kovdor Ultramafic Alkaline Complexes, Implications for Carbonatite Genesis. *J. Petrol.* **1998**, *39*, 2015–2031. [CrossRef]
87. Lee, W.J.; Wyllie, P.J. The system CaO–MgO–SiO₂–CO₂ at 1 GPa, metasomatic wehrlites, and primary carbonatite magmas. *Contrib. Mineral. Petrol.* **2000**, *138*, 214–228. [CrossRef]
88. Rosatelli, G.; Wall, F.; Stoppa, F. Calcio–carbonatite melts and metasomatism in the mantle beneath Mt. Vulture (Southern Italy). *Lithos* **2007**, *99*, 229–248. [CrossRef]
89. Fischer, T.P.; Burnard, P.; Marty, B.; Hilton, D.R.; Füre, E.; Palhol, F.; Sharp, Z.D.; Mangasini, F. Upper-mantle volatile chemistry at Oldoinyo Lengai volcano and the origin of carbonatites. *Nature* **2009**, *459*, 77–80. [CrossRef] [PubMed]
90. Potter, N.J.; Kamenetsky, V.S.; Simonetti, A.; Goemann, K. Different types of liquid immiscibility in carbonatite magmas, A case study of the Oldoinyo Lengai 1993 lava and melt inclusions. *Chem. Geol.* **2017**, *455*, 376–384. [CrossRef]
91. Cangelosi, D.; Smith, M.; Banks, D.; Yardley, B. The role of sulfate-rich fluids in heavy rare earth enrichment at the Dashigou carbonatite deposit, Huanglongpu, China. *Mineral. Mag.* **2020**, *84*, 65–80. [CrossRef]
92. Harmer, R.E.; Gittins, J. The Case for Primary, Mantle-derived Carbonatite Magma. *J. Petrol.* **1998**, *39*, 1895–1903. [CrossRef]
93. Brooker, R.A.; Kjarsgaard, B.A. Silicate–carbonate liquid immiscibility and phase relations in the system SiO₂–Na₂O–Al₂O₃–CaO–CO₂ at 0.1–2.5 GPa with applications to carbonatite genesis. *J. Petrol.* **2011**, *52*, 1281–1305. [CrossRef]
94. Wallace, M.E.; Green, D.H. An experimental determination of primary carbonatite magma composition. *Nature* **1988**, *335*, 343–346. [CrossRef]
95. Dalton, J.A.; Presnall, D.C. The Continuum of Primary Carbonatitic–Kimberlitic Melt Compositions in Equilibrium with Lherzolite, Data from the System CaO–MgO–Al₂O₃–SiO₂–CO₂ at 6 GPa. *J. Petrol.* **1998**, *39*, 1953–1964. [CrossRef]
96. Dasgupta, R.; Hirschmann, M.M.; Stalker, K. Immiscible transition from carbonatite-rich to silicate-rich melts in the 3 GPa melting interval of eclogite plus CO₂ and genesis of sili-ca-under-saturated ocean island lavas. *J. Petrol.* **2006**, *47*, 647–671. [CrossRef]

97. Martin, L.H.J.; Schmidt, M.W.; Mattsson, H.B.; Ulmer, P.; Hametner, K.; Günther, D. Element partitioning between immiscible carbonatite–kamafugite melts with application to the Italian ultrapotassic suite. *Chem. Geol.* **2012**, *320–321*, 96–112. [CrossRef]
98. Naby, Z.; Massuyeau, M.; Gaillard, F.; Tuduri, J.; Iacono-Marziano, G.; Rogerie, G.; Le Trong, E.; Di Carlo, I.; Melleton, J.; Bailly, L. A window in the course of alkaline magma differentiation conducive to immiscible REE-rich carbonatites. *Geochim. Cosmochim. Acta* **2020**, *282*, 297–323. [CrossRef]
99. Anenburg, M.; Mavrogenes, J.A.; Frigo, C.; Wall, F. Rare earth element mobility in and around carbonatites controlled by sodium, potassium, and silica. *Sci. Adv.* **2020**, *6*, eabb6570. [CrossRef]
100. Wei, C.W.; Xu, C.; Song, W.L.; Chen, W.; Shi, A.G.; Li, Z.Q.; Fan, C.X. Heavy rare earth element and crustal-derived silicon enrichment in Huayangchuan carbonatites, Qinling orogenic belt. *Lithos* **2023**, *436–437*, 106987. [CrossRef]
101. Li, F.C.; Zeng, Q.D.; Kang, Q.Q.; Fan, H.R.; Yang, K.F.; She, H.D.; Huang, L.L.; Yu, B.; Wu, J.J. Unusual HREE enrichment and mineralization age in the Jialu deposit from the Qinling Orogen, central China. *Ore Geol. Rev.* **2024**, *166*, 105932. [CrossRef]
102. Stracke, A.; Hofmann, A.W.; Hart, S.R. FOZO, HIMU, and the rest of the mantle zoo. *Geochem. Geophys. Geosyst.* **2005**, *6*, Q05007. [CrossRef]
103. Parai, R.; Mukhopadhyay, S.; Lassiter, J.C. New constraints on the HIMU mantle from neon and helium isotopic compositions of basalts from the Cook–Austral Islands. *Earth Planet. Sci. Lett.* **2009**, *277*, 253–261. [CrossRef]
104. Hanyu, T.; Tatsumi, Y.; Senda, R.; Miyazaki, T.; Chang, Q.; Hirahara, Y.; Takahashi, T.; Kawabata, H.; Suzuki, K.; Kimura, J.; et al. Geochemical characteristics and origin of the HIMU reservoir, A possible mantle plume source in the lower mantle. *Geochem. Geophys. Geosyst.* **2011**, *12*, 1–30. [CrossRef]
105. Xu, C.; Chakhmouradian, A.R.; Kynický, J.; Li, Y.X.; Song, W.L.; Chen, W. A Paleoproterozoic mantle source modified by subducted sediments under the North China craton. *Geochim. Cosmochim. Acta* **2019**, *245*, 222–239. [CrossRef]
106. She, H.D.; Fan, H.R.; Yang, K.F.; Li, X.H.; Wang, Z.Y. REEs upgrading by post-carbonatite fluids in the Huangshui’an Mo-REE deposit, eastern Qinling Orogen (central China). *Ore Geol. Rev.* **2022**, *150*, 105177. [CrossRef]
107. Hou, Z.Q.; Liu, Y.; Tian, S.H.; Yang, Z.M.; Xie, Y.L. Formation of carbonatite-related giant rare-earth-element deposits by the recycling of marine sediments. *Sci. Rep.* **2015**, *5*, 10231. [CrossRef] [PubMed]
108. Liu, Y.; Hou, Z.Q. A synthesis of mineralization styles with an integrated genetic model of carbonatite-syenite-hosted REE deposits in the Cenozoic Mianning-Dechang REE metallogenic belt, the eastern Tibetan Plateau, southwestern China. *J. Asian Earth Sci.* **2017**, *137*, 35–79. [CrossRef]
109. Woodard, J.; Huhma, H. Paleoproterozoic mantle enrichment beneath the Fennoscandian Shield: Isotopic insight from carbonatites and lamprophyres. *Lithos* **2015**, *236*, 311–323. [CrossRef]
110. Xu, C.; Kynický, J.; Chakhmouradian, A.R.; Li, X.H.; Song, W.L. A case example of the importance of multi-analytical approach in deciphering carbonatite petrogenesis in South Qinling orogen, Miaoya rare-metal deposit, central China. *Lithos* **2015**, *227*, 107–121. [CrossRef]
111. Ling, M.X.; Liu, Y.L.; Williams, I.S.; Teng, F.Z.; Yang, X.Y.; Ding, X.; Wei, G.J.; Xie, L.H.; Deng, W.F.; Sun, W.D. Formation of the world’s largest REE deposit through protracted fluxing of carbonatite by subduction-derived fluids. *Sci. Rep.* **2013**, *3*, 1776. [CrossRef]
112. Goodenough, K.M.; Schilling, J.; Jonsson, E.; Kalvig, P.; Charles, N.; Tuduri, J.; Dedy, E.A.; Sadeghi, M.; Schiellerup, H.; Müller, A.; et al. Europe’s rare earth element resource potential, An overview of REE metallogenic provinces and their geodynamic setting. *Ore Geol. Rev.* **2016**, *72*, 838–856. [CrossRef]
113. Yang, K.F.; Fan, H.R.; Pirajno, F.; Li, X.C. The Bayan Obo (China) giant REE accumulation conundrum elucidated by intense magmatic differentiation of carbonatite. *Geology* **2019**, *47*, 1198–1202. [CrossRef]
114. Amsellem, E.; Moynier, F.; Bertrand, H.; Bouyon, A.; Mata, J.; Tappe, S.; Day, J. Calcium isotopic evidence for the mantle sources of carbonatites. *Sci. Adv.* **2020**, *6*, eaba3269. [CrossRef]
115. Banerjee, A.; Chakrabarti, R.; Simonetti, A. Temporal evolution of $\delta^{44}/^{40}\text{Ca}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ of carbonatites: Implications for crustal recycling through time. *Geochim. Cosmochim. Acta* **2021**, *307*, 168–191. [CrossRef]
116. Huang, K.J.; Shen, B.; Lang, X.G.; Tang, W.B.; Peng, Y.; Ke, S.; Kaufman, A.J.; Ma, H.R.; Li, F.B. Magnesium isotopic compositions of the Mesoproterozoic dolostones, Implications for Mg isotopic systematics of marine carbonates. *Geochim. Cosmochim. Acta* **2015**, *164*, 333–351. [CrossRef]
117. Horton, F. Rapid recycling of subducted sedimentary carbon revealed by Afghanistan carbonatite volcano. *Nat. Geosci.* **2021**, *14*, 508–512. [CrossRef]
118. Meng, Q.R.; Zhang, G.W. Timing of collision of the North and South China blocks: Controversy and reconciliation. *Geology* **1999**, *27*, 123–126. [CrossRef]
119. Meng, Q.R.; Zhang, G.W. Geologic framework and tectonic evolution of the Qin-ling orogen, central China. *Tectonophysics* **2000**, *323*, 183–196. [CrossRef]
120. Xu, C.; Song, W.L.; Qi, L.; Wang, L.J. Geochemical characteristic and tectonic setting of ore-bearing carbonatite in Huanglongpu Mo ore field. *Acta Petrol. Sin.* **2009**, *25*, 422–430. (In Chinese with English Abstract)
121. Wu, Y.B.; Zheng, Y.F. Tectonic evolution of a composite collision orogen, An overview on the Qinling–Tongbai–Hong’an–Dabie–Sulu orogenic belt in central China. *Gondwana Res.* **2013**, *23*, 1402–1428. [CrossRef]

122. Dong, Y.P.; Santosh, M. Tectonic architecture and multiple orogeny of the Qinling Orogenic Belt, Central China. *Gondwana Res.* **2016**, *29*, 1–40. [CrossRef]
123. Chandra, J.; Paul, D.; Stracke, A.; Chabaux, F.; Granet, M. The Origin of Carbonatites from Amba Dongar within the Deccan Large Igneous Province. *J. Petrol.* **2019**, *60*, 1119–1134. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

The Nature of the Magma Source for Jurassic Mafic Rocks in the Yanbian Area, Eastern Jilin Province: Constraints on the Subduction Process of the Paleo-Pacific Ocean

Rui Geng¹, Zhenhua Fan², Zhixin Wang³, Yixin Li¹ and Bingyang Ye^{4,*}

¹ Shandong Gold Mining Co., Ltd., Jinan 250000, China; gengrui@sd-gold.com (R.G.); liyixin@sd-gold.com (Y.L.)

² NO.1 Geological team of Shandong Provincial Bureau of Geology and Mineral Resources, Jinan 250000, China; fanzhenhua006@163.com

³ 3th Geology & Mineral Resources Survey Institute, Yantai 264000, China; wzx61050304@126.com

⁴ School of Civil Engineering, Baicheng Normal University, Baicheng 131300, China

* Correspondence: yeby@bcnu.edu.cn

Abstract: Early Jurassic mafic–ultramafic igneous rocks are sporadically exposed in the eastern part of northeastern China. Understanding their petrogenesis and geological implications is essential for elucidating the evolution of magma in subduction zones and the evolutionary history of the Paleo-Pacific Ocean. This study presents a detailed petrological, zircon U–Pb geochronological, and whole-rock geochemical analysis of the Jurassic hornblende gabbro in the Yanbian area of northeastern China. The emplacement age of the hornblende gabbro is constrained to 175.3 ± 1.6 Ma. All samples exhibit low SiO₂ content, metaluminous properties, and geochemical characteristics indicative of a subduction environment. By integrating trace elemental ratios, such as Th/Sm, Th/Ce, Ba/La, Rb/Nb, Hf/Sm, Ba/Nb, and $\epsilon_{\text{Nd}(t)}$, our data propose that the hornblende gabbro originated from a mixture of depleted mantle and approximately 10%–20% continental sediment, and that the magmatism is generated by processes involving metasomatic addition to the source mantle wedge by ‘supercritical’ fluids. Contrasting with several recent hypotheses, the magma of the Early Jurassic gabbro originated from the mantle wedge, incorporating contributions from sediment melts and ‘supercritical’ fluids, and formed during the westward subduction of the Paleo-Pacific Ocean. The Yanbian area in Jilin Province was primarily influenced by this westward subduction during the Early Jurassic.

Keywords: zircon U–Pb ages; gabbros; magma source; Paleo-Pacific; Yanbian area

1. Introduction

Northeast China, located within the Central Asian Orogenic Belt (CAOB), is bordered to the north by the Siberian Craton, to the south by the North China Craton, and to the east by the Pacific Plate (Figure 1). This region features a complex geological landscape shaped by various tectonic processes and is characterized by an intricate network of micro-plates and subduction-accretionary complexes, resulting in a diverse array of geological features. The tectonic history of this region is particularly intricate, marked by significant events, such as the subduction and eventual closure of the Paleo-Asian Ocean. Additionally, the transformations associated with the Mongol–Okhotsk Ocean and the Paleo-Pacific Ocean have further shaped the area’s development [1–6]. As a result, Northeast China has become a focal point for geological research, particularly in understanding continental accretion, the interplay of microplates, and the transitions between oceanic and continental crust [7–10]. During the complex geological evolutionary process, numerous coeval igneous rocks were formed. The mafic–ultramafic rocks not only reflect magmatic activities at different stages but also reveal the geological environments and processes that contributed to their

formation. Therefore, studying the genesis of Early Jurassic gabbros plays a crucial role in understanding the properties of mantle-derived magmas and the tectonic evolution of the Paleo-Pacific.

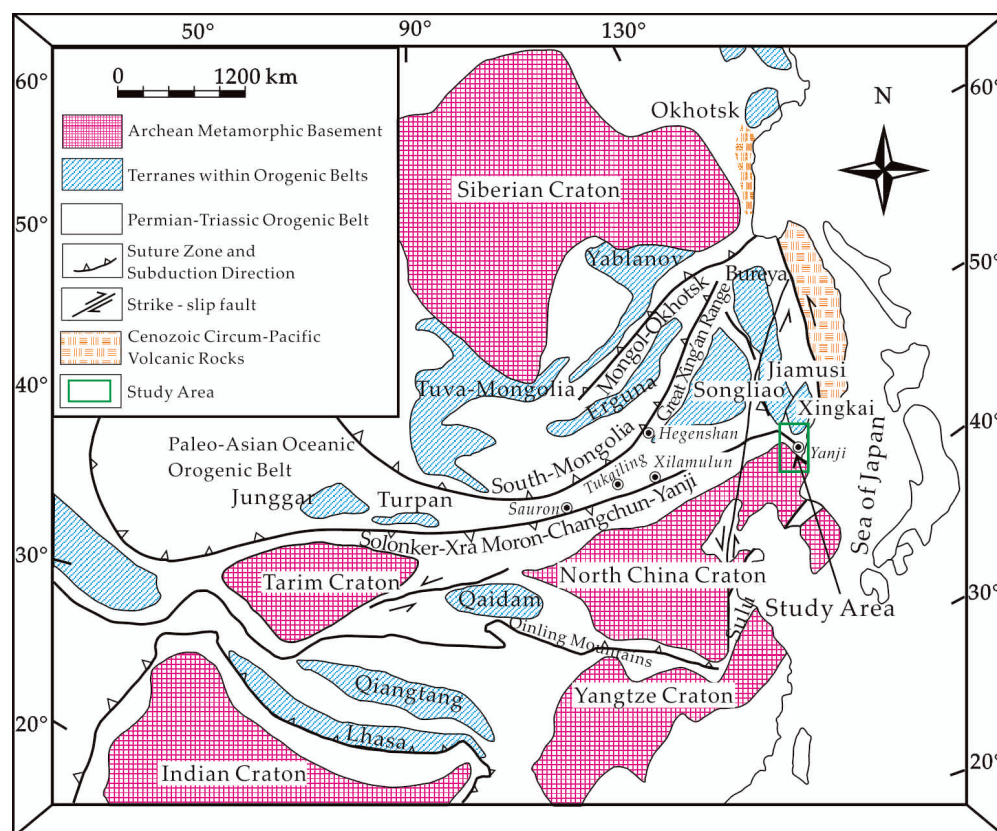


Figure 1. Tectonic unit division of the eastern part of the Central Asian Orogenic Belt (modified from [10]).

The Yanbian area in Jilin Province is structurally located in the eastern segment of the southern margin of the CAO and the western flank of the Circum-Pacific tectonic domain. Based on previous hypotheses, the Late Paleozoic to Early Mesozoic tectonic evolution of the Yanbian area remains a subject of considerable debate. One perspective suggests that the Yanbian area functions as an eastward extension of the Solonker–XraMoron–Changchun suture zone, influenced by the Paleo-Asian Ocean (PAO) tectonic domain during the Late Paleozoic to the Early Mesozoic [11–17]. According to this viewpoint, the subduction of the Paleo-Pacific Ocean (PPO) took place in the Yanbian area during the Late Triassic (~200 Ma) [11–17]. Alternatively, some argue that the Yanbian area is not an eastern extension of the Solonker–XraMoron–Changchun suture zone and was not influenced by the PAO tectonic domain during the Late Paleozoic to Early Mesozoic. Zhou et al. [3,18] defined the Changchun–Yanji suture zone and the Heilongjiang Complex west of Jiamusi as the Jilin–Heilongjiang high-pressure metamorphic belt, suggesting that its formation resulted from the westward subduction of the Pacific Plate between 210 Ma and 180 Ma, which amalgamated the Jiamusi–Xingkai block with the Songliao block and the North China Craton. Tang et al. [19] considered the Changchun–Yanji suture zone to be a product of the accretionary suture between the Late Jurassic Xingkai block and the North China Craton. Consequently, there are still differing opinions on when the Yanbian area began to be influenced by subduction processes. This study focuses on the geochronology, whole-rock geochemistry, and isotopic geochemistry of hornblende gabbro near Helong City in the Yanbian area, Jilin Province, aiming to analyze its magmatic sources and the tectonic setting, and ultimately constrain the Early Jurassic tectonic evolution of the Yanbian area in Jilin Province.

2. Geological Setting

The Yanbian area in Jilin Province is situated at the convergence of three tectonic units: the Jiamusi-Xingkai block, the Longgang block on the northern margin of the North China Craton, and the Zhangguangcai Range. The exposed strata in the study area encompass the Archaean, Paleozoic, Mesozoic, and Quaternary sediments. The intrusive rocks are also exposed widely in the study area, dominated by granitic intrusions with minor gabbros and diorites, accounting for approximately 60% of the area. These intrusive rocks can be broadly classified into three episodes: (1) Late Permian, characterized by granodiorites, quartz diorites, gneissic biotite diorites, and diorite–gabbro bodies, with granodiorite trending northwest from Changren village to Wolong village, and quartz diorite and gneissic biotite diorite distributed near the Bajiazi town; (2) Triassic, with the rocks primarily located north of the Gudonghe Fault, consisting of monzogranite, gabbro–diorite, and porphyritic monzogranite; and (3) Early-Middle Jurassic, during which the study area witnessed extensive exposure of Early-Middle Jurassic monzogranite and minor gabbro and diorite plutons, marking a period of intense magmatic activity.

3. Lithological Characteristics of Wolonghu Gabbro (D05)

The samples collected for this study are hornblende gabbro outcropped approximately 2 km east of Ji’nán village ($42^{\circ}41'9''$ N, $128^{\circ}53'8''$ E), with specific sampling locations illustrated in Figure 2. This gabbro pluton intrudes into the surrounding rocks of the Triassic granite and has an exposed area of about 1.5×1 km². Six samples, including the dating sample, were collected from the gabbro pluton, and all samples exhibit a mid-fine grain texture. The minerals of the gabbro are composed of quartz (5%), plagioclase (~55%), and hornblende (~40%). Accessory minerals include zircons, apatites, and pyrites (Figure 3).

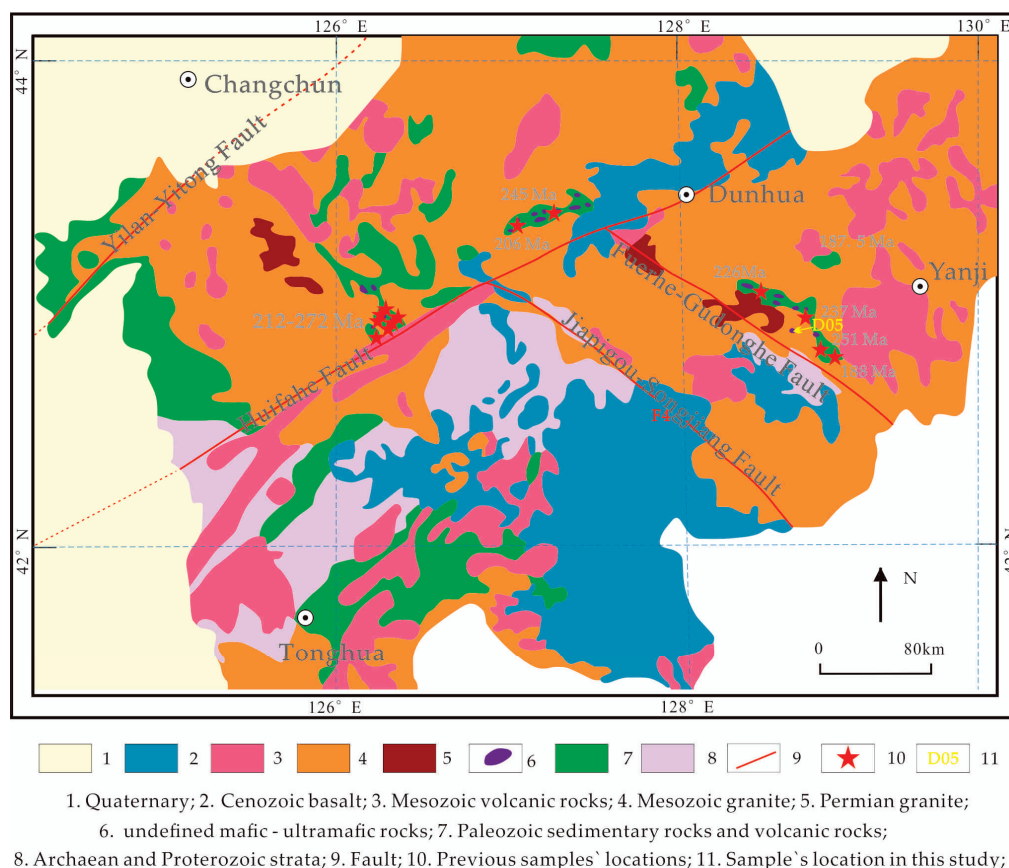


Figure 2. Distribution map of mafic and ultramafic rocks in the eastern Jilin province and the locations of the samples in the study area (modified from [20]).

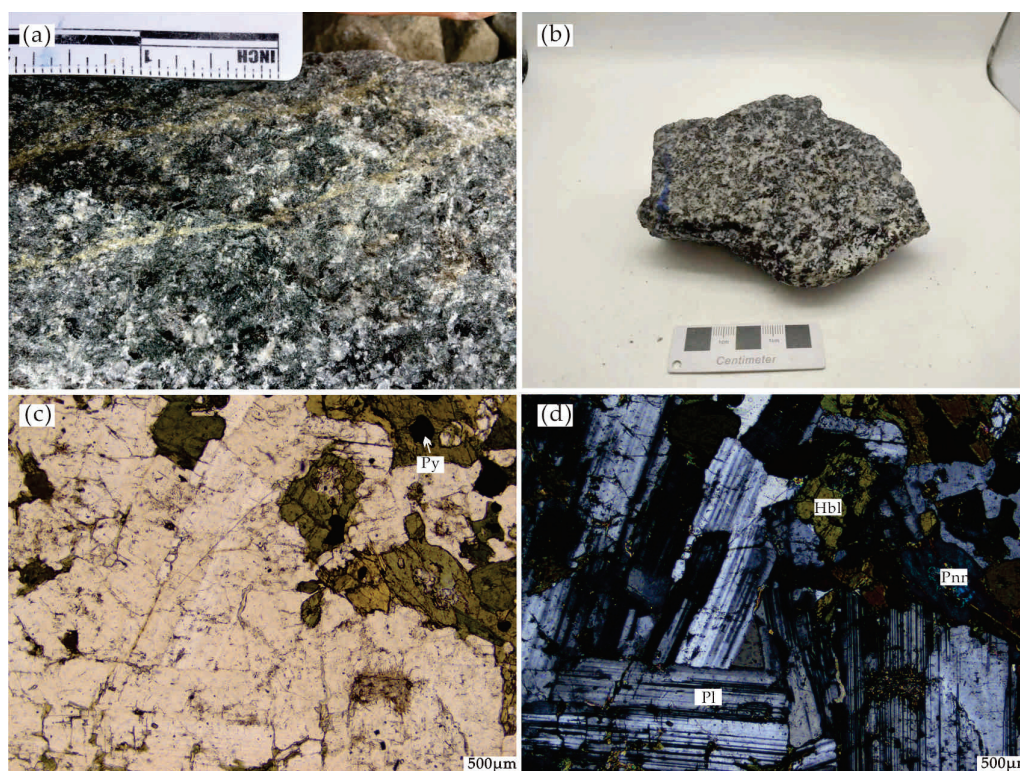


Figure 3. Representative field photographs (a,b), specimen photographs (c), and photomicrographs (d) of Wulonghu gabbro. Abbreviations: Hbl—Hornblende; Pnn—penninite; Pl—Plagioclase; Py—pyrites.

4. Analytical Methods

4.1. Zircon U-Pb Dating

This study employed the LA-ICP-MS technique to analyze the Wulonghu samples (D05). The zircon separation process for the rock samples was conducted at Yuheng Rock and Mineral Technology Services in Langfang City, Hebei Province. Initially, the samples were crushed using conventional methods and zircon grains were separated through magnetic and gravity separation. Subsequently, transparent zircons without cracks or visible inclusions were manually picked out under a binocular microscope. These zircon grains were then mounted on epoxy resin targets, polished to approximately half their thickness, and prepared as sample targets. Following preparation, the internal characteristics of the zircon grains were observed under a microscope to analyze their genetic types, and cathodoluminescence (CL) images were acquired. The CL imaging was performed using a JXA-8100 electron microprobe analyzer at Yuheng Rock and Mineral Technology Services in Langfang City, Hebei Province.

The zircon U-Pb ages were calculated using the ICPMSDataCal 9.0 data-processing software developed by the State Key Laboratory of GPMR, China University of Geosciences. Isotopic ratio corrections were applied using international standard zircons 91,500 and GJ-1 [21] as external standards for analysis and calculation. The errors for individual data points were reported at 1σ , while the errors for weighted averages were reported at 2σ . The calculation of weighted mean ages and the plotting of concordia diagrams were performed using the Isoplot R program [22], with the weighted averages exhibiting a confidence level of over 95%.

4.2. Major and Trace Element Analyses

Sample powder preparation was conducted at Guizhou Tongwei Testing Technology Co., Ltd. Based on hand specimen and petrographic analyses, representative samples were selected for major and trace element analyses. Initially, samples were sliced to remove

surface contaminants and weathered layers, then soaked in 0.5 mol/L diluted hydrochloric acid for two hours. After soaking, the samples were rinsed with distilled water and dried in an oven at 120 °C for 24 h. Subsequently, the dried fragments were ground to a 200-mesh powder for bulk rock major and trace element testing. Major elements were analyzed using an X-ray fluorescence spectrometer with an analytical error of less than 1%. Trace element analysis was performed on a Thermal Fisher iCAP RQ ICP-MS equipped with a Cetac ASX-560 AutoSampler made in Bremen, Germany. The detailed workflow is as follows: (1) Accurately weigh 50–100 mg of powdered sample into a Teflon digestion vessel, sequentially adding 1 mL of high-purity HNO₃ and HF, and shaking to mix thoroughly; (2) place the mixed digestion vessel in a steel jacket and heat in an oven at 190 °C for at least 24 h; (3) after complete cooling, open the vessel and evaporate the solution on a 140 °C hotplate before adding 1 mL of HNO₃ and evaporating again; (4) add 1 mL of high-purity HNO₃, 1 mL of MQ water, and 1 mL of internal standard solution (containing Rh, In, Re, and Bi as internal standards), replace the digestion vessel in the steel jacket, and heat in an oven for over 12 h; and (5) transfer the solution to a polyethylene bottle and dilute with 2% HNO₃ solution to 100 g for ICP-MS analysis. USGS standards W-2a and BHVO-2 were used as reference materials during data processing.

4.3. Bulk Rock Sr-Nd Isotope Analysis

The Sr-Nd isotope separation and purification processes were carried out at Guizhou Isotope Detection Technology Co., Ltd. Sample digestion was performed as follows: (1) Ground powdered samples to 50–100 µm and dry in an oven at 105 °C for 12 h; (2) accurately weigh 50–100 mg of the powdered sample into a Teflon digestion vessel; (3) sequentially add 1 mL of high-purity HNO₃ and 1 mL of high-purity HF; (4) place the Teflon digestion vessel in a steel jacket, tighten, and heat in an oven at 190 °C for over 24 h; (5) after cooling, evaporate the solution on a 140 °C hotplate, add 1 mL of HNO₃, and evaporate again; and (6) dissolve the evaporated sample with 1.5 mL of 2.5 mol/L HCl, 1.0 mol/L HBr, and 2.0 mol/L HF for subsequent chemical separation. Chemical separation involved centrifuging the samples and placing them in a clean column filled with resin. The column was sequentially rinsed with 2.5 mol/L HCl, 0.18 mol/L HCl, 3 mol/L HCl, 6 mol/L HCl, and 4 mol/L HCl + H₂O₂ to remove matrix elements. Finally, Sr and Nd were eluted and collected from the column using 2.5 mol/L HCl, 0.3 mol/L HCl, 6.0 mol/L HCl, and 2.0 mol/L HCl, respectively. The collected Sr and Nd solutions were evaporated to dryness for analysis. Isotope analysis was conducted using a Thermo Fisher Plus Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS). The experimental protocol employed two isotopic standards, USGS W-2a and BHVO-2, for normalization. The ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd ratios were calibrated against NIST987 (⁸⁷Sr/⁸⁶Sr = 0.710 249, 2σ) and NIST987 (¹⁴³Nd/¹⁴⁴Nd = 0.512 115, 2σ), respectively.

5. Results

5.1. Geochemical Characteristics of the Wolonghu Gabbro

The Wolonghu gabbro samples comprise SiO₂ = 46.38 wt% to 51.43 wt%, TiO₂ = 0.99 wt% to 1.185 wt%, Al₂O₃ = 17.31 wt% to 17.99 wt%, MgO = 4.86 wt% to 5.23 wt%, and Mg[#] = 50.23 to 52.55 (Table 1). In the TAS diagram, all the samples of the Wolonghu gabbros plot within the fields of monzogabbro and gabbro–diorite (Figure 4a), while belonging to the high-K calc-alkaline to shoshonitic series, with most samples falling within the high-K calc-alkaline series in the SiO₂–K₂O diagram (Figure 4b). The A/CNK values (Al₂O₃/[CaO+K₂O+Na₂O]) of the Wolonghu gabbros range from 0.78 to 0.84, indicative of a metaluminous character (Figure 4c). In the AFM diagram (Na₂O+K₂O–FeO^T–MgO), the samples plot within the calc-alkaline series (Figure 4d).

Table 1. The results of major (wt%) and trace element (ppm) analysis for the Wolonghu gabbros.

Sample No.	D05-1	D05-2	D05-3	D05-4	D05-5	D05-6
SiO ₂	49.24	51.43	51.10	51.10	46.38	50.41
Al ₂ O ₃	17.73	17.82	17.73	17.62	17.99	17.31
Fe ₂ O ₃	9.78	9.61	9.59	9.96	9.41	9.69
MgO	5.21	4.86	5.03	5.06	5.22	5.23
CaO	8.25	7.89	8.37	8.24	8.88	7.61
Na ₂ O	2.73	2.98	3.12	2.95	2.56	2.68
K ₂ O	2.29	1.88	1.53	1.62	2.51	2.16
MnO	0.17	0.15	0.16	0.17	0.17	0.16
P ₂ O ₅	0.20	0.22	0.26	0.26	0.20	0.23
TiO ₂	1.19	1.15	0.99	1.02	1.14	1.15
Cr	0.00	0.00	0.01	0.01	0.00	0.00
S	0.04	0.08	0.12	0.13	0.02	0.12
LOI	3.61	1.37	1.22	1.16	5.28	2.78
SUM	100.44	99.43	99.23	99.29	99.76	99.53
Mg [#]	51.53	50.23	51.15	50.35	52.54	51.86
Li	35.10	22.90	21.70	23.50	42.20	32.20
Mg	31,300.00	29,700.00	30,400.00	30,300.00	30,900.00	31,800.00
Sc	22.90	23.70	22.00	22.30	24.70	23.30
Ti	7020.00	6920.00	5950.00	6090.00	6920.00	6900.00
V	216.00	220.00	210.00	218.00	221.00	215.00
Cr	51.90	50.40	64.30	63.70	48.50	49.50
Mn	1330.00	1190.00	1280.00	1330.00	1330.00	1240.00
Fe	67,100.00	67,000.00	66,500.00	68,400.00	65,100.00	66,900.00
Co	25.90	28.60	32.00	33.60	22.50	29.40
Ni	31.00	19.00	25.40	22.10	19.70	20.30
Cu	24.00	67.20	146.00	116.00	6.34	31.20
Zn	116.00	99.70	91.00	93.50	123.00	113.00
Ga	21.00	21.10	20.70	20.90	21.60	20.60
Rb	93.20	69.30	56.30	59.10	105.00	85.50
Sr	634.00	667.00	703.00	689.00	663.00	624.00
Y	21.90	23.00	19.60	19.60	24.00	23.60
Zr	132.00	117.00	110.00	109.00	106.00	113.00
Nb	9.52	8.80	6.25	6.33	9.04	8.88
Cs	11.50	8.40	9.39	10.10	13.80	11.80
Ba	361.00	324.00	384.00	401.00	368.00	334.00
La	28.10	29.80	25.40	24.40	29.50	30.80
Ce	65.70	68.70	53.10	51.10	69.50	72.50
Pr	7.54	7.72	6.27	6.12	7.96	8.14
Nd	27.30	28.00	24.70	24.30	29.30	29.50
Sm	5.25	5.42	4.83	4.81	5.71	5.57
Eu	1.24	1.32	1.29	1.29	1.35	1.31
Gd	4.57	4.77	4.31	4.31	5.04	4.90
Tb	0.69	0.72	0.64	0.64	0.76	0.75
Dy	3.86	4.05	3.54	3.56	4.28	4.21
Ho	0.76	0.80	0.70	0.70	0.83	0.82
Er	2.11	2.19	1.87	1.88	2.27	2.27
Tm	0.32	0.33	0.27	0.28	0.34	0.34
Yb	2.01	2.05	1.68	1.68	2.13	2.13
Lu	0.31	0.31	0.25	0.25	0.32	0.32
Hf	4.06	3.69	3.18	3.15	3.42	3.56
Ta	0.45	0.43	0.41	0.42	0.45	0.44
Pb	10.60	9.40	9.75	9.67	12.40	9.47
Th	5.36	5.03	5.41	4.86	5.22	5.47
U	1.29	1.50	1.34	1.23	1.29	1.42
(La/Yb) _N	9.43	9.80	10.19	9.79	9.34	9.75
δEu	0.76	0.78	0.85	0.85	0.75	0.75
ΣREE	149.76	156.18	128.85	125.32	159.30	163.56
ΣLREE	135.13	140.96	115.59	112.02	143.32	147.82
ΣHREE	14.63	15.22	13.26	13.30	15.98	15.74

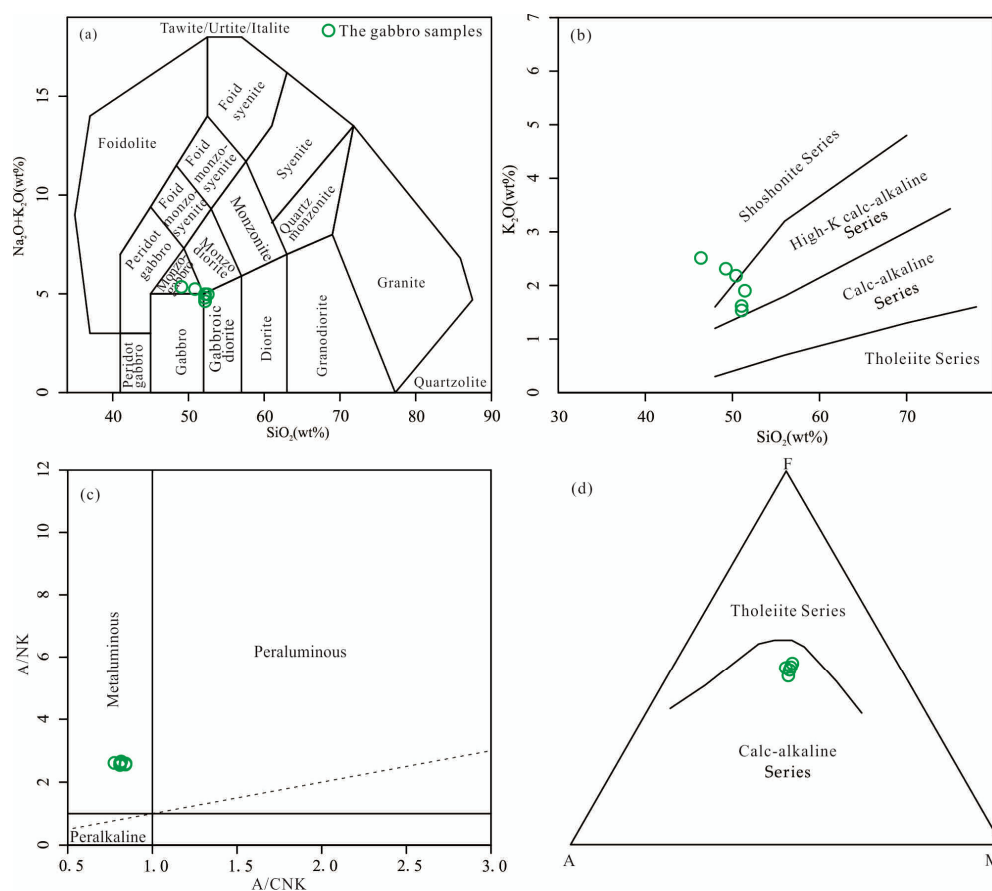


Figure 4. (a) TAS diagram (modified from [23]); (b) SiO_2 vs. K_2O diagram (modified from [24]); (c) ANK vs. A/NK diagram (modified from [25]); (d) AFM diagrams (modified from [23]) of the Wolonghu gabbros.

In the primitive mantle-normalized spider diagrams (Figure 5a), all the samples are enriched in large ion lithophile elements (LILEs, e.g., Rb, Ba, and K) and depleted in high-field-strength elements (HFSEs, e.g., Nb, Ta, and Ti), characteristic of basic magmatic rocks formed in a subduction setting. The total REE contents range from 125.32 ppm to 163.56 ppm, and the ratios of LREE/HREE (8.45 to 9.25) and $(\text{La}/\text{Yb})_N$ (9.33 to 10.19) display a pronounced right-leaning fractionation pattern (Figure 5b). The Eu anomalies (δEu) of the Wolonghu gabbros range from 0.75 to 0.85, indicating negative Eu anomalies.

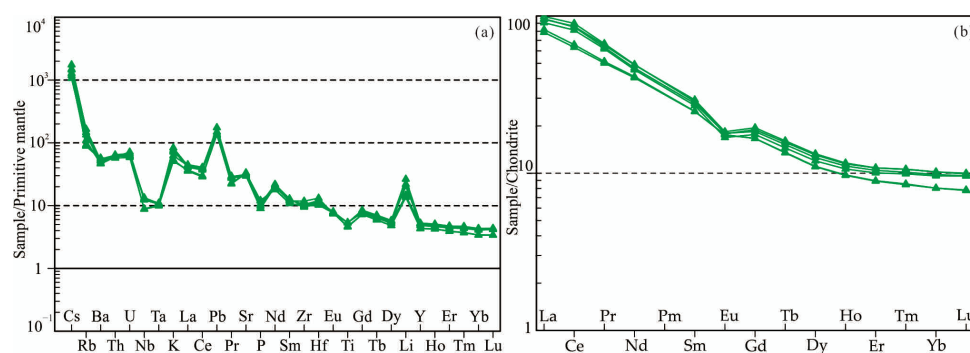


Figure 5. (a). Primitive mantle-normalized spider diagrams of Wolonghu gabbros (modified from [26]); (b) Chondrite-normalized REE patterns (modified from [27]) of Wolonghu gabbros.

5.2. Sr-Nd Isotopes of the Wolonghu Gabbros

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Wolonghu gabbros range from 0.706 463 to 0.706 954. These $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are higher than those of Hawaiian-type mid-ocean ridge basalts (MORBs) [28] (0.702 29–0.703 16) and ocean island basalts (OIBs) (0.703 17–0.704 12). Otherwise, the initial $^{143}\text{Nd}/^{144}\text{Nd}$ values range from 0.512 347 to 0.512 368 (Table 2), while the $\epsilon_{\text{Nd}}(t)$ values of the Wolonghu gabbros are -3.93 to -3.53 , with one-stage ages ranging from 1249 to 1286 Ma.

Table 2. The results of Sr-Nd isotopic analysis for the gabbros.

Sample	D05-1	D05-2	D05-3	D05-4
$^{87}\text{Sr}/^{86}\text{Sr}$	0.706 954	0.706 630	0.706 463	0.706 506
$\pm 2\sigma$	0.000 008	0.000 007	0.000 009	0.000 008
I_{Sr}	0.71	0.71	0.71	0.71
$^{143}\text{Nd}/^{144}\text{Nd}$	0.512 349	0.512 347	0.512 368	0.512 357
2σ	0.000 007	0.000 008	0.000 008	0.000 008
I_{Nd}	0.51	0.51	0.51	0.51
$\epsilon_{\text{Nd}}(t)$	-3.87	-3.94	-3.54	-3.78
2σ	0.07	0.07	0.08	0.08
T_{DM}	1254	1268	1249	1286
T_{DMC}	1274	1279	1247	1267

5.3. Geochronology of the Wolonghu Gabbros

Twenty spots from the Wolonghu gabbro sample (D05) were selected for zircon LA-ICP-MS dating, and the U-Pb isotope analysis results have been summarized in Table 3. The grain sizes of the zircons from the Wolonghu gabbros range from 150 μm to 400 μm (Figure 6). They are semihedral to euhedral in shape, with most displaying a high degree of euhedrality. The zircons, featuring distinct oscillatory zoning, possess Th/U ratios ranging from 0.53 to 1.22, indicative of magmatic zircon characteristics. The ages of the 20 analyzed zircons range from 169 ± 3 Ma to 185 ± 3 Ma, yielding a weighted mean age of 175.3 ± 1.6 Ma ($n = 20$, MSWD = 1.9; Figure 7).

Table 3. The LA-ICP-MS zircon U-Pb results of Wolonghu gabbros (D05).

Sample No.	Th	U	$^{207}\text{Pb}/^{235}\text{U}$	σ	$^{206}\text{Pb}/^{238}\text{U}$	σ	$^{206}\text{Pb}/^{238}\text{U}$
D05-1	87	151	0.189	0.011	0.028	0.0007	178.1 ± 4.2
D05-2	172	205	0.191	0.009	0.028	0.0006	179.2 ± 4.0
D05-3	99	167	0.193	0.010	0.028	0.0005	178.4 ± 3.4
D05-4	73	121	0.210	0.018	0.027	0.0008	171 ± 4.7
D05-5	141	264	0.201	0.007	0.029	0.0007	182.8 ± 4.5
D05-6	124	234	0.207	0.009	0.029	0.0005	182.9 ± 3.1
D05-7	114	199	0.202	0.008	0.029	0.0005	184.9 ± 3.3
D05-8	164	231	0.189	0.008	0.027	0.0006	170.5 ± 3.9
D05-9	95	165	0.200	0.008	0.028	0.0007	180.7 ± 4.3
D05-10	119	218	0.192	0.008	0.027	0.0006	170.9 ± 3.8
D05-11	199	224	0.196	0.007	0.028	0.0006	177.6 ± 3.9
D05-12	115	188	0.189	0.010	0.028	0.0006	177.5 ± 3.6
D05-13	198	200	0.191	0.009	0.027	0.0005	171.8 ± 3.1
D05-14	284	389	0.197	0.008	0.027	0.0005	168.9 ± 2.9
D05-15	274	257	0.200	0.008	0.029	0.0007	181.5 ± 4.3
D05-16	156	180	0.201	0.009	0.028	0.0006	178.1 ± 4.0
D05-17	297	244	0.175	0.008	0.027	0.0003	170.8 ± 2.1
D05-18	366	347	0.187	0.007	0.028	0.0005	175.9 ± 3.4
D05-19	144	170	0.189	0.009	0.028	0.0006	179.6 ± 3.8
D05-20	71	132	0.187	0.010	0.028	0.0007	177.1 ± 4.6

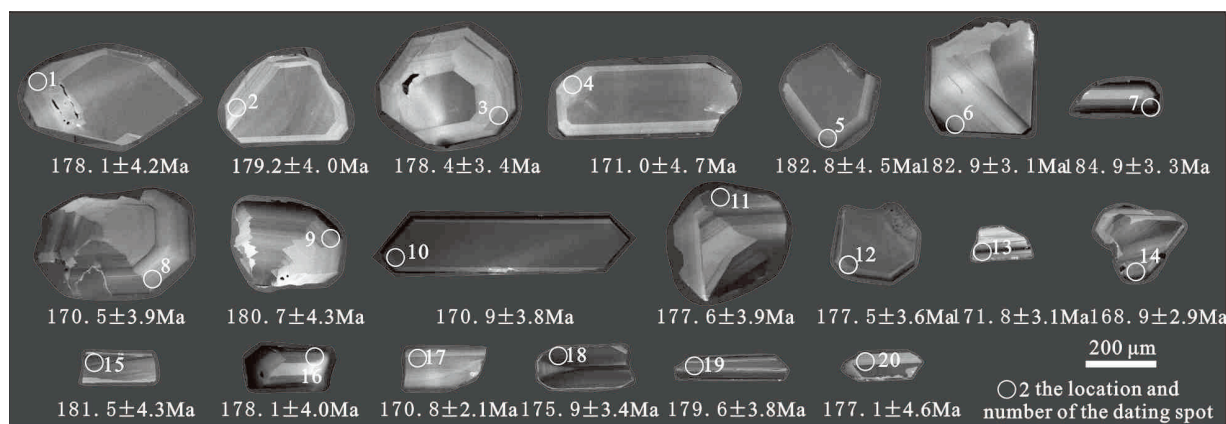


Figure 6. Cathodoluminescence (CL) image of the zircons for Wolonghu gabbros (D05).

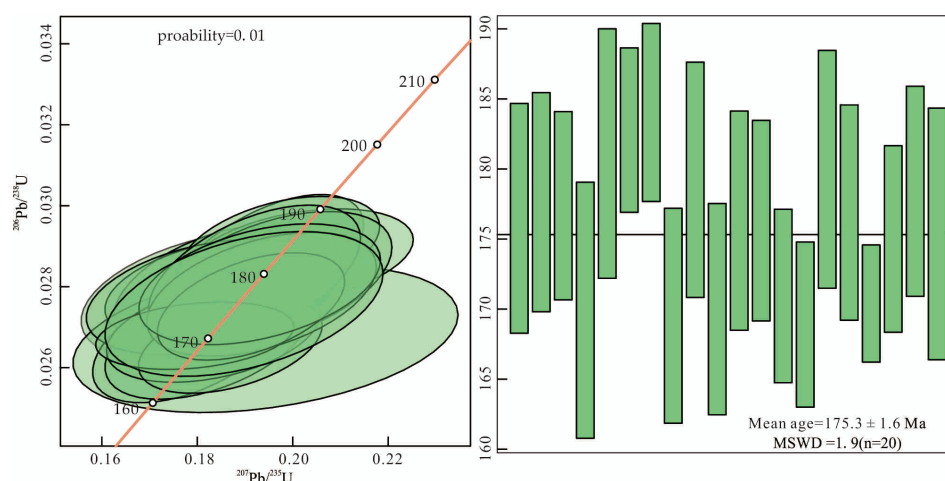


Figure 7. LA-ICP-MS zircon U-Pb concordia diagrams and weighted mean age of the Wolonghu gabbros (D05).

6. Discussion

6.1. Magma Source and Petrogenesis of the Wolonghu Gabbros

The Wolonghu gabbros are characterized by low SiO_2 and TiO_2 , and possess the MgO contents and $\text{Mg\#}$ values of typical gabbroic geochemical features. All samples have been plotted as monzogabbro and gabbro–diorite while enriched in Al_2O_3 and large ion lithophile elements (LILEs), with a depletion in high-field-strength elements (HFSEs). The petrology and geochemistry indicate that these rocks may have formed in an environment characterized by both mafic and slightly more evolved compositions. Additionally, the classifications in TAS and AFM diagrams highlight that the samples are likely derived from subduction zone-related magmatic activity consistent with high potassium content, which can indicate a more evolved source or interaction with crust materials. All in all, the geochemical characteristics of these gabbros imply a complex petrogenetic history, potentially involving multiple stages of melting, crystallization, and possibly interaction with crustal materials. The Ce/Pb and Nb/U ratios can serve as effective indicators for assessing crustal contamination in mafic magmas derived from the mantle [29–32], while Ce/Pb and Nb/U ratios are very different between those in continental crust ($\text{Ce/Pb} = 3.9$, $\text{Nb/U} = 6.2$ [33]) and those in oceanic crust ($\text{Ce/Pb} = 25 \pm 5$ and $\text{Nb/U} = 47 \pm 10$, [32]).

The Th/La ratios of the Wolonghu gabbro range from 0.17 to 0.21, aligning with subduction-related magmas ($\text{Th/La} < 0.2$) [34]. All the samples indicate an active continental margin setting (Figure 8) and plot within the continental arc field in the Th/Yb-Nb/Yb diagram (Figure 8c). Combined with the low $\text{Na}_2\text{O/K}_2\text{O}$ ratios (1.24–1.67) of the gabbros,

the Wolonghu gabbro formed in a continental arc setting rather than an oceanic arc setting (Figure 8). Additionally, the Wolonghu gabbro exhibits low Ce/Pb (5.28–7.66) and Nb/U (5.08–6.34) values, suggesting crustal contamination by the continental crust [34,35], while all the samples fall within the overlapping range between the crustal contamination and subducted-related mafic rocks (Figure 9).

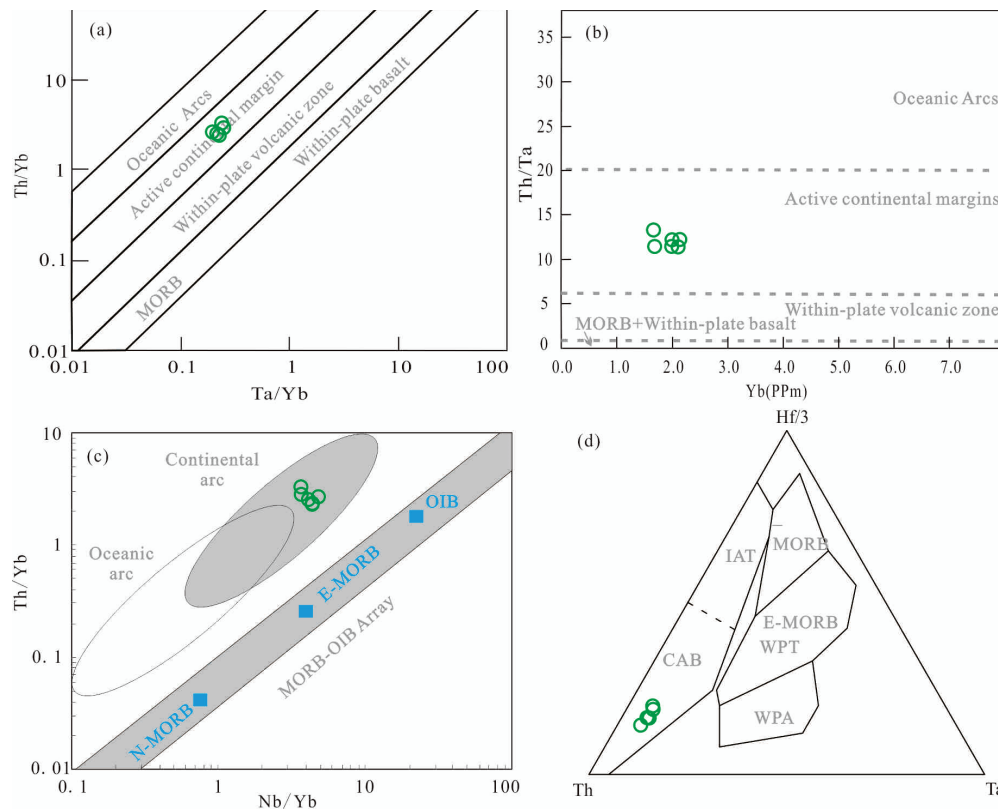


Figure 8. (a) Th/Yb-Ta/Yb diagram (modified from [29]); (b) Th/Ta-Yb diagram (modified from [29]); (c) Th/Yb-Nb/Yb (modified from [30]); (d) Hf/3-Th-Ta (modified from [31]) for Wolonghu gabbros. Abbreviations: N-MORB—Normal mid-ocean ridge basalt; E-MORB—Enriched mid-ocean ridge basalt; IAT—Island arc tholeiite; WPT—Tholeitic within-plate basalt; CAB—Calc-alkaline basalt; WPA—Alkaline within-plate basalt.

Within subduction arc systems, fluids or melts generated from subduction-related sediments play a crucial role in shaping the arc-type trace element distributions and isotopic enrichments observed in rocks [36,37]. Rare earth elements (REEs), Nb, Zr, Th, and Ba exhibit distinct geochemical behaviors in sediment-derived fluids and aqueous melts, enabling them to serve as indicators for distinguishing between melts and fluids evolved from subducted sediments [38–40]. The positive correlation between Th/Sm and Th/Ce ratios in the Wolonghu gabbro suggests significant sediment input into the mantle wedge (Figure 10a). Furthermore, the Wolonghu gabbros display distinct characteristics of sediment melt addition, indicating that its primary magma was affected by sediment melts (Figure 10b,c). Alternatively, the present work reports evidence that UHP ‘supercritical’ fluids released from subducting sediments along an intermediate geothermal gradient can be efficient metasomatic agents as hydrous silicate melts [41]. Our data reveal that the magmatism is generated by processes involving metasomatic addition to the source mantle wedge by ‘supercritical’ fluids (Figure 10d).

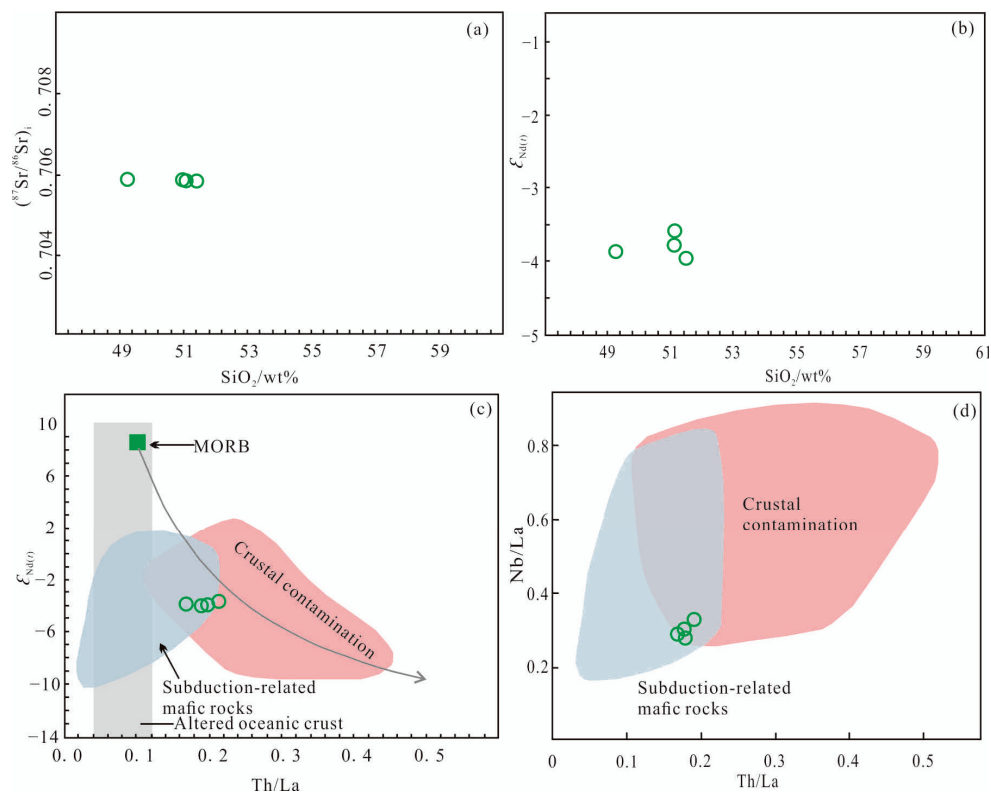


Figure 9. (a) SiO_2 - $(^{87}\text{Sr}/^{86}\text{Sr})_i$ diagram; (b) SiO_2 - $\epsilon\text{Nd}(t)$ diagram; (c) $\epsilon\text{Nd}(t)$ -Th/La diagram (modified from [35]); (d) Nb/La-Th/La diagram (modified from [35]) for Wolonghu gabbros.

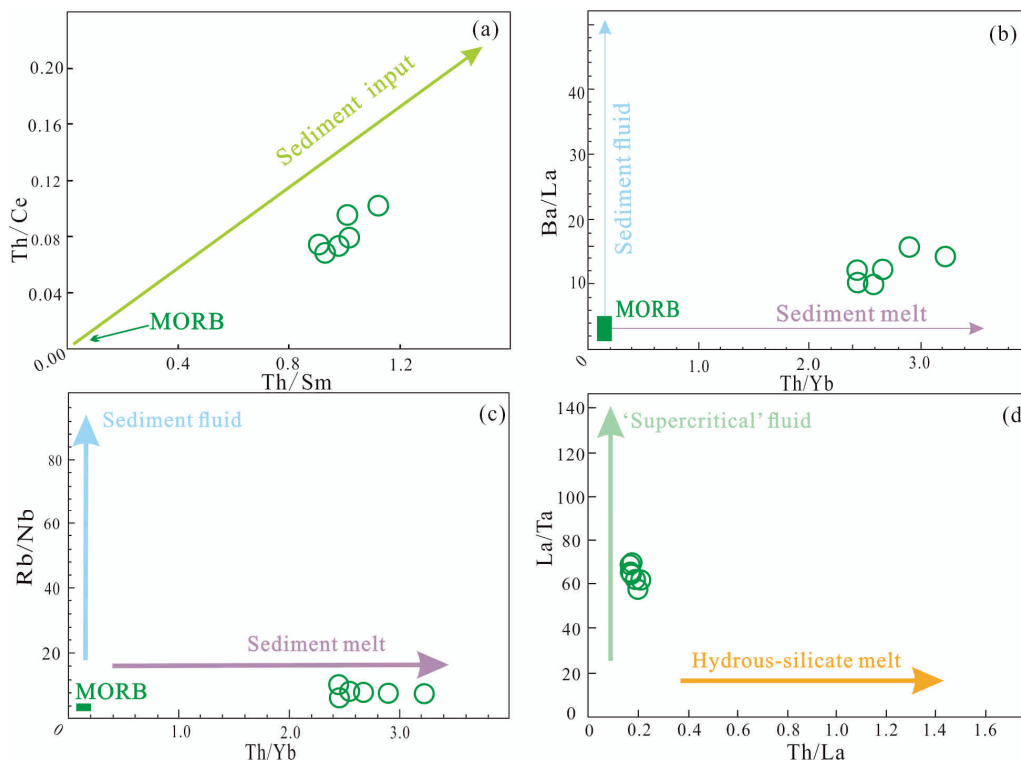


Figure 10. (a) Th/Ce vs. Th/Sm diagram (modified from [38]); (b) Ba/La vs. Th/Yb diagram (modified from [42]); (c) Rb/Nb vs. Th/Yb diagram (modified from [42]); (d) Th/La vs. La/Ta variations (modified from [41]) for Wolonghu gabbros.

Due to the distance of oceanic arcs from continental crusts, the oceanic sediments typically enter the mantle wedge from the subducting setting. Conversely, terrigenous sediments are more prevalent in continental arcs [42]. Furthermore, the concentration of Hf in zircon and Nd in clay minerals results in coarser-grained terrigenous sediment shaving with higher Hf/Nd ratios and lower Lu/Hf ratios, while finer-grained oceanic sediments typically exhibit lower Hf/Nd ratios and higher Lu/Hf ratios [43–48]. Consequently, the Th/REE and Hf/REE ratios of mafic rocks are widely used to trace the contributions of these two types of sediments to mantle enrichment processes [34]. The Wolonghu gabbro displays notably low Lu/Hf values and high Th/Yb and Th/La ratios, suggesting enrichment of continental sediments in its mantle source region, with a possible minor contribution from oceanic sediments (in Figure 11a,b).

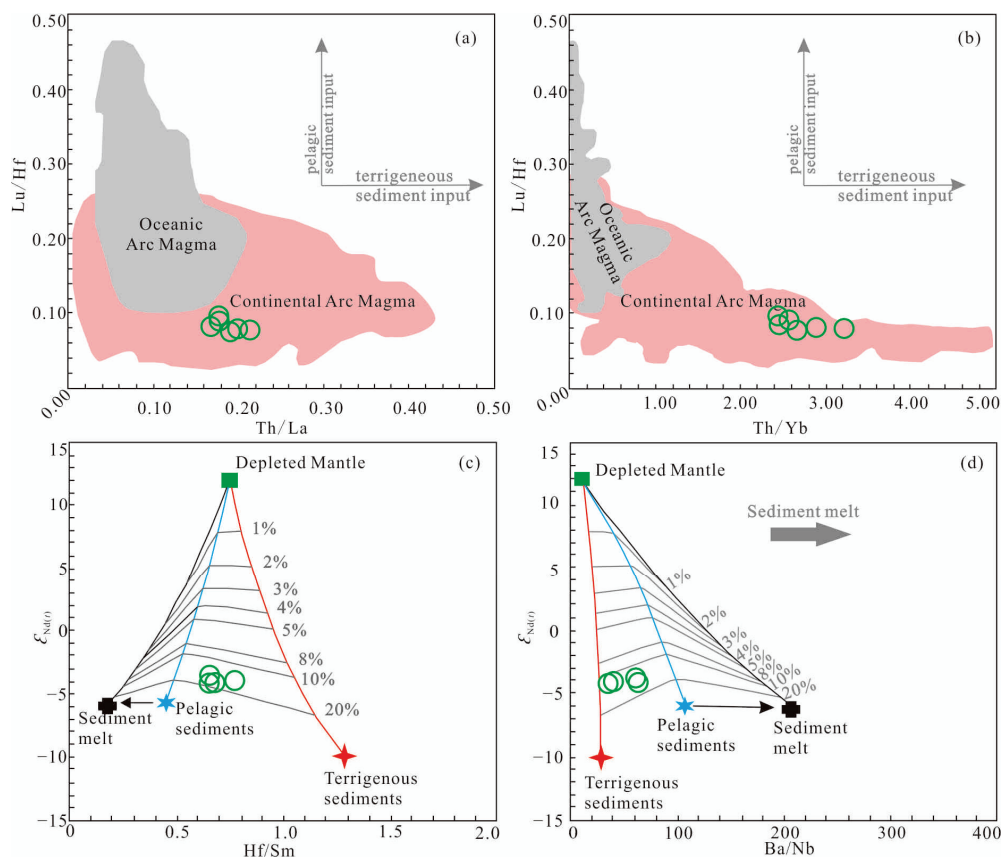


Figure 11. (a) Lu/Hf-Th/La diagram (modified from [42]); (b) Lu/Hf-Th/Yb diagram (modified from [42]); (c) $\epsilon_{\text{Nd}}(t)$ -Hf/Sm diagram (modified from [42]); (d) $\epsilon_{\text{Nd}}(t)$ -Ba/Nb diagram (modified from [42]) for Wolonghu gabbros.

To further confirm the contributions of these two sediment types to the magma evolution process, we employ the discrimination model proposed by Zhao et al. [42] to assess the sedimentary contributions in the Wolonghu gabbro. The discrimination results based on Hf/Sm, Ba/Nb, and $\epsilon_{\text{Nd}}(t)$ values (Figure 11c,d) indicate that the Wolonghu gabbro originated from a mantle wedge evolved from depleted mantle, with the addition of 10%–20% terrigenous sediments.

6.2. Tectonic Evolution of Early Jurassic Magmatic Activities

Zircon U-Pb age indicates that the emplacement age of Wolonghu gabbros is Early Jurassic. The Early to Middle Jurassic rock assemblages distributed in the Yanbian area exhibit a continuous sequence of basic–intermediate–acidic rocks (Figure 12a,b), with the majority belonging to the calc-alkaline to high-K calc-alkaline series. Among them, the granites are primarily I- or S-type arc magmatic rocks (Figure 12c,d). Furthermore, the

trace elements and isotopic signatures of the Early Jurassic mafic intrusive rocks in the Yanbian area are characteristic of those associated with the subduction of the Paleo-Pacific plate [42].

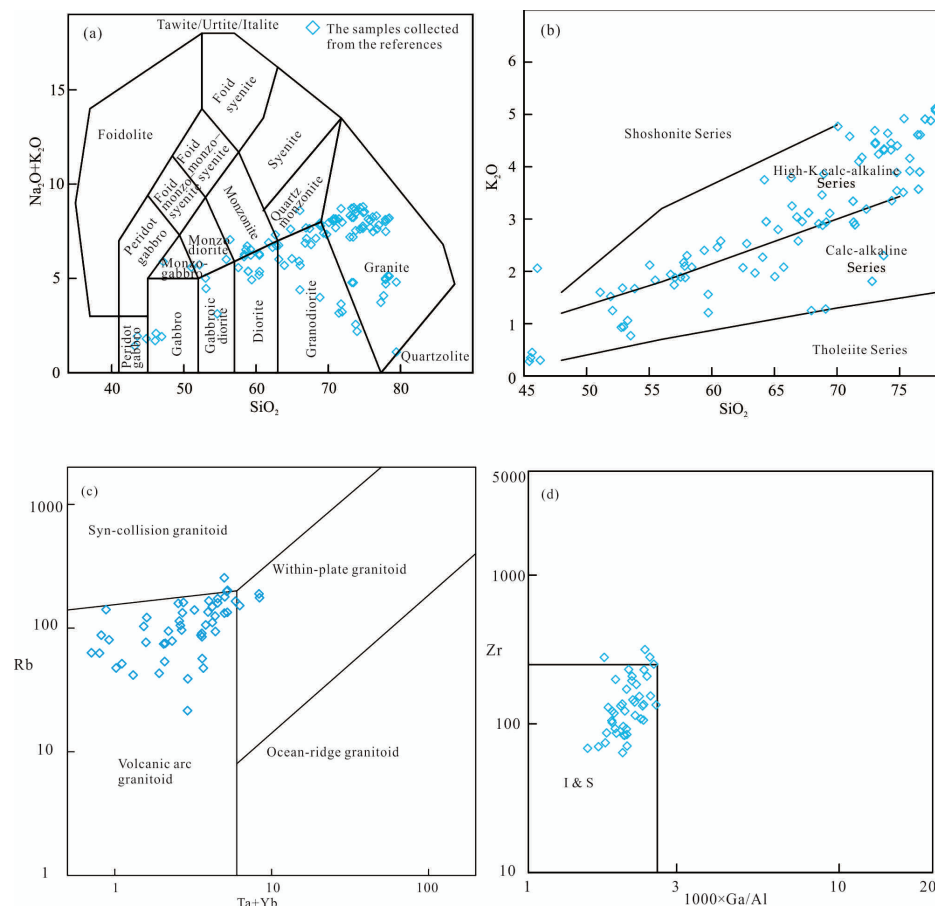


Figure 12. (a) TAS diagram (modified from [23]); (b) SiO₂-K₂O diagram (modified from [24]); (c) Rb-Y + Nb diagram (modified from [49]); (d) Zr-10,000 × Ga/Al diagram (modified from [49]) for Jurassic intrusive rocks in the Yanbian area.

Based on recent hypotheses, the eastern part of the CAOB experienced collisions and post-collision extensions following the final closure of the PAO, as well as subduction of the PPO and the Mongol–Okhotsk Ocean during the Mesozoic. These geological processes resulted in the development of extensive magmatic belts and substantial mineral resources [1,6,50–58]. The Yanbian region is located at the southeastern margin of the CAOB, serving as a direct area of interaction between the PAO tectonic domain and the PPO tectonic domain. The closure time of the PAO tectonic domain and the subduction timing of the PPO in this region have attracted significant attention from domestic and international scholars [1–3,6,14,59]. During the Late Triassic, the distribution of rocks, such as the orthopyroxene-bearing olivine rock, mafic–ultramafic intrusions, pyroxenite, and A2-type granodiorite, in the Yanbian region exhibits an east–west orientation. This rock assemblage suggests that the Yanbian area was in an extensional tectonic environment during the Late Triassic [1,6]. Combined with the metamorphic ages from the Late Triassic Dajiangou Formation [53,60], the Kedao Formation (210 Ma [61]), and the Hulan Group (220 Ma [62]), the Late Triassic extensional tectonic environment of the Yanbian area represents the final closure time of the PAO tectonic domain. Therefore, the magmatic rocks with active continental margin characteristics during the Jurassic in the eastern Yanbian area should be unrelated to the evolution of the PAO tectonic domain. Spatially, the Early to Middle Jurassic magmatic rocks in the Yanbian area exhibit a northeast–southwest trending

distribution (Figure 13); this distribution direction of the magmatic arcs is consistent with the subduction of the PPO. In addition, the Early to Middle Jurassic granitoid rocks also exhibit a rock assemblage and geochemical characteristics consistent with a subduction background. The Early Jurassic mafic intrusions and contemporaneous I-type granites form a bimodal magmatic assemblage. This bimodal magmatic assemblage has been interpreted as magmatic events in an extensional environment of the back-arc basin during the subduction of the Paleo-Pacific. The contemporaneous accretionary complexes (186–176 Ma) have also been reported as the Heilongjiang Complex, Khabarovsk Complex, and Minodanbo Complex [3]. These deformation ages' accretionary complexes range from 186 Ma to 176 Ma and are consistent with the emplacement age of Early Jurassic magmatic events [13]. In summary, the Early Jurassic metamorphic events and contemporaneous magmatic events are interpreted as products of the Early Jurassic subduction of the PPO, indicating that the Yanbian area was in a tectonic environment of westward subduction of the Paleo-Pacific during the Early Jurassic.

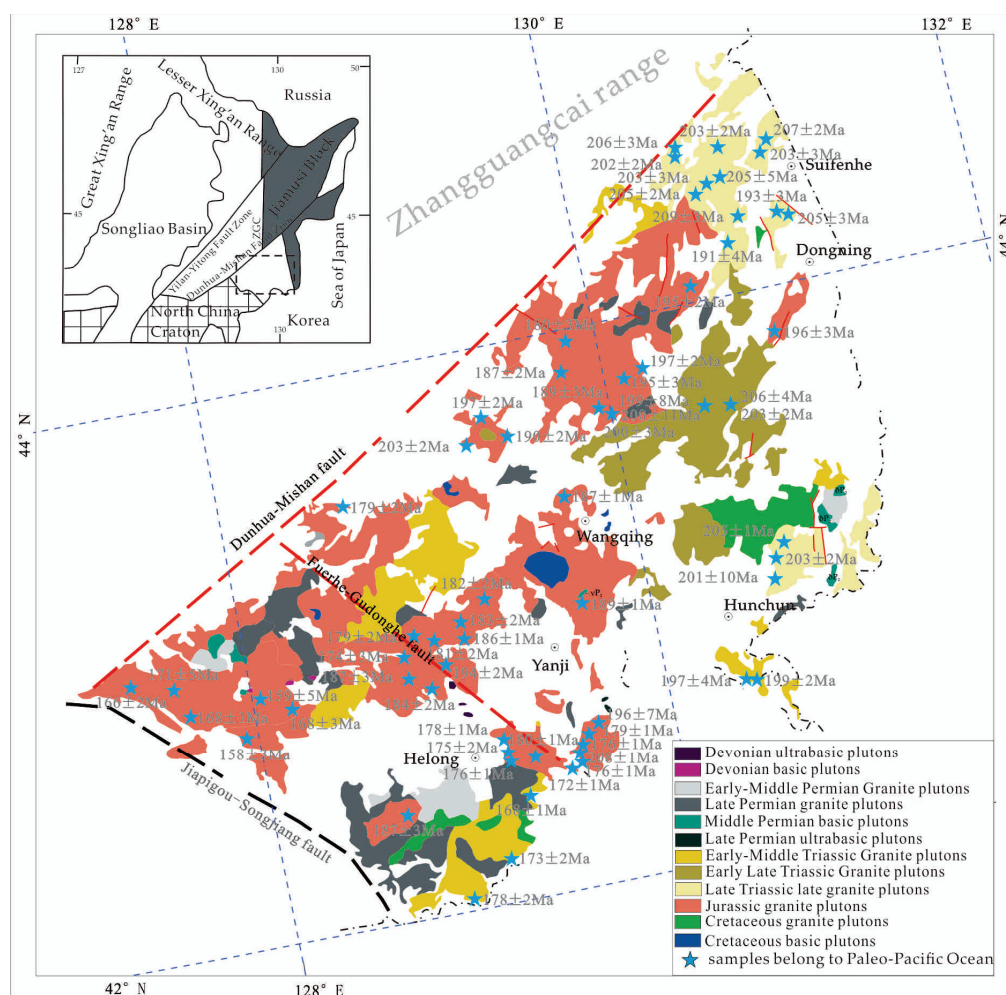


Figure 13. Distribution of Jurassic intrusive rocks in the Yanbian area (data from [1,16,50–58]).

7. Conclusions

The Early Jurassic gabbro has an emplacement age of 175.3 ± 1.6 Ma, and is the product of the subduction of the Paleo-Pacific Ocean.

The Wolonghu gabbro displays geochemical features characteristic of a metaluminous composition. Its trace element patterns exhibit a pronounced right-leaning fractionation pattern, with depletions in high-field-strength elements such as Nb and Ta, indicative of subduction-related geochemistry.

The magma of Wolonghu gabbros was formed by the mixing of 10%–20% terrigenous sediments with a mantle wedge evolved from depleted mantle, while the magmatism is generated by processes involving metasomatic addition to the source mantle wedge by ‘supercritical’ fluids.

Author Contributions: Conceptualization, R.G. and Y.L.; methodology, R.G.; software, Z.F.; validation, R.G., and B.Y.; formal analysis, Z.F.; investigation, Y.L.; data curation, Z.W. and B.Y.; writing—original draft preparation, R.G.; writing—review and editing, Z.W., Y.L. and B.Y.; project administration, B.Y.; funding acquisition, B.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science Foundation of Jilin Province (grant number YDZJ202401533ZYTS) and the Key Popular Science Project of the Jilin Province Science and Technology Association (grant number KPCX3).

Data Availability Statement: Data will be made available by the authors on request.

Acknowledgments: We acknowledge Luyuan Wang for his assistance during the writing process.

Conflicts of Interest: Authors Rui Geng and Yixin Li were employed by the company Shandong Gold Mining Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Wu, F.Y.; Sun, D.Y.; Ge, W.C.; Zhang, Y.B.; Grant, M.L.; Wilde, S.A.; Jahn, B.M. Geochronology of the Phanerozoic granitoids in Northeastern China. *Asian Earth Sci.* **2011**, *41*, 1–30. [CrossRef]
2. Liu, Y.J.; Li, W.M.; Feng, Z.Q.; Wen, Q.B.; Neubauer, F.; Liang, C.Y. A review of the Paleozoic tectonics in the eastern part of central Asian orogenic belt. *Gondwana Res.* **2017**, *43*, 123–148. [CrossRef]
3. Zhou, J.B.; Pu, X.G.; Hou, H.S.; Han, W.; Cao, J.L.; Li, G.Y. The Mesozoic accretionary complex in NE China and its tectonic implications for the subduction of the Paleo-Pacific plate beneath the Eurasia. *Acta Petrol. Sin.* **2018**, *34*, 2845–2856.
4. Liu, Y.J.; Feng, Z.Q.; Jiang, L.W.; Jin, W.; Li, W.M.; Guan, Q.B.; Wen, Q.B.; Liang, C.Y. Ophiolite in the eastern Central Asian Orogenic Belt, NE China. *Acta Petrol. Sin.* **2019**, *35*, 3017–3047. [CrossRef]
5. Li, J.Y.; Liu, J.F.; Qu, J.F.; Zheng, R.G.; Zhao, S.; Zhang, J.; Sun, L.X.; Li, Y.F.; Yang, X.P.; Wang, L.J.; et al. Major geological features and crustal tectonic framework of Northeast China. *Acta Petrol. Sin.* **2019**, *35*, 2989–3016. [CrossRef]
6. Zhang, C.; Liu, Y.J.; Cui, F.H.; Wang, L.Y.; Liu, Z.H. Deformation time and tectonic significance of the Gudonghe ductile shear belt in the Yanbian area, NE China. *Int. J. Earth Sci.* **2023**, *112*, 77–94. [CrossRef]
7. Li, J.Y. Permian geodynamic setting of Northeast China and adjacent regions: Closure of the Paleo-Asian Ocean and subduction of the Paleo-Pacific Plate. *J. Asian Earth Sci.* **2006**, *26*, 207–224. [CrossRef]
8. Xiao, W.J.; Windley, B.F.; Han, C.M.; Liu, W.; Wan, B.; Zhang, J.E.; Ao, S.J.; Zhang, Z.Y.; Song, D.F. Late Paleozoic to Early Triassic multiple roll-back and oroclinal bending of the Mongolia collage in Central Asia. *Earth Sci. Rev.* **2018**, *186*, 94–128. [CrossRef]
9. Zhao, Y.L.; Liu, Y.J.; Li, W.M.; Feng, Z.Q.; Wen, Q.B.; Liang, C.Y. Detrital zircon LA-ICP-MS U-Pb age of Late Carboniferous to Early Permian sandstones in central Great Xing’an Range and its geological significance. *Earth Sci.* **2018**, *43*, 2055–2075, (In Chinese with English abstract).
10. Xu, W.L.; Sun, C.Y.; Tang, J.; Luan, J.P.; Wang, F. Basement Nature and Tectonic Evolution of the Xing’an-Mongolian Orogenic Belt. *Earth Sci.* **2019**, *44*, 1620–1646. [CrossRef]
11. Zhang, C. The Mesozoic Tectonic Evolution of Yanbian Area in the Eastern Segment of Northern Margin of the North China Block. Ph.D. Thesis, Jilin University, Changchun, China, 2014. (In Chinese with English abstract).
12. Liu, Y.J.; Ma, Y.F.; Feng, Z.Q.; Li, W.M.; Li, S.Z.; Guan, Q.B.; Chen, Z.X.; Zhou, T.; Fang, Q.A. Paleozoic Orocline in the eastern Central Asian Orogenic Belt. *Acta Geol. Sin.* **2022**, *96*, 3468–3493.
13. Liu, S.; Hu, R.Z.; Gao, S.; Feng, C.X.; Feng, G.Y.; Ian, M.C.; Li, C.; Wang, T.; Qi, Y.Q. Zircon U–pb Age and Sr–Nd–Hf Isotope Geochemistry of Permian Granodiorite and Associated Gabbro in the Songliao Block, NE China and Implications for Growth of Juvenile Crust. *Lithos* **2010**, *114*, 423–436. [CrossRef]
14. Wilde, S.A. Final amalgamation of the Central Asian Orogenic Belt in NE China: Paleo-Asian Ocean closure versus Paleo-Pacific plate subduction—a review of the evidence. *Tectonophysics* **2015**, *662*, 345–362. [CrossRef]
15. Xu, B.; Zhao, P.; Wang, Y.Y.; Liao, W.; Luo, Z.W.; Bao, Q.Z.; Zhou, Y.H. The pre-Devonian tectonic framework of Xing’an–Mongolia orogenic belt (XMOB) in north China. *Asian Earth Sci.* **2015**, *97*, 183–196. [CrossRef]
16. Guan, Q.B.; Liu, Z.; Liu, Y.J.; Zhang, C. A tectonic transition from closure of the Paleo-Asian Ocean to subduction of the Paleo-Pacific Plate. *Gondwana Res.* **2021**, *102*, 332–353. [CrossRef]
17. Wei, J.Y.; Pei, F.P.; Zhou, H.; Jiao, J.; Wang, Y.P. Tectonic nature of Permian terrane in the Kaishantun area, Yanbian: Evidence from intrusive rocks and detrital zircons. *Acta Petrol. Sin.* **2020**, *36*, 759–780. [CrossRef]

18. Zhou, J.B.; Han, J.; Wilde, S.A.; Guo, X.D.; Zeng, W.S.; Cao, J.L. A primary study of the Jilin-Heilongjiang high-pressure metamorphic belt: Evidence and tectonic implications. *Acta Petrol. Sin.* **2013**, *29*, 386–398.
19. Tang, K.D.; Shao, J.A.; Li, J.C.; Kang, Z. Nature of the Yanbian suture zone and structure of Northeast Asia. *Geol. Bull. China* **2004**, *23*, 885–891.
20. Wei, Q.Q. Late Hercynian–Indosinian Mafic–Ultramafic Rocks of the Central–Eastern Part of Jilin Province and Cu–Ni Metallization. Ph.D. Thesis, Jilin University, Changchun, China, 2015. (In Chinese with English abstract).
21. Wiedenbeck, M.; Allé, P.; Corfu, F.; Griffin, W.L.; Meier, M.; Oberli, F.; Quadt, V.A.; Roddick, J.C.; Spiegel, W. Three natural zircon standards for U–Th–Pb, Lu–Hf, trace element and REE analyses. *Geostand. Geoanalytical Res.* **1995**, *19*, 1–23. [CrossRef]
22. Vermeesch, P. IsoplotR: A free and open toolbox for geochronology. *Geosci. Front.* **2018**, *9*, 1479–1493. [CrossRef]
23. Irvine, T.N.; Baragar, W.A. Guide to the Chemical Classification of the Common Volcanic Rocks. *Can. J. Earth Sci.* **1971**, *8*, 523–548. [CrossRef]
24. Rickwood, P.C. Boundary lines within petrologic diagrams which use oxides of major and minor elements. *Lithos* **1989**, *22*, 247–263. [CrossRef]
25. Maniar, P.; Piccoli, P. Tectonic Discrimination of Granitoids. *Geol. Soc. Am. Bull.* **1989**, *101*, 635–643. [CrossRef]
26. Sun, S.S.; McDonough, W.F. Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes. *Geol. Soc. Lond. Spec. Publ.* **1989**, *42*, 313–345. [CrossRef]
27. Boynton, W.V. Geochemistry of the rare earth elements: Meteorite studies. In *Rare Earth Element Geochemistry*; Henderson, P., Ed.; Elsevier: Amsterdam, The Netherlands, 1984; pp. 63–114.
28. Saunders, A.D.; Storey, M.; Kent, R.W.; Norry, M.J. Consequences of plume–lithosphere interactions. In *Magmatism and the Cause of Continental Breakup*; Geological Society Special Publication No. 68; Storey, B.C., Alabaster, T., Pankhurst, R.J., Eds.; Geological Society of London: London, UK, 1992; pp. 41–60.
29. Schandl, E.S.; Gorton, M.P. Application of high strength elements to discriminate tectonic settings in WMS environments. *Econ. Geol.* **2002**, *97*, 629–642. [CrossRef]
30. Pearce, J.A. Immobile element fingerprinting of ophiolites. *Elements* **2014**, *10*, 101–108. [CrossRef]
31. Wood, D.A. The application of a Th–Hf–Ta diagram to problems of tectonomagmatic classification and to establishing the nature of crustal contamination of basaltic lavas of the British Tertiary Volcanic Province. *Earth Planet. Sci. Lett.* **1980**, *50*, 11–30. [CrossRef]
32. Hofmann, A.W.; Jochum, K.P.; Seufert, M.; White, W.M. Nb and Pb in oceanic basalts: New constraints on mantle evolution. *Earth Planet. Sci. Lett.* **1986**, *79*, 33–45. [CrossRef]
33. Rudnick, R.L.; Gao, S. Composition of the continental crust. *Treat. Geochem* **2003**, *3*, 1–64.
34. Yang, H.; Ge, W.C.; Santosh, M.; Ji, Z.; Dong, Y.; Jing, Y.; Wu, H.R. The role of continental fragments in the formation of intra-oceanic arcs: Constraints from Sr–Nd–Hf–O isotopes of gabbro from the Jiamusi Block, NE China. *Gondwana Res.* **2022**, *103*, 297–313. [CrossRef]
35. Xu, W.J.; Xu, X.S.; Zeng, G. Crustal contamination versus an enriched mantle source for intracontinental mafic rocks: Insights from early Paleozoic mafic rocks of the South China Block. *Lithos* **2017**, *286–287*, 388–395. [CrossRef]
36. Grove, T.L.; Parman, S.W.; Bowring, S.A.; Price, R.C.; Baker, M.B. The role of an H₂O-rich fluid component in the generation of primitive basaltic andesites and andesites from the Mt. Shasta region, N California. *Contrib. Miner. Petrol* **2002**, *142*, 375–396. [CrossRef]
37. Handley, H.K.; Macpherson, C.G.; Davidson, J.P.; Berlo, K.; Lowry, D. Constraining fluid and sediment contributions to subduction-related magmatism in Indonesia: Ijen Volcanic Complex. *Petrol* **2007**, *48*, 1155–1183. [CrossRef]
38. Guo, F.; Li, H.X.; Fan, W.M.; Li, J.Y.; Zhao, L.; Huang, M.W. Variable sediment flux in generation of Permian subduction-related mafic intrusions from the Yanbian region, NE China. *Lithos* **2016**, *261*, 195–215. [CrossRef]
39. Kogiso, T.; Tatsumi, Y.; Nakano, S. Trace element transport during dehydration processes in the subducted oceanic crust: 1. Experiments and implications for the origin of ocean island basalts. *Earth Planet. Sci. Lett.* **1997**, *148*, 193–205. [CrossRef]
40. Spandler, C.; Pirard, C. Element recycling from subducting slabs to arc crust: A review. *Lithos* **2013**, *170–171*, 208–223. [CrossRef]
41. Zhao, L.; Guo, F.; Fan, W.; Huang, M. Roles of subducted pelagic and terrigenous sediments in Early Jurassic mafic magmatism in NE China: Constraints on the architecture of Paleo-Pacific subduction zone. *J. Geophys. Res. Solid Earth* **2019**, *124*, 2525–2550. [CrossRef]
42. Ferrando, S.; Petrelli, M.; Frezzotti, M.L. Gradual and selective trace-element enrichment in slab-released fluids at sub-arc depths. *Sci. Rep.* **2019**, *9*, 16393. [CrossRef]
43. Bayon, G.; Burton, K.; Soulet, G.; Vigier, N.; Dennielou, B.; Etoubleau, J.; Ponzevera, E.; German, C.R.; Nesbitt, R.W. Hf and Nd isotopes in marine sediments: Constraints on global silicate weathering. *Earth Planet. Sci. Lett.* **2009**, *277*, 318–326. [CrossRef]
44. David, K.; Frank, M.; O’Nions, R.K.; Belshaw, N.S.; Arden, J.W. The Hf isotope composition of global seawater and the evolution of the Hf isotopes in the deep Pacific Ocean from Fe–Mn crusts. *Chem. Geol.* **2001**, *178*, 23–42. [CrossRef]
45. Marini, J.C.; Chauvel, C.; Maury, R.C. Hf isotope compositions of northern Luzon arc lavas suggest involvement of pelagic sediments in their source. *Contrib. Mineral. Petrol.* **2005**, *149*, 216–232. [CrossRef]
46. Plank, T.; Langmuir, C.H. The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chem. Geol.* **1998**, *145*, 325–394. [CrossRef]
47. Valley, J.W. Oxygen isotopes in zircon. *Rev. Mineral. Geochem.* **2003**, *53*, 343–385. [CrossRef]

48. Valley, J.W.; Lackey, J.S.; Cavosie, A.J.; Clechenko, C.C.; Spicuzza, M.J.; Basei, M.A.S.; Bindeman, I.N.; Ferreira, V.P.; Sial, A.N.; King, E.M.; et al. 4.4 billion years of crustal maturation: Oxygen isotope ratios of magmatic zircon. *Contrib. Mineral. Petrol.* **2005**, *150*, 561–580. [CrossRef]
49. Whalen, J.B.; Currie, K.L.; Chappell, B.W. A-type granites: Geochemical characteristics, discrimination and petrogenesis. *Contrib. Mineral. Petrol.* **1987**, *95*, 407–419. [CrossRef]
50. Yu, J.J.; Wang, F.; Xu, W.L.; Gao, F.H.; Pei, F.P. Early Jurassic mafic magmatism in the Lesser Xing'an-Zhangguangcai Range, NE China, and its tectonic implications: Constraints from Zircon U-Pb chronology and geochemistry. *Lithos* **2012**, *142–143*, 256–266. [CrossRef]
51. Guo, F.; Li, H.X.; Fan, W.M.; Li, J.Y.; Zhao, L.; Huang, M.W.; Xu, W.L. Early Jurassic subduction of the Paleo-Pacific Ocean in NE China: Petrologic and geochemical evidence from the Tumen mafic intrusive complex. *Lithos* **2015**, *224–225*, 46–60. [CrossRef]
52. Huang, M.W. Nd-Hf-O Isotopic Constraints on the Phanerozoic Crustal Growth and Modification in the Yanbian Area, NE China. Master's Thesis, Guangzhou Institute of Geochemistry Chinese Academy of Sciences, Changchun, China, 2015. (In Chinese with English abstract).
53. Wang, Z.J. Late Paleozoic-Triassic Tectonic Evolution of Eastern Segment of the Southern Margin of the Xing'an-Mongolia Orogenic Belt: Evidence from Detrital Zircon U-Pb Geochronology and Igneous Rock Associations. Ph.D. Thesis, Jilin University, Changchun, China, 2016. (In Chinese with English abstract).
54. Ma, X.H.; Zhu, W.P.; Zhou, Z. Hua.; Qiao, S.L. Transformation from Paleo-Asian Ocean closure to Paleo-Pacific Subduction: New constraints from granitoids in the eastern Jilin-Heilongjiang Belt, NE China. *J. Asian Earth Sci.* **2017**, *144*, 261–286. [CrossRef]
55. Yang, D.G.; Sun, D.Y.; Gou, J.; Hou, X.G. U-Pb ages of zircons from Mesozoic intrusive rocks in the Yanbian area, Jilin Province, NE China: Transition of the Paleo-Asian oceanic regime to the circum-Pacific tectonic regime. *J. Asian Earth Sci.* **2017**, *143*, 171–190. [CrossRef]
56. Guo, W.K.; Zeng, Q.D.; Zhang, B.; Hu, Y.Z. Genesis of the Jurassic Dongfengbeishan porphyry Mo deposit in Eastern Yanbian, NE China inferred from molybdenite Re-Os and zircon U-Pb ages, and whole-rock elemental and zircon Hf isotopic compositions. *J. Asian Earth Sci.* **2018**, *1367–9120*, 256–269. [CrossRef]
57. Lu, Q. Petrogenesis of Mesozoic Granite in Songjianghe Region from Dunhua, Yanbian Korean Autonomous Prefecture. Master's Thesis, Jilin University, Changchun, China, 2019. (In Chinese with English abstract).
58. Zhang, C.; Wang, L.Y.; Geng, R.; Liu, Z.H.; Zhang, L.T. Paleo-Pacific Subduction in Early Jurassic: Geochronological and Geochemical Evidences of Gabbros in Helong Area of Yanbian, Jilin, China. *J. Earth Sci. Environ.* **2020**, *42*, 819–832, (In Chinese with English abstract).
59. Zhang, C.; Liu, Y.J.; Zhang, Z.L.; Cui, F.H.; Zhang, C.; Guan, Q.B.; Li, Y. Deformation and Geochronological Characteristics of Gudonghe Ductile Shear Zone in Yanbian Area. *Earth Sci.* **2019**, *44*, 3252–3264, (In Chinese with English abstract).
60. Zhou, Z.B.; Pei, F.P.; Wang, Z.W.; Cao, H.H.; Xu, W.L.; Wang, Z.J.; Zhang, Y. Using Detrital Zircons from Late Permian to Triassic Sedimentary Rocks in the South-Eastern Central Asian Orogenic Belt (NE China) to Constrain the Timing of the Final Closure of the Paleo-Asian Ocean. *J. Asian Earth Sci.* **2017**, *144*, 82–109. [CrossRef]
61. Du, Q.X.; Han, Z.Z.; Shen, X.L.; Han, C.; Song, Z.G. Geochronology and Geochemistry of Permo-Triassic Sandstones in Eastern Jilin Province (NE China): Implications for Final Closure of the Paleo-Asian Ocean. *Geosci. Front.* **2019**, *10*, 683–704. [CrossRef]
62. Liu, Z.H.; Wang, C.; Song, J.; Gao, X.; Sun, L.N. ⁴⁰Ar-³⁹Ar Dating and Its Tectonic Significance of the Hulan Group at the Northern Margin of the North China Plate. *Acta Petrol. Sin.* **2016**, *32*, 2757–2764, (In Chinese with English abstract).

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Petrogenesis of Diorite-Porphyrite in the Southern Xintai Area of the Mid-Western Shandong Peninsula, North China Craton: Insights from Geochronology, Mineralogy, Geochemistry, and Sr-Nd-Hf Isotopes

Lijie Jin ^{1,2,3,*}, Jilin Wang ⁴, Pinrui Qin ^{2,*}, Chunjia Li ², Shuang Xu ⁴, Zhixin Han ⁵, Wei Wang ², Wei Liu ², Zisheng Wang ², Jilei Gao ^{2,3} and Fangfang Li ⁶

¹ School of Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China

² No. 1 Institute of Geology and Mineral Resources of Shandong Province, Jinan 250100, China; chunjia7788@126.com (C.L.); www86_0@126.com (W.W.); sddky_lw@163.com (W.L.); wangzisheng06@126.com (Z.W.); gjln@163.com (J.G.)

³ Shandong Engineering Research Center of High-Grade Iron Deposits Exploration and Exploitation, Jinan 250100, China

⁴ The Testing Center of Shandong Bureau, China Metallurgical Geology Bureau, Jinan 250013, China; wangjilin22126@126.com (J.W.); xushuang901129@163.com (S.X.)

⁵ Geological Exploration Institute of Shandong Zhengyuan, Shandong Bureau of China Metallurgical Geology Bureau, Jinan 250101, China; 15588555535@163.com

⁶ Aerospace Information Research Institute, Chinese Academy of Sciences, Beijing 100190, China; fflil@mail.ie.ac.cn

* Correspondence: jinlijie1987@163.com (L.J.); qinpinrui1982@126.com (P.Q.)

Abstract: The Early Cretaceous intermediate intrusive rocks have important significance in understanding the crust–mantle interaction, iron mineralization, and tectonic evolution in the western Shandong Peninsula. In this study, we present new zircon U–Pb ages, and Hf isotope, whole-rock geochemistry, Sr–Nd isotopes, and the mineral chemistry of the diorite-porphyrite in the southern Xintai area, mid-western Shandong Peninsula. The diorite-porphyrite formed at ca. 125 Ma. They have intermediate SiO₂ (59.57–62.29 wt.%) and MgO (2.78–3.58 wt.%) contents, high Mg# values (53–56), high Sr (589–939 ppm) and low Y (9.2–10.8 ppm) contents, and high Sr/Y ratios (54–94), showing adakitic affinity. The diorite-porphyrite exhibits lower zircon $\epsilon_{\text{Hf}}(t)$ values (–30.1 to 7.5) and whole-rock $\epsilon_{\text{Nd}}(t)$ values (–3.5 to –6.0), with (⁸⁷Sr/⁸⁶Sr)_i ratios of 0.70514–0.70567. We suggest that the diorite-porphyrite was derived from the partial melting of the local delamination of lower continental crust and then by the interaction with the enriched lithospheric mantle. The genesis of diorite-porphyrite may be related to the rollback process of the Paleo-Pacific slab in the Early Cretaceous. This geodynamic process induced the melting of the enriched lithospheric mantle, subducted oceanic crust, and local delamination of lower continental crust, which produced different types of adakitic magmatism in the western Shandong Peninsula.

Keywords: Early Cretaceous; diorite-porphyrite; petrogenesis; North China Craton; Shandong Peninsula

1. Introduction

The eastern North China Craton (NCC) underwent significant craton destruction during the Mesozoic and Cenozoic periods, with mechanisms primarily attributed to the westward subduction of the Paleo-Pacific plate [1–5]. This destruction is closely linked to the large-scale magmatism and metal mineralization processes during the Late Mesozoic [6–9]. These Late Mesozoic igneous rocks encompass a broad spectrum, ranging from mafic to felsic intrusive and volcanic rocks, with their origin traced to multiple sources [10–15]. The Shandong Peninsula holds a pivotal position for investigating the eastern NCC evolution in Late Mesozoic and its associated mineralization processes [16–23].

During the Early Cretaceous period, a variety of magmatic rocks and iron mineralization emerged in the western Shandong Peninsula [24–28]. Among these igneous rocks, diorites predominate and play a crucial role in the formation of skarn-type iron deposits [29]. However, the origins and evolution of these diorites and their coeval igneous rocks are still unclear. Investigations into intermediate-acidic intrusive rocks have suggested multiple genetic processes, including the reworking of ancient crust, the growth of new continental crust, or crust–mantle interactions [24,26,30–32]. Moreover, a portion of intrusive rocks exhibits adakitic geochemical characteristics, indicative of significant geodynamic processes [26,27,31,33]. Furthermore, analogous Cretaceous intrusions and skarn-related iron mineralization events have been observed in the Xingtai–Handan regions, located in the central NCC [34–36].

Remarkably, the western Shandong Peninsula’s central and northern regions boast three significant skarn-type iron ore fields, notably in the Laiwu, Zibo, and Jinan areas [37]. Among these, the Zhangjiawa deposit in the Laiwu area stands out as one of China’s largest skarn-type iron ore deposit. These skarn-type iron deposits are primarily associated with the medium- to large-sized intermediate-acid intrusive plutons that formed during the Early Cretaceous [38,39]. To the south of this metallogenic belt, several diorite-porphyrite rocks emerge as minor intrusions and stocks. In this study, we sampled the diorite-porphyrite from the southern Xintai area, mid-western Shandong Peninsula. We present new zircon U–Pb ages, Hf isotopes, mineral chemistry, whole-rock geochemistry, and Sr–Nd isotopes of diorite-porphyrite in Xintai to discuss their petrogenesis and regional tectonic implications.

2. Geological Background and Samples

The NCC comprises an Archean to Paleoproterozoic basement, which is typically segmented into the Eastern and Western blocks, along with the Trans-North China Orogen [40,41] (Figure 1a). The Shandong Peninsula lies in the southeast part of the eastern NCC, which has a basement divided into western and eastern segments by the Tancheng–Luijiang fault zone [42–44] (Figure 1b). The Luzhong uplift belt, which lies in the middle part of the western Shandong Peninsula, encompasses an array of geological formations. These include the Mesoarchean–Neoproterozoic basement, Cambrian to lower-middle Ordovician strata indicative of a marine sedimentary environment, Upper Carboniferous to Permian strata reflective of a marine–continental transitional environment, as well as Mesozoic–Cenozoic terrestrial sedimentary strata [45,46]. The Cretaceous magmatic rocks predominantly consist of intermediate-acidic intrusive rocks, exemplified by diorite and granitoid plutons, along with volcanic rocks [22,27,32,47].

We have collected nine typical diorite-porphyrite samples from the southern region of Liudu town (abbreviated as LD) and Fengshan (abbreviated as FS) in Xintai City, situated in the mid-western section of the Shandong Peninsula (Figure 1b,c). Diorite-porphyrite is well exposed in the field and intrudes into tonalite of the Archean basement and sandstone of the Early Cambrian Mantou Formation in the form of veins. There are no skarn-type iron deposits at the contact. These samples display a striking porphyritic texture, featuring phenocrysts that predominantly comprise plagioclase (40%–60%) and hornblende (30%–40%), with the plagioclase grains being notably larger than those of hornblende. The matrix predominantly consists of plagioclase (70%–80%), quartz (5%–10%), and hornblende (10%–20%) (Figure 2). The grain size of minerals in the matrix ranges from 0.1 mm to 0.3 mm. Furthermore, the samples contain accessory minerals like magnetite, apatite, and zircon.

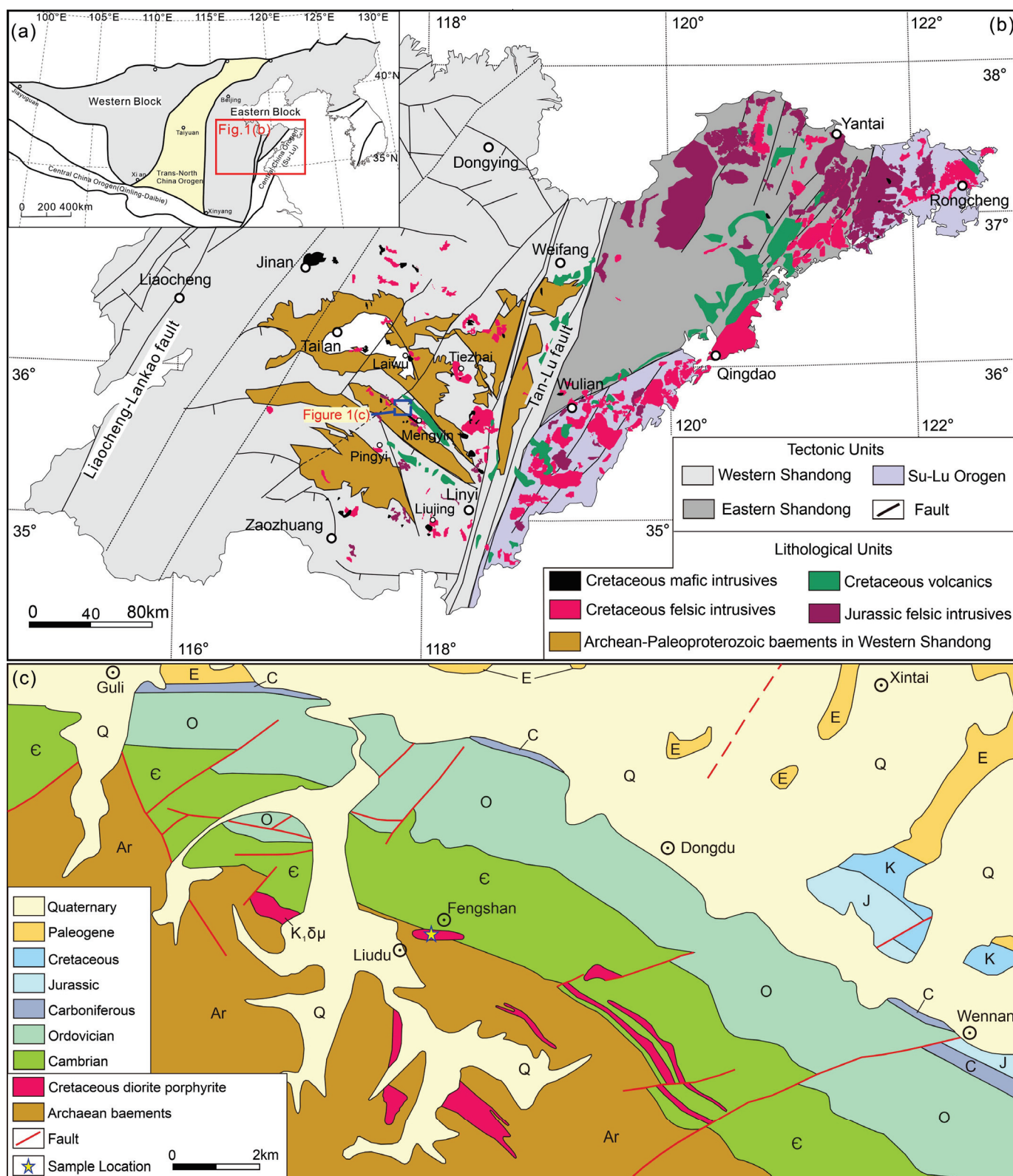


Figure 1. (a) Tectonic subdivision of the NCC (after [43]). (b) Simplified geological map of Shandong Peninsula (after [27]). (c) Geological sketch map of the southern Xintai area of the mid-western Shandong Peninsula.

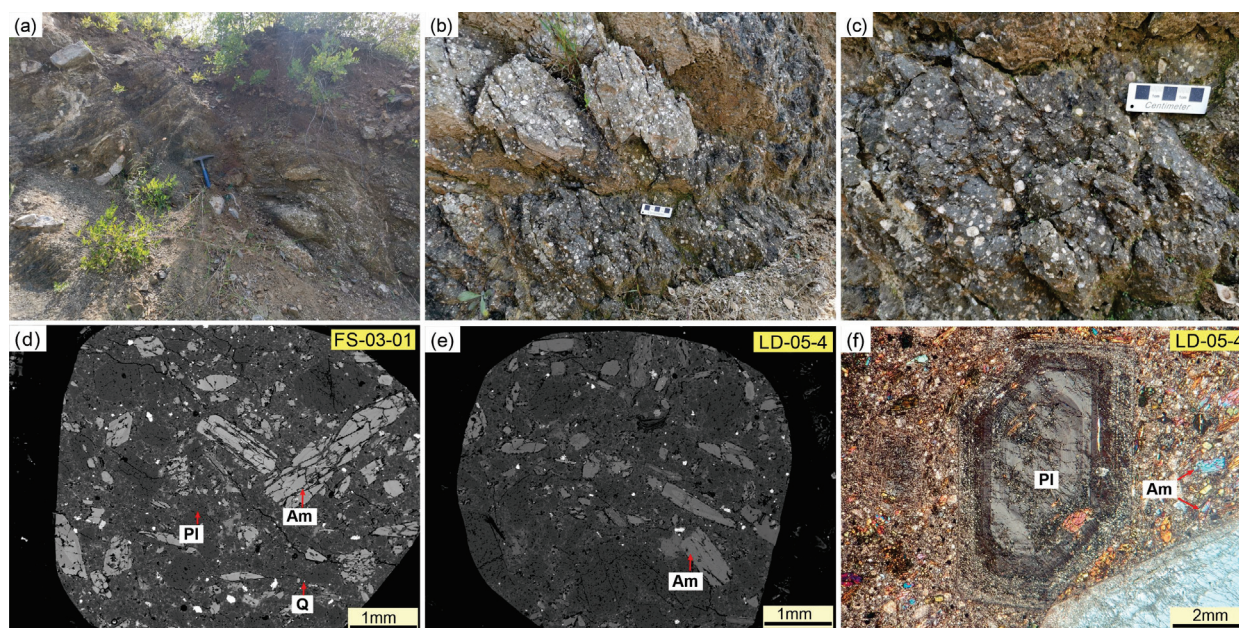


Figure 2. Representative photographs and photomicrographs of diorite-porphyrite in the Xintai area. (a) The diorite-porphyrite intruded into the Lower Cambrian Mantou Formation; (b,c) Field photographs of diorite-porphyrite; (d,e) SEM images of porphyritic texture in diorite-porphyrite; (f) Representative plagioclase phenocryst in cross-polarized light.

3. Analytical Methods

3.1. Zircon U–Pb Dating

Zircon cathodoluminescence (CL) imaging was conducted using a JEOL (JSM-6510, Akishima, Japan) scanning electron microscope equipped with a Gatan MiniCL detector to reveal the internal structures. The instruments used include the JEOL (JSM-6510) scanning electron microscope which is produced by JEOL from Japan and the Gatan MiniCL detector which is made by Gatan in the United States. In situ zircon U–Pb dating was analyzed at the Testing Center of Shandong Bureau, China Metallurgical Geology Bureau (TCSB, CMGB). The analysis was facilitated by a Thermo Scientific iCAP Q ICP-MS (Waltham, MA, USA), which was manufactured by Thermo Fisher Scientific of the United States. It also was equipped with a GeoLasPro 193 nm ArF Excimer Laser (Coherent Inc., Butler, PA, USA) laser ablation system, which is from Coherent Inc. in the United States. The laser ablation craters were 32 μm in diameter. For external calibration, the zircon standard Plešovice (337 ± 0.37 Ma) [48] was utilized. The analytical procedure and precision are documented by [49].

3.2. Whole-Rock Elemental Geochemistry and Sr–Nd Isotopes Analyses

Whole-rock elemental compositions were analyzed at the Wuhan SampleSolution Analytical Technology Co., Ltd in Wuhan city. Major element compositions were measured by an X-ray fluorescence spectrometry (XRF, Rigaku ZSX Primus II, Tokyo, Japan), and relative standard deviation is less than 2%. As for the trace elements, after the samples underwent acid digestion within high-pressure Teflon bombs, an Agilent 7700e ICP-MS was employed, achieving a relative standard deviation superior to 15%. The instrument is produced by Agilent Technologies in the Santa Clara, CA, United States.

Whole-rock Sr–Nd isotopic analyses were conducted using a Finnigan MAT-262 thermal ionization mass spectrometer at the Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China. The instrument is produced by Thermo Fisher Scientific in the United States. Detailed separation and analytical procedures are described by Chen et al. (2002) [50]. The acquired data have been standardized to $^{86}\text{Sr}/^{87}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. In the case of the Jndi Nd standard,

the measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratio is 0.512109 ± 0.000006 . The standard NBS987 boasts a measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710260 ± 0.000010 . As for the BCR-2 standard, the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is reported as 0.705020 ± 0.000007 , while the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio is 0.512634 ± 0.000010 .

3.3. Zircon Hf Isotope Analyses

An analysis of the in situ zircon Hf isotopes was conducted using the Neptune Plus MC-ICP-MS instrument, in collaboration with the Geolas HD excimer ArF laser ablation technology at the Wuhan SampleSolution Analytical Technology Co., Ltd. (Wuhan, China). The Neptune Plus MC-ICP-MS instrument is produced by Thermo Fisher Scientific in the United States. The analytical procedure and precision are described by [51]. The laser beam is 44 μm in diameter. Zircon standards 91500 and GJ-1 were utilized to monitor data quality. Zircon standard Plešovice served as an external calibration reference. The Hf isotope results incorporated the following parameters: chondritic ratios [52], decay constant for $\lambda^{176}\text{Lu}$ [53], and a depleted mantle source ratio [54]. Both the chondritic ratios and the decay constant for $\lambda^{176}\text{Lu}$ were utilized for the calculation of the $\varepsilon_{\text{Hf}}(t)$ values. As for the Hf model ages (T_{DM1}), they were calculated with reference to a depleted mantle source ratio.

3.4. Mineral Chemistry Analyses

The mineral chemistry underwent analysis utilizing a JEOL JXA-8230 electron microprobe analyzer in the TCSB, CMGB. The JEOL JXA-8230 is produced by JEOL in Japan. The analysis was conducted with the following precise operational conditions: an accelerating voltage of 15 kV and a beam current of 20 nA. The diameters of the analyzed spot beams were meticulously set to 5 μm for hornblende and 8 μm for plagioclase. The ZAF method, which is short for the Atomic Number Correction Factor (Z), Absorption Correction Factor (A), and Fluorescence Correction Factor (F) method, was employed to correct the analytical data. Elements with different atomic numbers possess different absorption and scattering properties for X-rays, and the Z factor is utilized to adjust for these differences. The elements within the sample absorb a portion of the X-rays, which leads to a reduction in fluorescence intensity. The A factor is used to correct this absorption effect. Additionally, factors such as secondary fluorescence and scattering also influence the fluorescence intensity, and the F factor is employed to correct for these effects. The measurement durations were tailored to the characteristics of the respective elements, with 10 s allocated for peaks indicative of Si, Al, Fe, Na, K, Cr, F, and Cl, and 20 s for Mg, Ca, Ti, Mn, and Ni. The analytical uncertainties were generally less than 2% for contents > 10 wt.%, and less than 5% for contents < 10 wt.%.

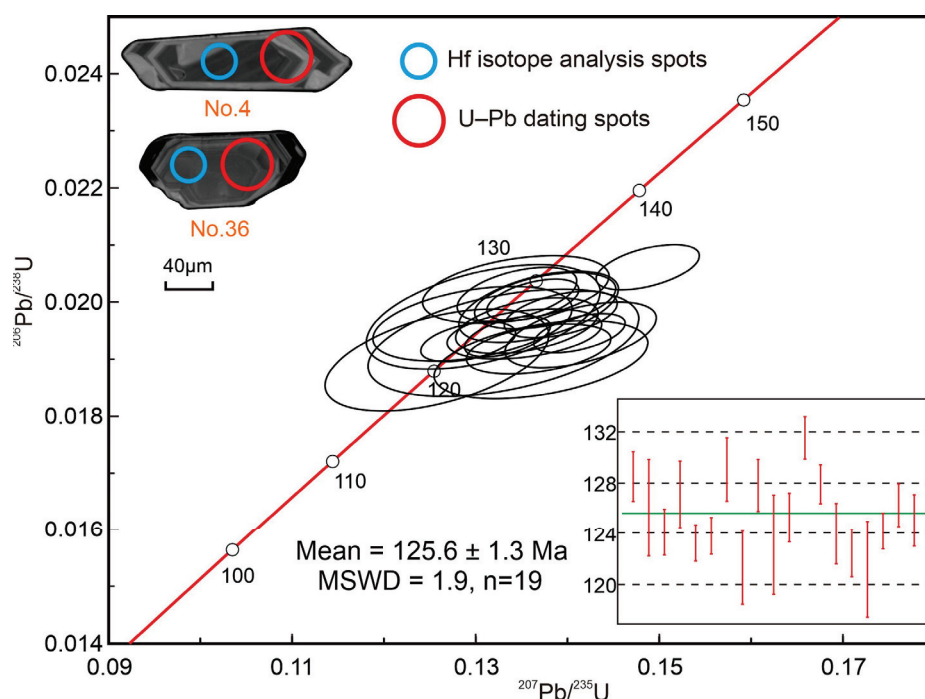
4. Results

4.1. Zircon U–Pb Age

A total of 19 zircon grains were analyzed from the diorite-porphyry sample (FS-01), all of which yielded concordant U–Pb ages (Table 1). The zircon of the diorite-porphyry displays a euhedral morphology, characterized by oscillatory magmatic zoning. The zircons show concentrations of Th (8–388 ppm) and U (194–2664 ppm), along with Th/U ratios spanning from 0.02 to 0.51. These zircon grains yield a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages of 125.6 ± 1.3 Ma (MSWD = 1.9, $n = 19$) (Figure 3), indicating the crystallization age of diorite-porphyry.

Table 1. Zircon U–Pb isotopic data of the samples from the diorite-porphyrite in the southern Xintai area of the mid-western Shandong Peninsula, eastern NCC.

Sample	Content (ppm)		Th/U	Ratios								Age (Ma)			
	Th	U		$^{207}\text{Pb}/^{206}\text{Pb}$	1 σ	$^{207}\text{Pb}/^{235}\text{U}$	1 σ	$^{206}\text{Pb}/^{238}\text{U}$	1 σ	$^{207}\text{Pb}/^{206}\text{Pb}$	1 σ	$^{207}\text{Pb}/^{235}\text{U}$	1 σ	$^{206}\text{Pb}/^{238}\text{U}$	1 σ
FS-01-01	163	1677	0.10	0.0482	0.0014	0.1344	0.0043	0.0201	0.0003	109	76.8	128	3.9	129	2.0
FS-01-02	8	345	0.02	0.0488	0.0037	0.1307	0.0084	0.0197	0.0006	200	105.5	125	7.6	126	3.8
FS-01-03	303	2047	0.15	0.0495	0.0026	0.1352	0.0055	0.0194	0.0003	172	122.2	129	5.0	124	1.8
FS-01-04	297	2145	0.14	0.0490	0.0015	0.1367	0.0057	0.0199	0.0004	146	72.2	130	5.1	127	2.6
FS-01-05	183	2185	0.08	0.0480	0.0013	0.1291	0.0034	0.0193	0.0002	102	64.8	123	3.1	123	1.5
FS-01-06	388	2664	0.15	0.0494	0.0011	0.1334	0.0031	0.0194	0.0002	165	53.7	127	2.8	124	1.5
FS-01-07	60	1115	0.05	0.0478	0.0043	0.1342	0.0067	0.0202	0.0004	87	200.0	128	6.0	129	2.5
FS-01-08	257	506	0.51	0.0517	0.0026	0.1370	0.0077	0.0190	0.0004	272	117.6	130	6.9	121	2.8
FS-01-09	72	839	0.09	0.0493	0.0018	0.1374	0.0051	0.0200	0.0003	161	91.7	131	4.5	128	2.0
FS-01-10	14	194	0.07	0.0494	0.0037	0.1329	0.0097	0.0193	0.0006	165	166.6	127	8.7	123	3.9
FS-01-11	69	325	0.21	0.0486	0.0027	0.1296	0.0072	0.0196	0.0004	128	125.9	124	6.4	125	2.7
FS-01-12	125	1718	0.07	0.0502	0.0016	0.1486	0.0037	0.0206	0.0003	211	70.4	141	3.3	132	1.7
FS-01-13	317	1052	0.30	0.0491	0.0012	0.1361	0.0033	0.0200	0.0002	150	52.8	130	3.0	128	1.5
FS-01-14	141	1582	0.09	0.0524	0.0017	0.1413	0.0054	0.0194	0.0004	302	71.3	134	4.8	124	2.4
FS-01-15	30	700	0.04	0.0517	0.0020	0.1367	0.0052	0.0192	0.0003	272	88.9	130	4.7	122	1.9
FS-01-16	40	528	0.08	0.0477	0.0028	0.1257	0.0080	0.0190	0.0006	83	137.0	120	7.2	121	3.7
FS-01-17	193	2120	0.09	0.0524	0.0012	0.1412	0.0033	0.0195	0.0002	302	49.1	134	2.9	124	1.5
FS-01-18	99	801	0.12	0.0507	0.0014	0.1392	0.0040	0.0198	0.0003	228	66.7	132	3.6	126	1.7
FS-01-19	63	391	0.16	0.0505	0.0020	0.1354	0.0051	0.0196	0.0003	217	90.7	129	4.6	125	2.0

**Figure 3.** Typical zircon CL images and zircon U–Pb concordia diagrams of diorite-porphyrite.

4.2. Whole-Rock Elements and Sr–Nd Isotopes

The major and trace elemental data are shown in Table 2. The diorite-porphyrite samples belong to the monzonite in the TAS diagram (SiO_2 , 59.57–62.29 wt.%) (Figure 4a). They are high-K calc-alkaline to calc-alkaline series based on the SiO_2 versus K_2O diagram (Figure 4b). Harker diagrams reveal that the SiO_2 contents of the samples increase as the MgO (2.78–3.92 wt.%), $\text{Fe}_2\text{O}_3^{\text{T}}$ (4.91–6.15 wt.%), CaO (3.50–4.64 wt.%), and TiO_2 (0.52–0.61 wt.%) contents decrease (Figure 5a–c,e). The Al_2O_3 (15.76–16.33 wt.%) contents remain unchanged (Figure 5f). The Na_2O contents (4.57–5.56 wt.%) and K_2O contents (1.80–2.33 wt.%) increased with the increase in SiO_2 content (Figure 5d,g). The A/CNK (aluminum saturation index) values of diorite-porphyrite are between 0.82 and 1.01, and A/NK are between 1.44 and 1.66. As shown in the A/CNK–A/NK diagram, most of the diorite-porphyrite samples plot in the field of metaluminous, only one sample plot in the

field of metaluminous peraluminous. Meanwhile, we have collected the geochemical data of Early Cretaceous adakitic rocks in western Shandong Peninsula (e.g., Mengyin, Tiezhai, Liujing) from the literature and compared them with the data of this study [11,22,33,55].

Table 2. Whole-rock major and trace element compositions of the samples from the diorite-porphyrite in the southern Xintai area of the mid-western Shandong Peninsula, eastern NCC.

Sample No.	LD-02	LD-03	LD-04	LD-05	LD-06	LD-07	FS-01	FS-03	FS-04
Major elements (wt.%)									
SiO ₂	60.76	62.29	61.44	61.07	61.72	61.12	59.57	60.33	59.98
TiO ₂	0.61	0.56	0.52	0.55	0.53	0.57	0.60	0.56	0.58
Al ₂ O ₃	15.76	16.25	16.33	15.79	16.07	16.04	16.02	16.25	16.30
TFe ₂ O ₃	6.15	5.38	4.91	5.06	4.91	4.94	6.14	5.51	5.85
MnO	0.08	0.07	0.07	0.07	0.07	0.06	0.09	0.08	0.09
MgO	3.92	3.03	2.78	3.12	3.04	2.98	3.58	3.13	3.38
CaO	3.74	3.50	4.09	3.91	3.85	3.84	4.64	4.40	4.34
Na ₂ O	4.81	4.57	4.69	5.06	5.11	4.62	5.56	5.30	5.19
K ₂ O	2.21	2.07	2.21	2.31	2.33	2.25	1.80	1.88	2.04
P ₂ O ₅	0.20	0.20	0.18	0.18	0.18	0.19	0.20	0.19	0.20
LOI	1.72	1.69	2.44	2.08	2.13	2.66	1.37	1.61	1.51
Total	99.96	99.59	99.65	99.20	99.94	99.25	99.56	99.23	99.46
A/CNK	0.92	1.01	0.93	0.88	0.90	0.94	0.82	0.87	0.87
A/NK	1.53	1.66	1.62	1.46	1.47	1.60	1.44	1.51	1.52
Mg#	56	53	53	55	55	55	54	53	53
Trace elements (ppm)									
Li	42.1	42.1	40.5	32.5	32.6	46.1	30.9	40.0	39.6
Be	1.30	1.43	1.34	1.51	1.68	1.52	1.27	1.46	1.38
Sc	12.8	10.5	9.55	9.68	9.77	9.96	12.5	11.3	11.8
V	121	103	95.3	99.7	99.9	103	122	110	115
Cr	197	129	114	114	118	120	122	117	120
Co	20.5	16.2	14.4	15.6	15.5	14.8	19.7	16.7	18.7
Ni	72.1	52.6	47.9	54.4	49.1	47.9	56.7	50.2	52.3
Cu	45.4	29.6	29.5	34.5	29.7	29.0	41.3	23.9	27.6
Zn	69.8	74.3	66.6	71.7	70.8	69.4	76.5	72.5	77.4
Ga	20.9	22.1	21.5	21.3	22.2	22.2	20.7	21.6	21.2
Rb	56.1	55.3	61.6	62.3	65.7	60.3	39.8	42.1	47.1
Sr	589	792	817	741	785	821	913	939	914
Y	10.8	9.67	9.75	9.58	9.37	9.24	10.7	9.92	10.6
Zr	100	110	102	104	101	108	100	94.1	98.8
Nb	5.35	6.09	5.61	5.65	5.70	5.83	4.94	5.22	5.15
Sn	1.01	0.94	0.85	0.97	0.91	0.86	0.82	0.83	0.80
Cs	2.66	2.94	3.33	2.66	3.35	2.79	2.53	2.73	3.19
Ba	920	974	1049	1027	1041	1081	1009	1031	1100
La	14.7	14.9	14.8	14.5	14.5	14.2	14.7	14.4	15.4
Ce	30.3	31.5	29.7	30.9	31.2	30.4	30.3	30.1	31.3
Pr	3.68	3.76	3.70	3.76	3.71	3.65	3.73	3.57	3.81
Nd	15.7	15.3	15.3	15.3	15.1	14.9	15.5	14.5	15.7
Sm	3.17	3.25	3.19	3.20	3.03	2.94	3.32	3.21	3.37
Eu	1.00	0.99	0.95	0.98	0.98	0.92	1.03	1.04	1.04
Gd	2.76	2.57	2.66	2.74	2.67	2.44	2.77	2.60	2.80
Tb	0.39	0.38	0.35	0.33	0.34	0.33	0.37	0.36	0.39
Dy	2.01	1.87	1.80	1.72	1.77	1.77	1.89	1.89	1.96

Table 2. Cont.

Sample No.	LD-02	LD-03	LD-04	LD-05	LD-06	LD-07	FS-01	FS-03	FS-04
Ho	0.38	0.34	0.33	0.34	0.34	0.35	0.38	0.36	0.38
Er	1.12	1.03	0.94	0.91	0.95	0.91	1.11	0.96	1.04
Tm	0.14	0.13	0.13	0.12	0.12	0.12	0.15	0.13	0.14
Yb	0.95	0.87	0.83	0.80	0.81	0.82	0.91	0.84	0.86
Lu	0.13	0.12	0.12	0.12	0.12	0.12	0.13	0.12	0.12
Hf	2.62	2.97	2.71	2.88	2.80	2.94	2.70	2.59	2.74
Ta	0.32	0.37	0.32	0.33	0.36	0.33	0.28	0.29	0.30
Tl	0.53	0.50	0.54	0.57	0.62	0.49	0.28	0.32	0.34
Pb	14.6	15.7	17.2	13.3	14.4	14.3	15.4	16.6	16.9
Th	3.39	3.39	3.26	3.31	3.14	3.35	3.48	3.43	3.43
U	1.13	0.96	1.04	1.18	1.15	1.11	1.12	1.15	1.03
Sr/Y	54.64	81.83	83.80	77.31	83.81	88.89	85.47	94.68	86.30
ΣREE	76.30	77.06	74.74	75.82	75.64	73.83	76.23	74.12	78.27
LREE	68.45	69.76	67.59	68.72	68.50	66.99	68.52	66.85	70.59
HREE	7.86	7.30	7.15	7.09	7.13	6.85	7.71	7.26	7.68
L/HREE	8.71	9.55	9.46	9.69	9.60	9.78	8.89	9.20	9.19
δCe	0.98	1.00	0.96	1.00	1.02	1.01	0.98	1.00	0.97
δEu	1.01	1.01	0.97	0.99	1.03	1.02	1.01	1.06	1.01
(La/Yb) _N	11.1	12.4	12.7	13.1	12.9	12.4	11.6	12.4	12.8
(La/Sm) _N	2.98	2.97	2.99	2.94	3.09	3.13	2.86	2.90	2.94
(Gd/Lu) _N	2.65	2.60	2.81	2.71	2.67	2.49	2.71	2.79	2.81

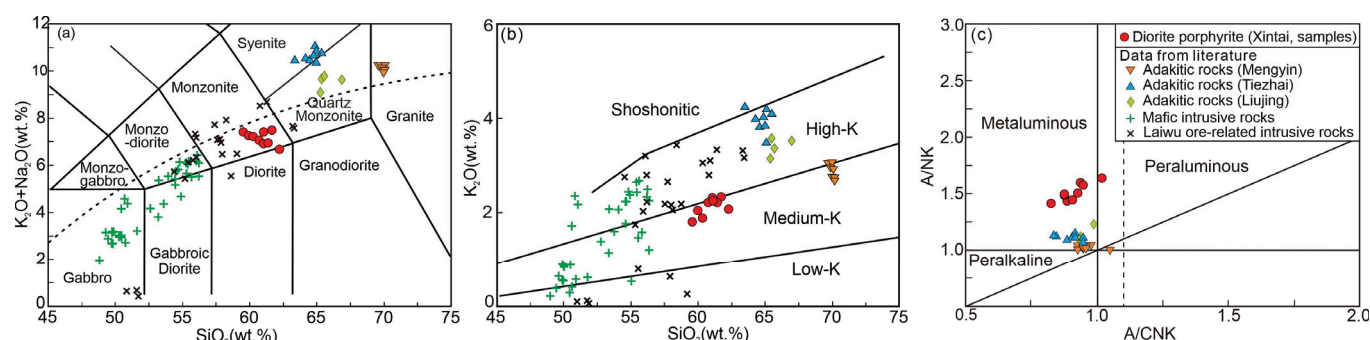


Figure 4. Diagrams of (a) $(K_2O + Na_2O)$ versus SiO_2 (TAS; [56]); (b) SiO_2 versus K_2O [57]; A/CNK versus A/NK [58]. (c) Data sources: Adakitic rocks from Tiezhai [22]; Mengyin and Liujiing [33]; Mafic intrusive rocks [11]; Laiwu ore-related intrusive rocks [55].

The diorite-porphyrite samples exhibit an enrichment of LREEs and a near-flat HREE pattern (Figure 6a), with $(La/Sm)_N$ ratios of 2.86–3.13. They exhibit high $(La/Yb)_N$ ratios (11.10–13.00) and low $(La/Sm)_N$ (2.86–3.12) and $(Gd/Lu)_N$ (2.51–2.82) ratios. In primitive mantle-normalized spidergrams, the samples exhibit the variable enrichment of LILEs (e.g., Rb, Ba, Th, U) and the depletion of HFSEs (e.g., Nb, Ta) (Figure 6b). The samples show no obvious Eu (δEu of 0.97–1.07) and Ce (δCe of 0.96–1.02) anomalies. Compared with other types of intermediate-acidic rocks, they show high Sr (589–939 ppm) content, low Y (9.24–10.80 ppm) and Yb (0.80–0.95 ppm) contents, and high Sr/Y (54.54–94.66) ratios.

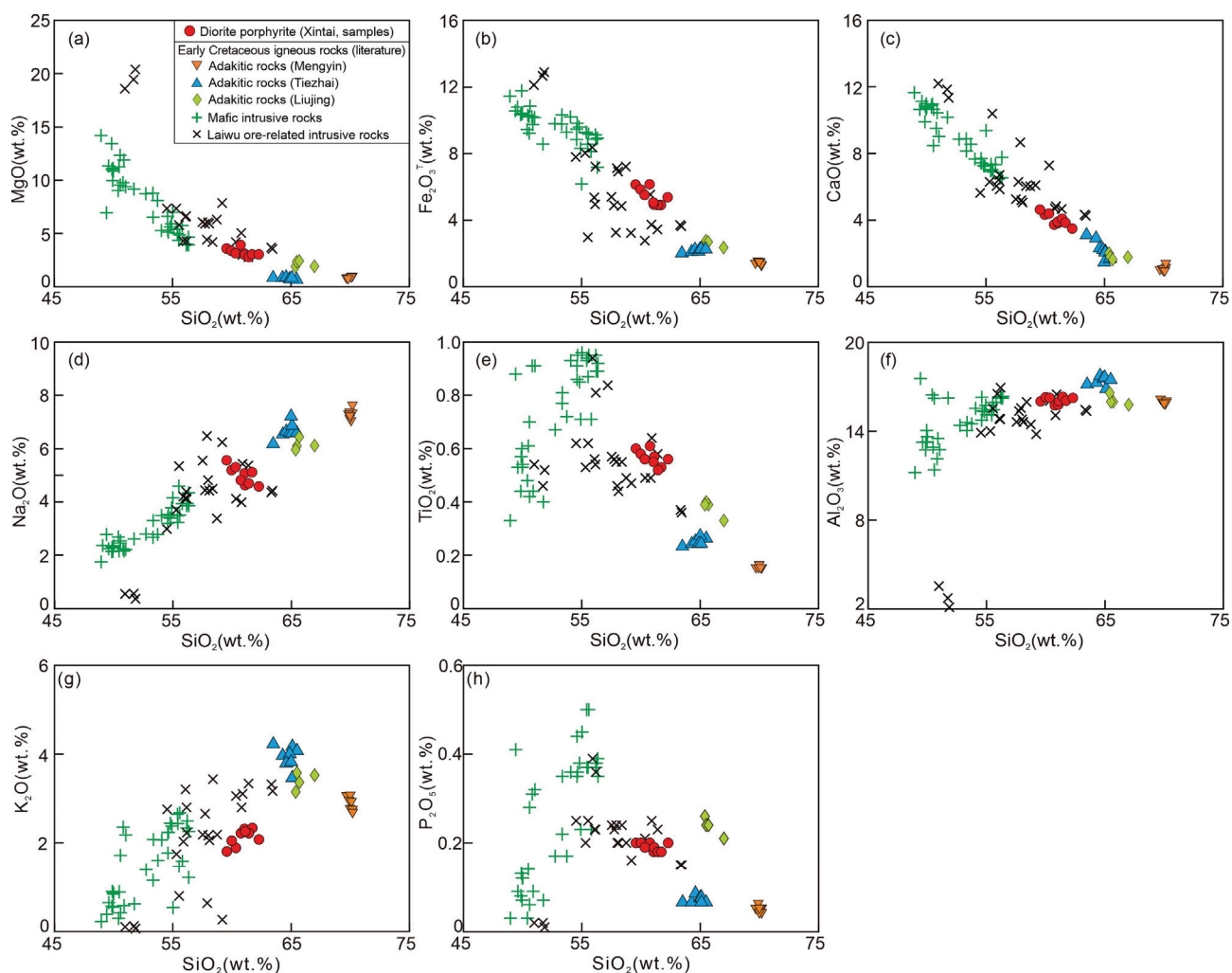


Figure 5. Variation in (a) MgO, (b) Fe_2O_3^T , (c) CaO, (d) Na_2O , (e) TiO_2 , (f) Al_2O_3 , (g) K_2O , and (h) P_2O_5 versus SiO_2 for the samples. Data sources are the same as Figure 4.

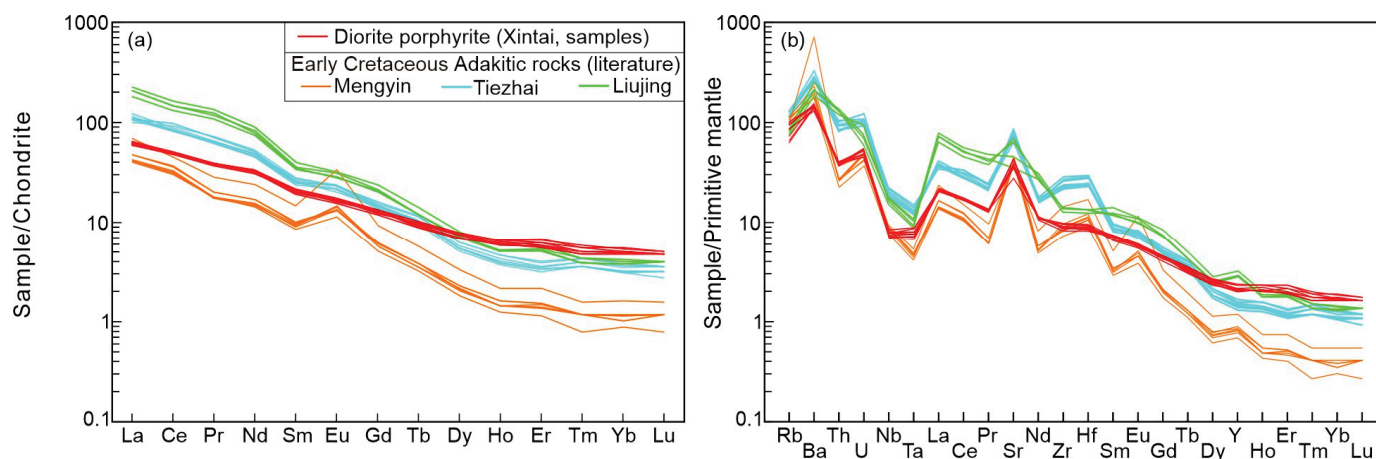


Figure 6. (a) Chondrite-normalized REE patterns and (b) primitive mantle-normalized element spidergrams. The values used for normalization are adopted from [59]. Data sources are the same as Figure 4.

The Sr–Nd isotopic data are presented in Table 3. The Sr–Nd isotopic values were calculated using the zircon U–Pb dating results. The ratios of $^{147}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$

of diorite-porphyrity are 0.512274–0.512398 and 0.705361–0.706290, respectively. The diorite-porphyrity sample exhibits lower $(^{87}\text{Sr}/^{86}\text{Sr})_i$ ratios (0.70514–0.70567) and negative $\varepsilon_{\text{Nd}}(t)$ values from -3.5 to -6.0 (Figure 7). All samples share similar Nd model ages ($T_{\text{DM}}^{\text{Nd}}$) (1.2–1.6 Ga) and two-stage Nd model ages ($T_{\text{DM}}^{\text{Nd}2}$) (1.2–1.4 Ga).

Table 3. Whole-rock Sr–Nd isotopic compositions of the samples from the diorite-porphyrity in the southern Xintai area of the mid-western Shandong Peninsula, eastern NCC.

Sample	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	($\pm 2s_m$)	Sm (ppm)	Nd (ppm)
FS-01	40.58	948.4	0.124	0.705361	0.000008	4.151	19.09
FS-04	35.66	297.0	0.347	0.706290	0.000008	3.478	17.44
LD-06	65.7	785	0.242	0.705863	0.000012	3.03	15.1
Sample	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	($\pm 2s_m$)	$(^{87}\text{Sr}/^{86}\text{Sr})_i$	$\varepsilon_{\text{Nd}}(t)$	T_{DM1} (Ga)	T_{DM2} (Ga)
FS-01	0.1315	0.512274	0.000005	0.705141	−6.0	1.6	1.4
FS-04	0.1205	0.512398	0.000010	0.705673	−3.5	1.2	1.2
LD-06	0.1216	0.512310	0.000006	0.705433	−5.2	1.4	1.3

The formulas and parameters used for calculation were: $(^{87}\text{Sr}/^{86}\text{Sr})_i = (^{87}\text{Sr}/^{86}\text{Sr})_s - (^{87}\text{Rb}/^{86}\text{Sr})_s \times (e^{\lambda t} - 1)$, $\varepsilon_{\text{Nd}}(t) = [(^{143}\text{Nd}/^{144}\text{Nd})_s / (^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} - 1] \times 10,000$, $T_{\text{DM1}} = \ln\{1 + [(^{143}\text{Nd}/^{144}\text{Nd})_s - (^{143}\text{Nd}/^{144}\text{Nd})_{\text{DM}}] / [(^{147}\text{Sm}/^{144}\text{Nd})_s - (^{147}\text{Sm}/^{144}\text{Nd})_{\text{DM}}] / \lambda\}$ [60]; $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} = 0.512638$ [61]; $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}} = 0.1967$ [62], $\lambda^{147}\text{Sm} = 6.54 \times 10^{-12}/\text{a}$ [63]; $t = 125.6$ Ma.

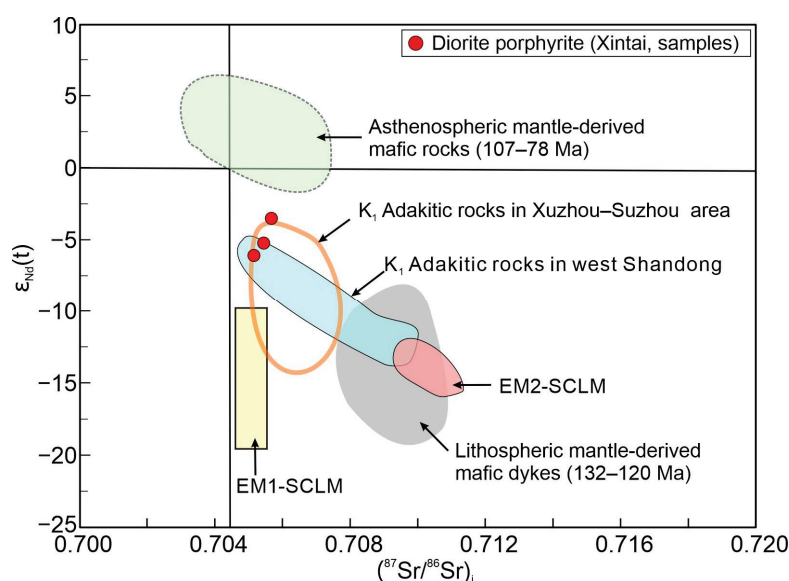


Figure 7. Diagram of $(^{87}\text{Sr}/^{86}\text{Sr})_i$ versus $\varepsilon_{\text{Nd}}(t)$ values.

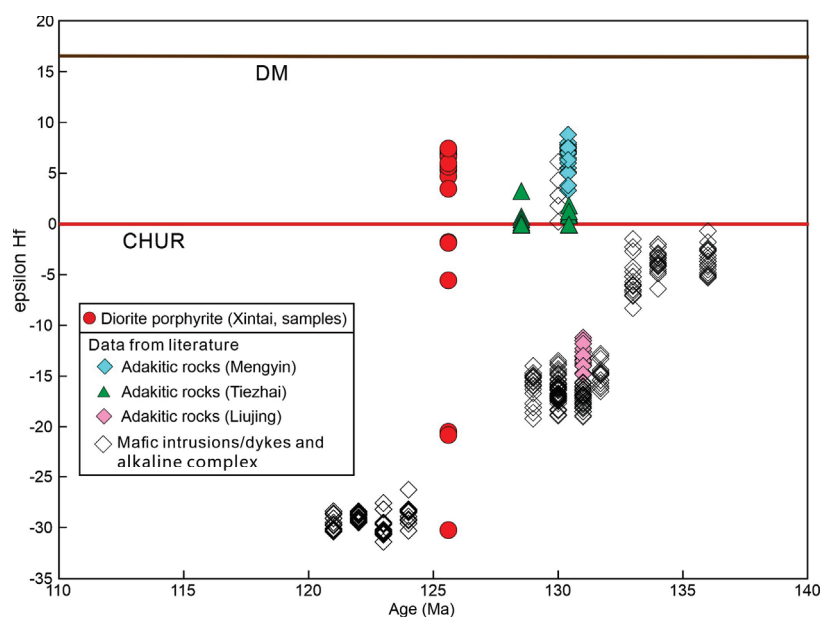
4.3. Zircon Hf Isotope

Zircon Hf isotope data are presented in Table 4. The ratios of $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ of zircons from the Xintai diorite-porphyrity are 0.000162–0.001526 and 0.281842–0.282905, respectively. The zircon from the diorite-porphyrity sample shows $\varepsilon_{\text{Hf}}(t)$ values range from -30.1 to 7.5 (Figure 8). The Hf model ages (T_{DM1}), which stand for the minimum age of the parental magma from which the zircon originated, range from 0.5 to 2.0 Ga. Meanwhile, the two-stage Hf model ages (T_{DM2}), signifying the age of a parental magma generated from an average continental crust, fall within the range of 0.7 to 3.1 Ga.

Table 4. Zircon Hf isotopic compositions of the samples from the diorite-porphyrityrite in the southern Xintai area of the mid-western Shandong Peninsula, eastern NCC.

Sample	t (Ma)	$^{176}\text{Hf}/^{177}\text{Hf}$	1 σ	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Yb}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$	$\epsilon_{\text{Hf}}(0)$	1 σ	T_{DM1} (Ga)	T_{DM2} (Ga)
FS-01-02	125.6	0.282119	0.000030	0.000674	0.019782	0.282118	−20.4	1.1	1.6	2.5
FS-01-03	125.6	0.282649	0.000022	0.001526	0.041300	0.282645	−1.7	0.8	0.9	1.3
FS-01-04	125.6	0.282848	0.000012	0.001336	0.042138	0.282844	5.3	0.4	0.6	0.8
FS-01-05	125.6	0.282645	0.000014	0.001178	0.034729	0.282642	−1.8	0.5	0.9	1.3
FS-01-06	125.6	0.282829	0.000012	0.000520	0.016975	0.282828	4.7	0.4	0.6	0.9
FS-01-07	125.6	0.282796	0.000012	0.001199	0.033952	0.282793	3.5	0.4	0.7	1.0
FS-01-08	125.6	0.281845	0.000014	0.001128	0.034541	0.281842	−30.1	0.5	2.0	3.1
FS-01-10	125.6	0.282890	0.000012	0.000312	0.008822	0.282890	6.9	0.4	0.5	0.7
FS-01-11	125.6	0.282901	0.000017	0.000162	0.005377	0.282901	7.3	0.6	0.5	0.7
FS-01-12	125.6	0.282858	0.000014	0.001328	0.034245	0.282855	5.7	0.5	0.6	0.8
FS-01-13	125.6	0.282111	0.000021	0.001107	0.036502	0.282108	−20.7	0.7	1.6	2.5
FS-01-14	125.6	0.282541	0.000015	0.000808	0.020575	0.282539	−5.5	0.5	1.0	1.5
FS-01-16	125.6	0.282888	0.000010	0.000334	0.009538	0.282887	6.8	0.4	0.5	0.7
FS-01-17	125.6	0.282885	0.000011	0.001274	0.035562	0.282882	6.7	0.4	0.5	0.8
FS-01-18	125.6	0.282866	0.000011	0.000702	0.019472	0.282864	6.0	0.4	0.5	0.8
FS-01-19	125.6	0.282907	0.000017	0.000772	0.022335	0.282905	7.5	0.6	0.5	0.7

The parameters used for the calculation were: $(^{176}\text{Hf}/^{177}\text{Hf})_{\text{CHUR},0} = 0.282772$, $(^{176}\text{Lu}/^{177}\text{Hf})_{\text{CHUR}} = 0.0332$ [52], $\lambda^{176}\text{Lu} = 1.865 \times 10^{-11} \text{ a}^{-1}$ [53], $(^{176}\text{Hf}/^{177}\text{Hf})_{\text{DM},0} = 0.28325$, $(^{176}\text{Lu}/^{177}\text{Hf})_{\text{DM}} = 0.0384$ [54].

**Figure 8.** Diagram of zircon $^{206}\text{Pb}/^{238}\text{U}$ ages versus $\epsilon_{\text{Hf}}(t)$ values of adakitic rocks, mafic intrusions/dykes and alkaline complex.

4.4. Mineral Chemistry

Mineral chemical composition is presented in Table S1. The hornblendes from diorite-porphyrityrite are mainly calcic amphibole compositions [64], with Ca ranging from 1.6 to 1.86 a.p.f.u. (atoms per formula unit) (Figure 9a). They exhibit CaO contents of 1.71–2.39 wt.% and high Al_2O_3 (8.8–14.38 wt.%) and TiO_2 (0.69–1.77 wt.%). The plagioclases from diorite-porphyrityrite are mainly oligoclase and albite (Figure 9c). The plagioclase matrixes have relatively low CaO (0.15–4.26 wt.%, average of 1.86 wt.%), intermediate Al_2O_3 (19.17–22.54 wt.%, average of 20.68 wt.%), and high Na_2O (8.25–11.24 wt.%, average of 9.90 wt.%) contents. The compositions of the seven analyzed plagioclase grains of matrix range from An_1 to An_{22} . Specifically, there are 4 data points with values between An_1 and An_5 , and 3 data points with values ranging from An_{16} to An_{22} . Meanwhile, a total of

75 data points were analyzed for six plagioclase phenocrysts. The result shows plagioclase phenocrysts have relatively high CaO (0.39–5.87 wt.%, average of 4.06 wt.%), intermediate Al_2O_3 (19.54–23.99 wt.%, average of 22.51 wt.%), and low Na_2O (7.75–11.11 wt.%, average of 8.51 wt.%) contents. The plagioclase phenocryst compositions range from An_2 to An_{29} , the most common values being in the ranges An_{16-29} .

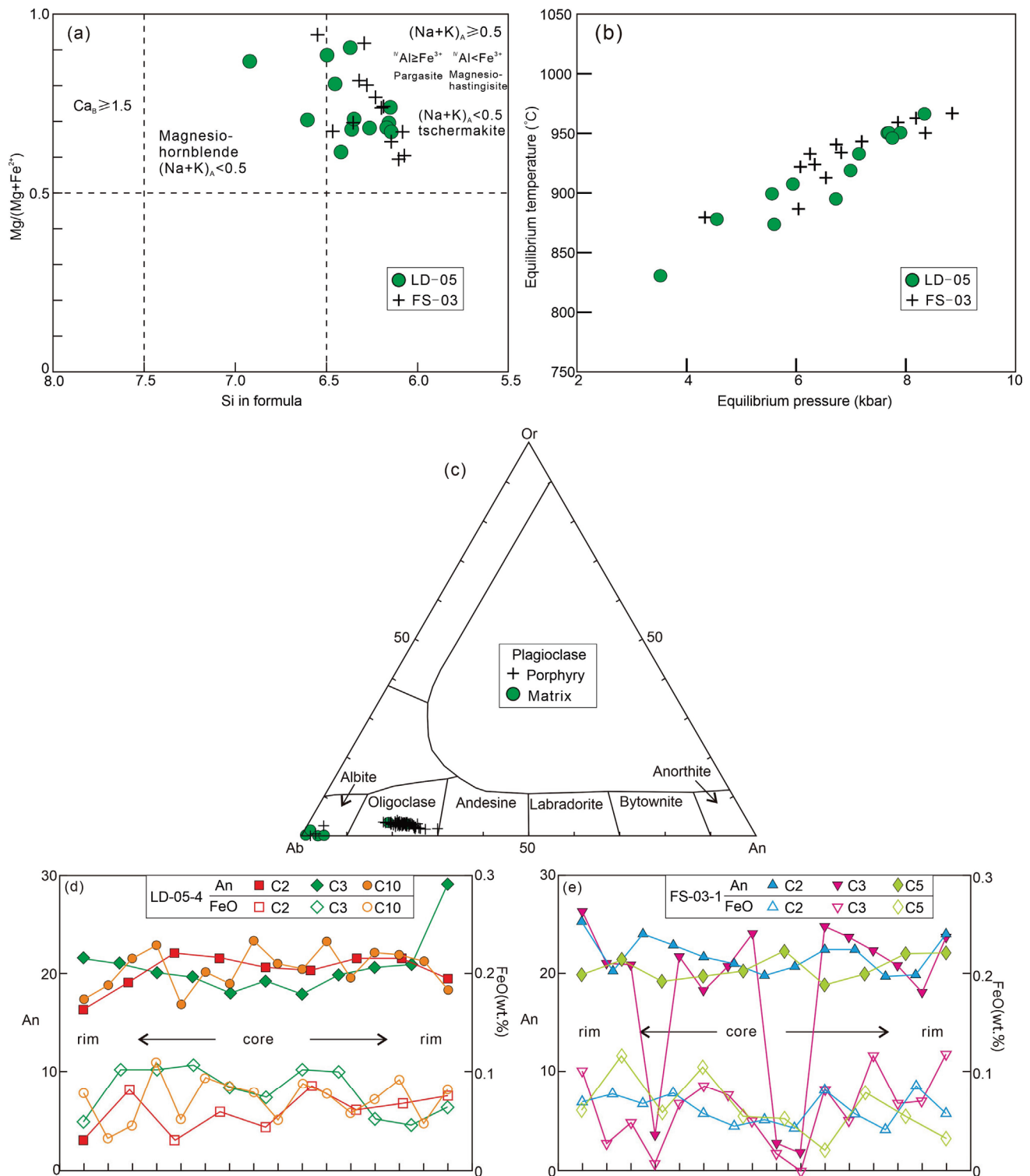


Figure 9. Diagrams of (a) hornblende classification [64]; (b) hornblende equilibrium temperature versus equilibrium pressure; (c) plagioclase Or-Ab-An [65]; (d,e) variation in An and FeO values of plagioclase phenocrysts.

5. Discussion

5.1. Crystallization and Magma Condition of Diorite-Porphyrite

The diorite-porphyrite samples from the Xintai area exhibit fractional crystallization process during magma evolution according to the Harker diagram (Figure 5). The contents of Fe_2O_3^T , MgO , CaO , and TiO_2 in the diorite-porphyrite samples show a negative correlation with SiO_2 , which may be caused by the fractional crystallization of hornblende and Fe-Ti oxides. The contents of Ni and $\text{CaO}/\text{Al}_2\text{O}_3$ ratios show a positive correlation with MgO , suggesting that the diorite-porphyrite of the Xintai area experienced the process of olivine fractional crystallization (Figure 10). The diorite-porphyrite in the Xintai area and the adakitic rocks in the Liujing and Tiezhai areas have similar REE pattern curves, but the magmatic differentiation in the Liujing and Tiezhai areas is stronger (Figure 4). The adakitic rocks in the Mengyin area have different REE pattern curves (obvious positive Eu anomalies), indicating that they have experienced different magmatic evolution processes.

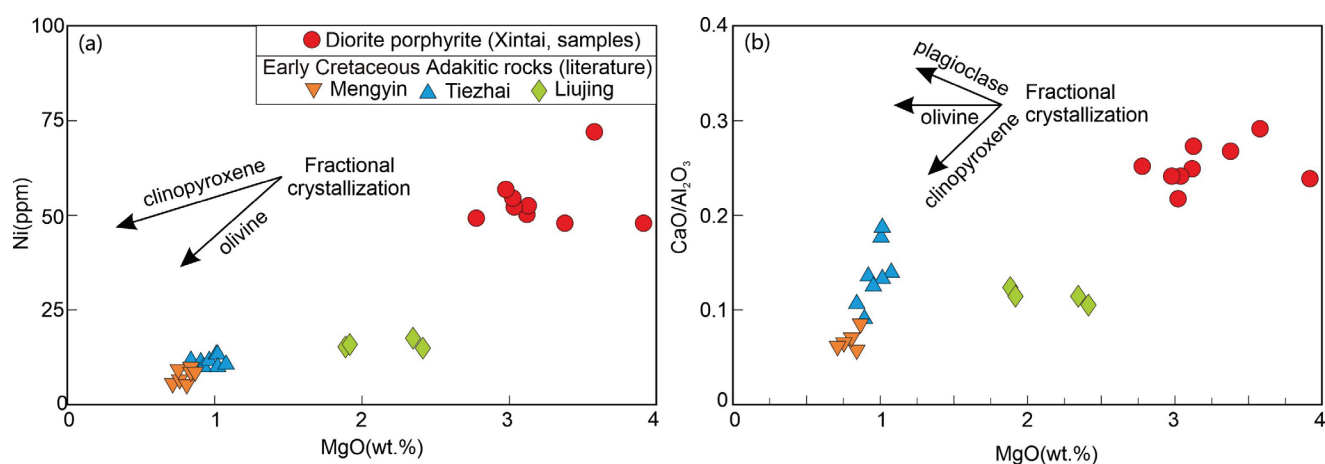


Figure 10. Diagrams of (a) Ni versus MgO; (b) $\text{CaO}/\text{Al}_2\text{O}_3$ versus MgO [27]. Data sources are the same as Figure 4.

In intermediate rocks, the aluminum (Al) of hornblende shows a strong correlation with the equilibrium pressure of mineral crystallization. Consequently, a large number of geobarometers have been put forward to compute the crystallization equilibrium pressure [66,67]. The relation between Al^T and pressure is $P = -3.92 + 5.03\text{Al}^T$, where P is the pressure measured in kbar, and Al^T is based on the total number of Al cations in each formula of 23 oxygen atoms. Our samples reveal phenocryst hornblende have equilibrium pressure of crystallization equivalent to 3.5–8.8 kbar. Most of the hornblende phenocrysts formed in 6–8.8 kbar, and crystallization depth shows that most of the hornblende crystallized at a depth of 19.8–29 km. The other hornblende formed in 3.6–6 kbar, with depth estimated as 11.8–19.8 km. The thermometer used to calculate the equilibrium temperature of the phenocryst hornblende by [68] showed that most of the hornblende in the samples have equilibrium temperature in the 830–967 °C range. The equilibrium pressure and temperature of hornblende show a positive correlation in Figure 9b. The calculated results show that the hornblende formed in a wide range of depth.

The plagioclase phenocrysts in the Xintai area of diorite-porphyrite exhibit three kinds of textural and compositional zoning patterns, oscillatory zoning, normal zoning, and reverse zoning. This suggests the growth history of plagioclase crystals may be complex, potentially involving multiple stages of growth and readjustment. In particular, a sharp decrease in An value from the core to the rim was shown by the FS-03-1-C2 samples, and the FeO content also decreased at the same time. These changes might represent one pulse of magma mixing.

5.2. Origin of Diorite-Porphyrite in the Xintai Area

In comparison to other types of intermediate-acidic rocks, such as normal island arc andesites, dacites, and rhyolites, the diorite-porphyrite samples from the Xintai area exhibit distinct geochemical characteristics, intermediate SiO_2 (>56 wt.%), high Al_2O_3 and Sr contents, low Y and Yb contents, and high Sr/Y and $(\text{La}/\text{Yb})_N$ ratios. These samples exhibited characteristics of adakitic rock. For example, in the Sr/Y-Y and $(\text{La}/\text{Yb})_N$ -Yb_N diagrams, they are plotted within the area of adakitic rocks (Figure 11a,b). However, the characteristic feature of normal island arc andesite-dacite-rhyolites is that their Sr content generally remains below 400 ppm, while both the Sr/Y and La/Yb ratios are relatively low [69]. The formation mechanisms of rocks displaying adakitic affinities have been variously proposed, including the partial melting of subducted oceanic crust [70], partial melts of the delaminated mafic continental lower crust [27,33,71], crystal fractionation [72,73], or the magma mixing model [74]. Meanwhile, the adakitic magmas are also inferred to have been derived from a mantle source metasomatized by slab-derived melts or subducted sediment [75]. The diorite-porphyrite samples from the Xintai area exhibited characteristics of adakitic rocks. Adakitic rocks appear in different types in different areas of the Western Shandong Peninsula, such as the Tiezhai, Mengyin and Liujing areas (Figures 4–6 and 11). The adakitic rocks in the Tiezhai area were most likely derived from partial melting of the newly underplated thick lower crust and assimilated the ancient NCC upper crust material during ascent [22]. The Mengyin adakitic porphyry was most likely derived from partial melting of subducted oceanic slab with some input of Neoproterozoic–Paleoproterozoic lower crust components, and the Liujing adakitic porphyry was probably derived from the partial melting of delaminated newly underplated thick lower crust [33].

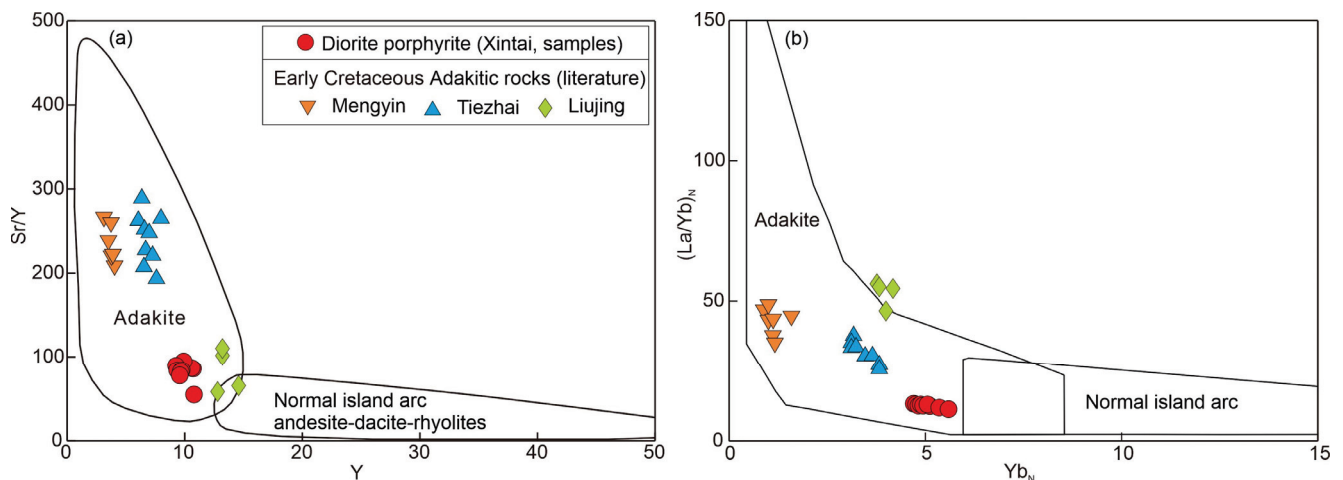


Figure 11. Plots of (a) Sr/Y versus Y and (b) $(\text{La}/\text{Yb})_N$ versus Yb_N (after [68]). Data sources are the same as Figure 4.

The diorite-porphyrite samples exhibit MgO contents ranging from 2.78% to 6.60%, which are higher than the typical MgO contents of adakites (usually less than 3%, rarely exceeding 6%). The adakitic magma, derived from subducted oceanic crust or delaminated lower crust, often results from the subsequent interaction with mantle peridotites, leading to relatively high MgO and compatible elements (Cr, Ni, Co) contents [76–78]. The Mg# value serves as an important indicator for assessing the involvement of mantle components. It is generally accepted that the Mg# values of magmatic rocks resulting from the partial melting of basaltic rocks are typically lower than 40, whereas those formed with the contribution of mantle components exceed 40 [79]. With Mg# values ranging from 53 to 63, these samples indicate the incorporation of mantle components in the source region of the magma. These occur in the fields of the Late Mesozoic high-Mg adakitic rocks in eastern China, as defined by [18] (Figure 12a).

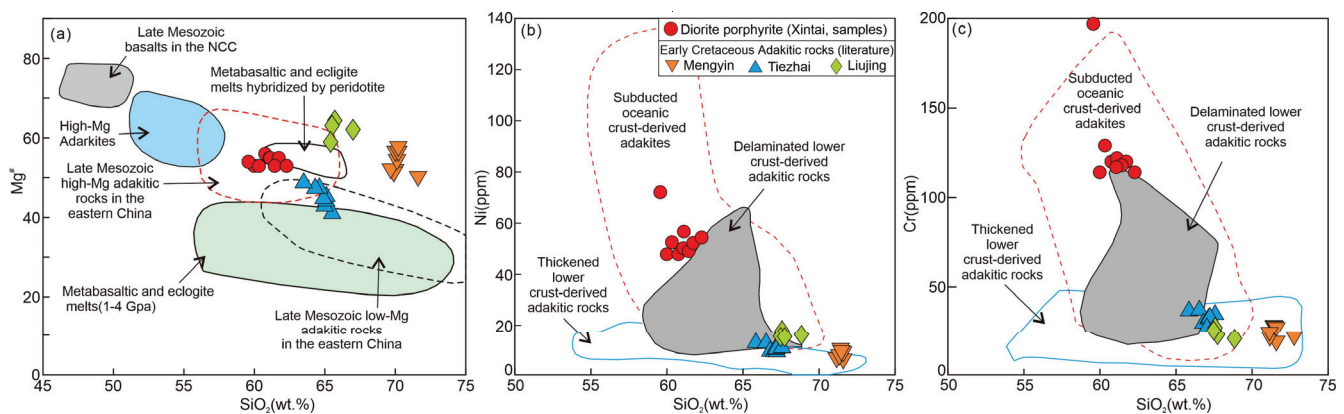


Figure 12. Plots of (a) Mg# versus SiO₂ (after [80]), (b) Ni versus SiO₂, and (c) Cr versus SiO₂ (after [81]). Data sources are the same as Figure 4.

Compatible elements such as Cr (114–197 ppm), Co (14–31 ppm), and Ni (50–153 ppm) exhibit elevated concentrations in the diorite-porphyrite from the Xintai area. The geochemical compositions of the samples plot within the field of subducted oceanic crust-derived adakitic rocks, near the field of delaminated lower crust-derived adakitic rocks (Figure 12b,c), but are different from the thickened lower crust-derived adakitic rocks. The diorite-porphyrite samples exhibit sodium-rich and potassium-poor ($K_2O/Na_2O = 0.32\text{--}0.49$) characteristics, as well as high $(La/Yb)_N$ values (11.10–13.00), which are reminiscent of oceanic crust components [82]. During the subduction process, the pressure and temperature increase with depth. Elements such as LILEs (e.g., Ba, Sr) become enriched due to the release of aqueous fluids generated by the dehydration of the Paleo-Pacific plate, while elements such as Nb, Th, and La accumulate in the melt of sediments [83,84]. The diagrams of trace elements indicate that the formation of Xintai diorite-porphyrite was dominated by slab-related enrichment, with weaker enrichment from sediment melts (Figure 13). The $\epsilon_{Hf}(t)$ values ranging from -30.1 to 7.5 (Figure 8), and the two-stage Hf model age (T_{DM2}) between 0.7 Ga and 3.1 Ga, indicate that the origin of diorite-porphyrite derived from both mantle and lower continental crust [85]. The conclusion indicated by the Hf isotopes is inconsistent with the conclusion of slab subduction indicated by LILEs (e.g., Ba, Sr). This may be because the mantle source of Early Cretaceous diorite-porphyrite samples had been affected by the interaction with melt derived from delaminated continental crust. The fluids released during the slab subduction process have led to the enrichment of the lithospheric mantle, making it exhibit the characteristics of slab subduction. Subsequently, the adakitic magma formed via the interactions of enriched lithospheric mantle with delaminated lower continental crust.

The depletion of HREEs, coupled with Y/Yb ratios ranging from 11.11 to 12.33 and $(Ho/Yb)_N$ values between 1.17 and 1.33, indicate that the residual phase primarily comprises garnet. The absence of any significant Eu anomaly (δEu values between 0.97 and 1.06) suggests that the residual phase did not include plagioclase.

Therefore, it is concluded that the diorite-porphyrite in the Xintai area comprises adakitic rocks derived from the partial melting of enriched lithospheric mantle and delaminated lower continental crust.

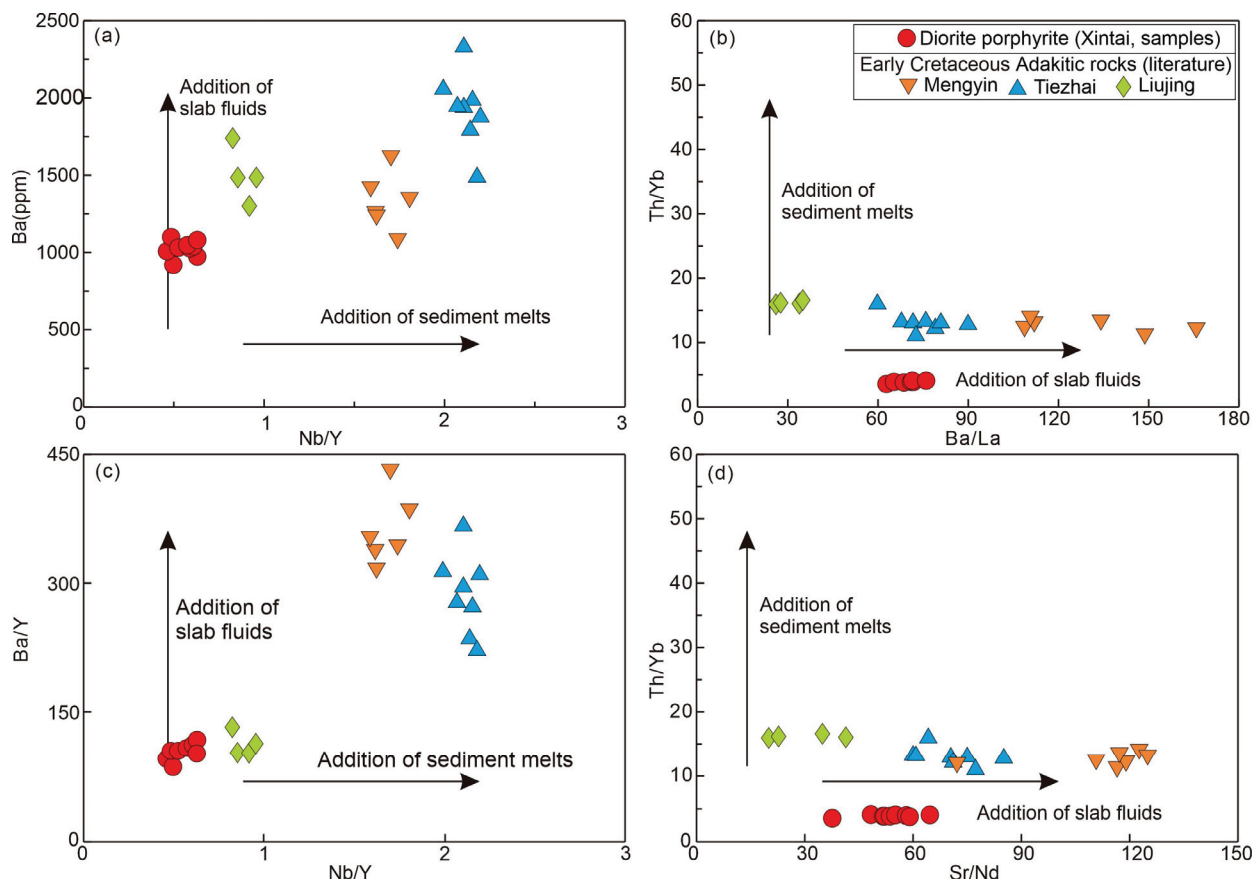


Figure 13. Plots of (a) Ba versus Nb/Y, (b) Th/Yb versus Ba/La, (c) Ba/Y versus Nb/Y, (d) Th/Yb versus Sr/Nd (after [76]). Data sources are the same as Figure 4.

5.3. Early Cretaceous Magmatism and Tectonic Implications

The magmatic activity during the Mesozoic era in Western Shandong was characterized by two distinct episodes in the Middle Jurassic and Early Cretaceous [7,24]. The Middle Jurassic magmatic activity was relatively limited in its distribution, prominently exemplified by the Tongshi monzonite complex [32]. The Early Cretaceous magmatic activity was more intense and widespread, varying from mafic to intermediate intrusions in the early stages to diorite-porphyrite and syenite in the later stages [17,26,47,86,87]. The intrusive rocks are mainly distributed in the central and northern parts of Western Shandong, including the Jinan, Zibo, Laiwu, Xintai, Yiyuan, and Mengyin regions, and there is also a small distribution in the Cangshan region in southwestern Shandong [24]. Meanwhile, the intermediate volcanic rocks are primarily andesite and andesite porphyrite, distributed in the Mengyin, Zibo, Anqiu, and other regions [26,27]. The Mesozoic ore-bearing/barren intermediate (dioritic) intrusions in the Western Shandong are mainly formed in the Early Cretaceous [29,37]. Regionally, the skarn-type iron ore deposits in northwest Shandong, which are closely related to the Early Cretaceous intermediate-mafic intrusions, are mainly distributed in the Jinan, Laiwu, Zibo, and other areas [87]. The investigations into the magmatism of the early Cretaceous era illuminate a lithospheric extensional environment prevalent during this period [88,89]. Concurrently, the coeval adakitic intrusive rocks, which are of significant geological importance, hint at the potential occurrence of delamination within the lower crust beneath the Western Shandong Peninsula [33,90].

During the Cretaceous, the eastern NCC underwent an important period of craton destruction, accompanied by intense magmatism, metamorphic core complexes, detachment faults, and rifted basins [57]. Specifically, the magmatic activity in the Shandong Peninsula during this Cretaceous epoch was predominantly concentrated towards the latter stages

of the Early Cretaceous [7]. Recently, a widespread consensus has crystallized regarding the causal nexus between the west Pacific plate subduction and NCC disintegration [8]. This subduction process had its inception as far back as the Early Jurassic era, while the retreat of the subducting west Pacific plate commenced approximately 145 million years ago, coinciding with the inception of the vast mantle wedge system during the Early Cretaceous.

The proposed slab rollback of the Paleo-Pacific subduction slab has been postulated to significantly contribute to the Cretaceous-era geodynamics beneath the eastern NCC [4]. This phenomenon is intricately linked to the Pacific slab's subduction, which underwent the following two distinct phases: an initial rapid, low-angle subduction phase corresponding to approximately 165–138 Ma, and a subsequent phase marked by a decreasing subduction angle, particularly after 138 Ma [4]. During 130 Ma to 120 Ma, the west Pacific plate subduction underwent a pivotal transformation, characterized by a pronounced increase in the subduction angle [4]. During the subduction process, the Paleo-Pacific plate broke into different slabs [91], one slab accompanied by slab rollback and a swift retreat of the trench [4], another slab leading to the final stagnation of the subducting slab within the mantle transition zone. The extension of the lithosphere was triggered by the retreat of the Paleo-Pacific slab. These processes lead to the partial melting of the pre-existing ancient enriched lithospheric mantle (including the EM1-type and EM2-type sources), resulting in the formation of mafic lavas and associated intermediate-felsic magmatic rocks. The rapid rollback of the subducting Paleo-Pacific slab may have been accompanied by fast hinge retreat and slab stagnation (Figure 14). Meanwhile, the retreat of the plate led to the upwelling of the asthenosphere, resulting in extensive magmatic activities [92,93]. In this study, the diorite-porphyrite in the Xintai area comprises adakitic rocks derived from the partial melting of enriched lithospheric mantle and delaminated lower continental crust.

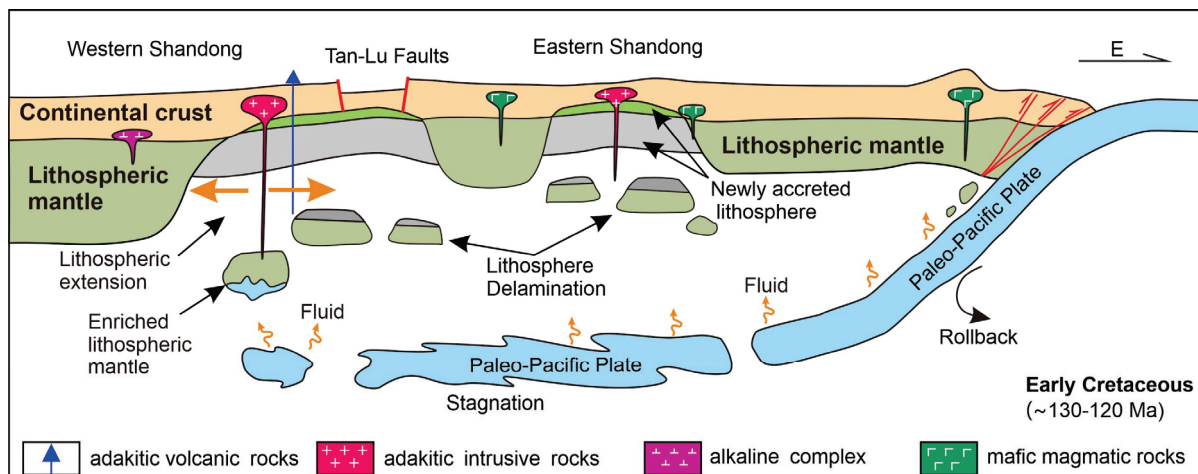


Figure 14. Schematic diagram of the evolution in the Early Cretaceous. Modified form [27].

6. Conclusions

The diorite-porphyrite in the southern Xintai area of the mid-western Shandong Peninsula has adakitic features with an EM2-like Sr–Nd isotopic signature and relatively low $(La/Yb)_N$ but variable high Sr/Y ratios, similar to oceanic adakites from slab melting but distinct from magmas from either the thickened or delaminated lower continental crust. In addition, their higher Mg# and MgO, Cr, and Ni contents are also similar to oceanic adakites.

The genesis of early Cretaceous diorite-porphyrite in the southern Xintai area of the mid-western Shandong Peninsula may be related to the enriched lithospheric mantle and delaminated lower continental crust. During the process of magma emplacement, there exist magma mixing and crystallization differentiation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14121220/s1>, Table S1: Microprobe analyses (wt%) of hornblende and plagioclase in the Xintai diorite-porphyrite.

Author Contributions: L.J. led the conceptualization, collected and curated data, and also wrote the initial draft. J.W., S.X. and Z.H. participated in fieldwork and sample analysis, and they also helped with data curation. L.J., C.L., W.W., W.L. and Z.W. provided expertise for data analysis and contributed to the interpretation of results. L.J., P.Q., J.G. and F.L. played integral roles in writing—review and editing. Collectively, all authors collaborated throughout the research process to ensure the integrity and quality of this geological study. All authors have read and agreed to the published version of the manuscript.

Funding: This work is supported by the Shandong Province geological exploration projects (SDZS-2015-GTT01) and the National Natural Science Foundation of China (No. 62171435).

Data Availability Statement: The data used to support the findings of this study are included within this article.

Acknowledgments: The authors would like to convey their heartfelt gratitude to the three anonymous reviewers and the academic editor for their constructive feedback on this paper.

Conflicts of Interest: The authors confirm that there are no financial, personal, or other conflicts of interest relevant to the research and writing of this paper.

References

1. Zhang, H.F. Peridotite-melt interaction: A key point for the destruction of cratonic lithospheric mantle. *Chin. Sci. Bull.* **2009**, *54*, 3417–3437. [CrossRef]
2. Zheng, Y.F.; Xu, Z.; Zhao, Z.F.; Dai, L.Q. Mesozoic mafic magmatism in North China: Implications for thinning and destruction of cratonic lithosphere. *Sci. China Earth Sci.* **2018**, *61*, 353–385. [CrossRef]
3. Wu, F.; Yang, J.; Xu, Y.; Wilde, S.A.; Walker, R.J. Destruction of the North China Craton in the Mesozoic. *Annu. Rev. Earth Planet. Sci.* **2019**, *47*, 173–195. [CrossRef]
4. Zhu, R.; Xu, Y. The subduction of the west Pacific plate and the destruction of the North China Craton. *Sci. China Earth Sci.* **2019**, *62*, 1340–1350. [CrossRef]
5. Chen, L.; Jiang, M.M.; Yang, J.H.; Wei, Z.G.; Liu, C.Z.; Ling, Y. Presence of an intralithospheric discontinuity in the central and western North China Craton: Implications for destruction of the craton. *Geology* **2015**, *42*, 223–226. [CrossRef]
6. Yang, J.H.; Wu, F.Y.; Wilde, S.A.; Belousova, E.; Griffin, W.L. Mesozoic decratonization of the North China block. *Geology* **2008**, *36*, 467–470. [CrossRef]
7. Li, H.Y. Destruction of North China Craton: Insights from temporal and spatial evolution of the proto-basins and magmatism. *Sci. China Earth Sci.* **2013**, *56*, 464–478. [CrossRef]
8. Zhu, R.; Sun, W. The big mantle wedge and decratonic gold deposits. *Sci. China Earth Sci.* **2021**, *64*, 1451–1462. [CrossRef]
9. Wu, F.; Xu, Y.; Zhu, R.X.; Zhang, G.W. Thinning and destruction of the cratonic lithosphere: A global perspective. *Sci. China Earth Sci.* **2014**, *57*, 2878–2890. [CrossRef]
10. Yang, J.H.; Wu, F.Y.; Wilde, S.A.; Chen, F.K.; Liu, X.M.; Xie, L.W. Petrogenesis of an Alkali Syenite–Granite–Rhyolite Suite in the Yanshan Fold and Thrust Belt, Eastern North China Craton: Geochronological, Geochemical and Nd–Sr–Hf Isotopic Evidence for Lithospheric Thinning. *J. Petrol.* **2008**, *49*, 315–351. [CrossRef]
11. Huang, X.; Zhong, J.; Xu, Y. Two tales of the continental lithospheric mantle prior to the destruction of the North China Craton: Insights from Early Cretaceous mafic intrusions in western Shandong, East China. *Geochim. Cosmochim. Acta* **2012**, *96*, 193–214. [CrossRef]
12. Pang, C.; Wang, X.; Xu, Y.; Wen, S.; Kuang, Y.; Hong, L. Pyroxenite-derived early cretaceous lavas in the Liaodong Peninsula: Implication for metasomatism and thinning of the lithospheric mantle beneath North China Craton. *Lithos* **2015**, *227*, 77–93. [CrossRef]
13. Dai, L.; Zheng, Y.; Zhao, Z. Termination time of peak decratonization in North China: Geochemical evidence from mafic igneous rocks. *Lithos* **2016**, *240–243*, 327–336. [CrossRef]
14. Ma, Q.; Xu, Y.G.; Zheng, J.P.; Griffin, W.L.; Hong, L.B.; Ma, L. Coexisting Early Cretaceous High-Mg Andesites and Adakitic Rocks in the North China Craton: The Role of Water in Intraplate Magmatism and Cratonic Destruction. *J. Petrol.* **2016**, *57*, 1279–1308. [CrossRef]
15. Pei, F.; Xu, W.; Yang, D.; Yu, Y.; Wang, W.; Zhao, Q. Geochronology and geochemistry of Mesozoic mafic–ultramafic complexes in the southern Liaoning and southern Jilin provinces, NE China: Constraints on the spatial extent of destruction of the North China Craton. *J. Asian Earth Sci.* **2011**, *40*, 636–650. [CrossRef]
16. Zheng, J.P.; O'Reilly, S.Y.; Griffin, W.L.; Lu, F.X.; Zhang, M. Nature and evolution of Cenozoic lithospheric mantle beneath Shandong Peninsula, Sino-Korean Craton, Eastern China. *Int. Geol. Rev.* **1998**, *40*, 471–499. [CrossRef]

17. Liu, S.; Hu, R.; Gao, S.; Feng, C.; Qi, L.; Zhong, H.; Xiao, T.; Qi, Y.; Wang, T.; Coulson, I.M. Zircon U–Pb geochronology and major, trace elemental and Sr–Nd–Pb isotopic geochemistry of mafic dykes in western Shandong Province, east China: Constrains on their petrogenesis and geodynamic significance. *Chem. Geol.* **2008**, *255*, 329–345. [CrossRef]
18. Gu, H.; Xiao, Y.; Santosh, M.; Li, W.; Yang, X.; Pack, A.; Hou, Z. Spatial and temporal distribution of Mesozoic adakitic rocks along the Tan-Lu fault, Eastern China: Constraints on the initiation of lithospheric thinning. *Lithos* **2013**, *177*, 352–365. [CrossRef]
19. Guo, F.; Guo, J.T.; Wang, C.Y.; Fan, W.M.; Li, C.W.; Zhao, L.; Li, H.X.; Li, J.Y. Formation of mafic magmas through lower crustal AFC processes—An example from the Jinan gabbroic intrusion in the North China Block. *Lithos* **2013**, *179*, 157–174. [CrossRef]
20. Huang, X.L.; He, P.L.; Wang, X.; Zhong, J.W.; Xu, Y.G. Lateral variation in oxygen fugacity and halogen contents in early Cretaceous magmas in Jiaodong area, East China: Implication for triggers of the destruction of the North China Craton. *Lithos* **2016**, *248–251*, 478–492. [CrossRef]
21. Ma, L.; Jiang, S.; Hofmann, A.W.; Xu, Y.; Dai, B.; Hou, M. Rapid lithospheric thinning of the North China Craton: New evidence from cretaceous mafic dikes in the Jiaodong Peninsula. *Chem. Geol.* **2016**, *432*, 1–15. [CrossRef]
22. Wang, H.; Wang, S.; Xu, Z.; Fu, B.; Zhao, Z.; Li, Z.; Dong, Y.; Tang, L.; Li, J. Geochemical and Sr–Nd–Pb–Hf–O isotopic compositions of the Tiezhai complex: Implications for lithosphere destruction of the North China Craton. *Gondwana Res.* **2018**, *61*, 203–221. [CrossRef]
23. Xu, W.L.; Hergt, J.M.; Gao, S.; Pei, F.P.; Wang, W.; Yang, D.B. Interaction of adakitic melt-peridotite: Implications for the high-Mg# signature of Mesozoic adakitic rocks in the eastern North China Craton. *Earth Planet. Sci. Lett.* **2008**, *265*, 123–137.
24. Xu, Y.G.; Huang, X.; Ma, J.; Wang, Y.; Iizuka, Y.; Xu, J.; Wang, Q.; Wu, X. Crust–mantle interaction during the tectono-thermal reactivation of the North China Craton: Constraints from SHRIMP zircon U–Pb chronology and geochemistry of Mesozoic plutons from western Shandong. *Contrib. Mineral. Petrol.* **2004**, *147*, 750–767. [CrossRef]
25. Ying, J.; Zhou, X.; Zhang, H. The geochemical variations of mid-Cretaceous lavas across western Shandong Province, China and their tectonic implications. *Int. J. Earth Sci.* **2006**, *95*, 68–79. [CrossRef]
26. Liu, S.; Hu, R.; Gao, S.; Feng, C.; Zhong, H.; Qi, Y.; Wang, T.; Qi, L.; Feng, G. K–Ar Ages and Geochemical + Sr–Nd Isotopic Compositions of Adakitic Volcanic Rocks, Western Shandong Province, Eastern China: Foundering of the Lower Continental Crust. *Int. Geol. Rev.* **2008**, *50*, 763–779. [CrossRef]
27. Li, X.Y.; Li, S.Z.; Suo, Y.H.; Somerville, I.D.; Huang, F.; Liu, X.; Wang, P.C.; Han, Z.X.; Jin, L.J. Early Cretaceous diabases, lamprophyres and andesites-dacites in western Shandong, North China Craton: Implications for local delamination and Paleo-Pacific slab rollback. *J. Asian Earth Sci.* **2018**, *160*, 426–444. [CrossRef]
28. Xu, W.L.; Zhou, Q.J.; Pei, F.P.; Yang, D.B.; Gao, S.; Li, Q.L.; Yang, Y.H. Destruction of the North China Craton: Delamination or thermal/chemical erosion? Mineral chemistry and oxygen isotope insights from websterite xenoliths. *Gondwana Res.* **2013**, *23*, 119–129. [CrossRef]
29. Duan, Z.; Li, J. Zircon and titanite U–Pb dating of the Zhangjiawa iron skarn deposit, Luxi district, North China Craton: Implications for a craton-wide iron skarn mineralization. *Ore Geol. Rev.* **2017**, *89*, 309–323. [CrossRef]
30. Guo, F.; Fan, W.; Wang, Y.; Lin, G. Geochemistry of late Mesozoic mafic magmatism in west Shandong Province, eastern China: Characterizing the lost lithospheric mantle beneath the North China Block. *Geochem. J.* **2003**, *37*, 63–77. [CrossRef]
31. Yang, C.H.; Xu, W.L.; Yang, D.B.; Wei, W.; Wang, W.D.; Liu, J.M. Petrogenesis of Shangyu gabbro-diorites in western Shandong: Geochronological and geochemical evidence. *Sci. China Earth Sci.* **2008**, *51*, 481–492. [CrossRef]
32. Lan, T.; Fan, H.; Santosh, M.; Hu, F.; Yang, K.; Yang, Y.; Liu, Y. Early Jurassic high-K calc-alkaline and shoshonitic rocks from the Tongshi intrusive complex, eastern North China Craton: Implication for crust–mantle interaction and post-collisional magmatism. *Lithos* **2012**, *140–141*, 183–199. [CrossRef]
33. Wang, H.; Xu, Z.; Lu, X.; Fu, B.; Lu, J.; Yang, X.; Zhao, Z. Two-types of Early Cretaceous adakitic porphyries from the Luxi terrane, eastern North China Block: Melting of subducted Paleo-Pacific slab and delaminated newly underplated lower crust. *Lithos* **2016**, *240–243*, 140–154. [CrossRef]
34. Deng, X.D.; Li, J.W.; Wen, G. U–Pb Geochronology of Hydrothermal Zircons from the Early Cretaceous Iron Skarn Deposits in the Handan-Xingtai District, North China Craton. *Econ. Geol.* **2015**, *110*, 2159–2180. [CrossRef]
35. Sun, Y.; Xiao, L.; Zhan, Q.Y.; Wu, J.X.; Zhu, D.; Huang, W.; Bai, M.; Zhang, Y.H. Petrogenesis of the Kuangshancun and Hongshan intrusive complexes from the Handan–Xingtai district: Implications for iron mineralization associated with Mesozoic magmatism in the North China Craton. *J. Asian Earth Sci.* **2015**, *113*, 1162–1178. [CrossRef]
36. Li, X.Y.; Li, S.Z.; Huang, F.; Wang, Y.M.; Yu, S.Y.; Cao, H.H.; Xie, W.M. Petrogenesis of high Ba–Sr plutons with high Sr/Y ratios in an intracontinental setting: Evidence from Early Cretaceous Fushan monzonites, central North China Craton. *Geol. Mag.* **2019**, *156*, 1965–1981. [CrossRef]
37. Xie, Q.; Zhang, Z.; Hou, T.; Santosh, M.; Jin, Z.; Han, L.; Cheng, Z. Petrogenesis of the Zhangmatun gabbro in the Ji’nan complex, North China Craton: Implications for skarn-type iron mineralization. *J. Asian Earth Sci.* **2015**, *113*, 1197–1217. [CrossRef]
38. Yang, Q.; Zhao, Z.; Zheng, Y. Slab–mantle interaction in continental subduction channel: Geochemical evidence from Mesozoic gabbroic intrusives in southeastern North China. *Lithos* **2012**, *155*, 442–460. [CrossRef]
39. Yang, Q.L.; Zhao, Z.F.; Zheng, Y.F. Modification of subcontinental lithospheric mantle above continental subduction zone: Constraints from geochemistry of Mesozoic gabbroic rocks in southeastern North China. *Lithos* **2012**, *146–147*, 164–182. [CrossRef]
40. Zhao, G.C.; Cawood, P.A. Precambrian geology of China. *Precambrian Res.* **2012**, *222–223*, 13–54. [CrossRef]

41. Zhao, G.C.; Zhai, M.G. Lithotectonic elements of Precambrian basement in the North China Craton: Review and tectonic implications. *Gondwana Res* **2013**, *23*, 1207–1240. [CrossRef]
42. Li, S.Z.; Zhao, G.C.; Santosh, M.; Liu, X.; Dai, L.M.; Suo, Y.H.; Tam, P.Y.; Song, M.C.; Wang, P.C. Paleoproterozoic structural evolution of the southern segment of the Jiao-Liao-Ji Belt, North China Craton. *Precambrian Res.* **2012**, *200–203*, 59–73. [CrossRef]
43. Zhao, G.C.; Cawood, P.A.; Li, S.Z.; Wilde, S.A.; Sun, M.; Zhang, J.; He, Y.H.; Yin, C.Q. Amalgamation of the North China Craton: Key issues and discussion. *Precambrian Res.* **2012**, *222–223*, 55–76. [CrossRef]
44. Zhu, G.; Wang, W.; Gu, C.C.; Zhang, S.; Liu, C. Late Mesozoic evolution history of the Tan-Lu Fault Zone and its indication to destruction processes of the North China Craton. *Acta Petrol. Sin.* **2016**, *32*, 935–949.
45. Li, S.Z.; Wang, J.D.; Liu, J.Z.; Yu, J.G.; Lv, H.Q.; Hou, F.H. Mesozoic structure and its tectonic setting in the western Shandong block. *Acta Geol. Sin.* **2005**, *79*, 487–497.
46. Wan, Y.; Dong, C.; Wang, S.; Kröner, A.; Xie, H.; Ma, M.; Zhou, H.; Xie, S.; Liu, D. Middle Neoarchean magmatism in western Shandong, North China Craton: SHRIMP zircon dating and LA-ICP-MS Hf isotope analysis. *Precambrian Res.* **2014**, *255*, 865–884. [CrossRef]
47. Lan, T.; Fan, H.; Hu, F.; Tomkins, A.G.; Yang, K.; Liu, Y. Multiple crust–mantle interactions for the destruction of the North China Craton: Geochemical and Sr–Nd–Pb–Hf isotopic evidence from the Longbaoshan alkaline complex. *Lithos* **2011**, *122*, 87–106. [CrossRef]
48. Sláma, J.; Košler, J.; Condon, D.J.; Crowley, J.L.; Gerdes, A.; Hanchar, J.M.; Horstwood, M.S.A.; Morris, G.A.; Nasdala, L.; Norberg, N.; et al. Plešovice zircon—A new natural reference material for U–Pb and Hf isotopic microanalysis. *Chem. Geol.* **2008**, *249*, 1–35. [CrossRef]
49. Li, X.Y.; Li, S.Z.; Suo, Y.H.; Dai, L.M.; Guo, L.L.; Ge, F.J.; Lin, P.J. Late Cretaceous basalts and rhyolites from Shimaoshan Group in eastern Fujian Province, SE China: Age, petrogenesis, and tectonic implications. *Int. Geol. Rev.* **2018**, *60*, 1721–1743. [CrossRef]
50. Chen, F.K.; Satir, M.; Ji, J.; Zhong, D. Nd–Sr–Pb isotopes of Tengchong Cenozoic volcanic rocks from western Yunnan, China: Evidence for an enriched-mantle source. *J. Asian Earth Sci.* **2002**, *21*, 39–45. [CrossRef]
51. Hu, Z.C.; Liu, Y.S.; Gao, S.; Liu, W.; Zhang, W.; Tong, X.R.; Lin, L.; Zong, K.Q.; Li, M.; Chen, H.; et al. Improved in situ Hf isotope ratio analysis of zircon using newly designed X skimmer cone and jet sample cone in combination with the addition of nitrogen by laser ablation multiple collector ICP-MS. *J. Anal. At. Spectrom.* **2012**, *27*, 1391–1399. [CrossRef]
52. Bouvier, A.; Vervoort, J.D.; Patchett, P.J. The Lu–Hf and Sm–Nd isotopic composition of CHUR: Constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets. *Earth Planet. Sci. Lett.* **2008**, *273*, 48–57. [CrossRef]
53. Scherer, E.; Münker, C.; Mezger, K. Calibration of the lutetium-hafnium clock. *Science* **2001**, *293*, 683–687. [CrossRef] [PubMed]
54. Vervoort, J.D.; Blichert-Toft, J. Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. *Geochim. Cosmochim. Acta* **1999**, *63*, 533–556. [CrossRef]
55. Duan, Z. The Mineralization and Mechanism of the Iron Skarn Deposits in Laiwu District, Shandong Province. Ph.D. Thesis, China University of Geosciences (Wuhan), Wuhan, China, 2019.
56. Middlemost, E.A.K. Naming materials in the magma/igneous rock system. *Earth-Sci. Rev.* **1994**, *37*, 215–224. [CrossRef]
57. Peccerillo, A.; Taylor, S.R. Geochemistry of eocene calc-alkaline volcanic rocks from the Kastamonu area, Northern Turkey. *Contrib. Mineral. Petrol.* **1976**, *58*, 63–81. [CrossRef]
58. Maniar, P.D.; Piccoli, P.M. Tectonic discrimination of granitoids. *Geological society of America bulletin* **1989**, *101*, 635–643. [CrossRef]
59. McDonough, W.F.; Sun, S.S. The composition of the Earth. *Chem. Geol.* **1995**, *120*, 223–253. [CrossRef]
60. DePaolo, D.J.; Wasserburg, G.J. Nd isotopic variations and petrogenetic models. *Geophys. Res. Lett.* **1976**, *3*, 249–252. [CrossRef]
61. Goldstein, S.L.; O’Nions, R.K.; Hamilton, P.J. A Sm–Nd study of atmospheric dusts and particulates from major river systems. *Earth Planet. Sci. Lett.* **1984**, *70*, 221–236. [CrossRef]
62. Lugmair, G.W.; Marti, K. Lunar initial $^{143}\text{Nd}/^{144}\text{Nd}$: Differential evolution of the lunar crust and mantle. *Earth Planet. Sci. Lett.* **1978**, *39*, 349–357. [CrossRef]
63. Peucat, J.J.; Vidal, P.; Bernard-Griffiths, J.; Condie, K.C. Sr, Nd and Pb isotopic systematics in the Archaean low- to high-grade transition zone of southern India: Syn accretion vs. post-accretion granulites. *J. Geol.* **1988**, *97*, 537–550. [CrossRef]
64. Leake, B.E.; Woolley, A.R.; Arps, C.E.S.; Birch, W.D.; Gilbert, M.C.; Grice, J.D.; Hawthorne, F.C.; Kato, A.; Kisch, H.J.; Krivovichev, V.G.; et al. Nomenclature of amphiboles: Report of the subcommittee on amphiboles of the International Mineralogical Association, Commission on New Minerals and Mineral Names. *Can. Mineral.* **1997**, *35*, 219–246.
65. Deer, W.A.; Howie, R.A.; Zussman, J. *An Introduction to the Rock-Forming Minerals*, 2nd ed.; Longman Group: Harlow, UK, 1992; p. 232.
66. Hammarstrom, J.M.; Zen, E. Aluminum in hornblende: An empirical igneous geobarometer. *Am. Miner.* **1986**, *71*, 1297–1313.
67. Schmidt, M.W. Amphibole composition in tonalite as a function of pressure: An experimental calibration of the Al-in-hornblende barometer. *Contrib. Mineral. Petrol.* **1992**, *110*, 304–310. [CrossRef]
68. Ridolfi, F.; Renzulli, A.; Puerini, M. Stability and chemical equilibrium of amphibole in calc-alkaline magmas: An overview, new thermobarometric formulations and application to subduction-related volcanoes. *Contrib. Mineral. Petrol.* **2010**, *160*, 45–66. [CrossRef]
69. Wang, Q.; Hao, L.; Zhang, X.; Zhou, J.; Wang, J.; Li, Q.; Ma, L.; Zhang, L.; Qi, Y.; Tang, G.; et al. Adakitic rocks at convergent plate boundaries: Compositions and petrogenesis. *Sci. China Earth Sci.* **2020**, *63*, 1992–2016. [CrossRef]

70. Drummond, M.S.; Defant, M.J. A model for Trondhjemite-Tonalite-Dacite Genesis and crustal growth via slab melting: Archean to modern comparisons. *J. Geophys. Res. Solid Earth* **1990**, *95*, 21503–21521. [CrossRef]
71. Xu, W.; Gao, S.; Wang, Q.; Wang, D.; Liu, Y. Mesozoic crustal thickening of the eastern North China Craton: Evidence from eclogite xenoliths and petrologic implications. *Geology* **2006**, *34*, 721–724. [CrossRef]
72. Gao, Y.F.; Santosh, M.; Hou, Z.Q.; Wei, R.H.; Ma, G.X.; Chen, Z.K.; Wu, J.L. High Sr/Y magmas generated through crystal fractionation: Evidence from Mesozoic volcanic rocks in the northern Taihang orogen, North China Craton. *Gondwana Res.* **2012**, *22*, 152–168. [CrossRef]
73. Gao, Y.F.; Santosh, M.; Wei, R.H.; Ma, G.X.; Chen, Z.K.; Wu, J.L. Origin of high Sr/Y magmas from the northern Taihang Mountains: Implications for Mesozoic porphyry copper mineralization in the North China Craton. *J. Asian Earth Sci.* **2013**, *78*, 143–159. [CrossRef]
74. Chen, B.; Jahn, B.M.; Suzuki, K. Petrological and Nd-Sr-Os isotopic constraints on the origin of high-Mg adakitic rocks from the North China Craton: Tectonic implications. *Geology* **2013**, *41*, 91–94. [CrossRef]
75. Gao, Y.; Hou, Z.; Kamber, B.S.; Wei, R.; Meng, X.; Zhao, R. Adakite-like porphyries from the southern Tibetan continental collision zones: Evidence for slab melt metasomatism. *Contrib. Mineral. Petrol.* **2007**, *153*, 105–120. [CrossRef]
76. Smithies, R.H. The Archaean tonalite-trondhjemite-granodiorite (TTG) series is not an analogue of Cenozoic adakite. *Earth Planet. Sci. Lett.* **2000**, *182*, 115–125. [CrossRef]
77. Martin, H.; Smithies, R.H.; Rapp, R.; Moyen, J.F.; Champion, D. An overview of adakite, tonalite-trondhjemite-granodiorite (TTG), and sanukitoid: Relationships and some implications for crustal evolution. *Lithos* **2005**, *79*, 1–24. [CrossRef]
78. Sun, H.; Zhao, Z.; Zhu, D.; Liu, D.; Wang, Q.; Tang, Y.; Qi, N.; Dong, G. Geochronology, geochemistry and petrogenesis of Miocene adakitic rocks in Milashan, Southern Tibet. *Acta Petrol. Sin.* **2021**, *37*, 3479–3500.
79. Rapp, R.P.; Watson, E.B. Dehydration Melting of Metabasalt at 8–32 kbar: Implications for Continental Growth and Crust-Mantle Recycling. *J. Petrol.* **1995**, *36*, 891–931. [CrossRef]
80. Stern, C.R.; Kilian, R. Role of the subducted slab, mantle wedge and continental crust in the generation of adakites from the Andean Austral Volcanic Zone. *Contrib. Mineral. Petrol.* **1996**, *123*, 263–281. [CrossRef]
81. Yu, S.Y.; Zhang, J.X.; Qin, H.P.; Sun, D.Y.; Zhao, X.L.; Cong, F.; Li, Y.S. Petrogenesis of the early Paleozoic low-Mg and high-Mg adakitic rocks in the North Qilian orogenic belt, NW China: Implications for transition from crustal thickening to extension thinning. *J. Asian Earth Sci.* **2015**, *107*, 122–139. [CrossRef]
82. Liu, S.; Li, S.; He, Y.; Huang, F. Geochemical contrasts between early Cretaceous ore-bearing and ore-barren high-Mg adakites in central-eastern China: Implications for petrogenesis and Cu–Au mineralization. *Geochim. Cosmochim. Acta* **2010**, *74*, 7160–7178. [CrossRef]
83. Pearce, J.A.; Peate, D.W. Tectonic Implications of the Composition of Volcanic ARC Magmas. *Earth Planet. Sci.* **1995**, *23*, 251–285. [CrossRef]
84. Castillo, P.R. Adakite petrogenesis. *Lithos* **2012**, *134–135*, 304–316. [CrossRef]
85. Belousova, E.A.; Kostitsyn, Y.A.; Griffin, W.L.; Begg, G.C.; O'reilly, S.Y.; Pearson, N.J. The growth of the continental crust: Constraints from zircon Hf-isotope data. *Lithos* **2010**, *119*, 457–466. [CrossRef]
86. Yang, D.; Xu, W.; Pei, F.; Yang, C.; Wang, Q. Spatial extent of the influence of the deeply subducted South China Block on the southeastern North China Block: Constraints from Sr–Nd–Pb isotopes in Mesozoic mafic igneous rocks. *Lithos* **2012**, *136–139*, 246–260. [CrossRef]
87. Jiang, Y.H.; Jiang, S.Y.; Ling, H.F.; Ni, P. Petrogenesis and tectonic implications of Late Jurassic shoshonitic lamprophyre dikes from the Liaodong Peninsula, NE China. *Mineral. Petrol.* **2010**, *100*, 127–151. [CrossRef]
88. Kusky, T.M.; Windley, B.F.; Wang, L.; Wang, Z.; Zhu, P. Flat slab subduction, trench suction, and craton destruction: Comparison of the north China, wyoming, and brazilian cratons. *Tectonophysics* **2014**, *630*, 208–221. [CrossRef]
89. Windley, B.F.; Maruyama, S.; Xiao, W.J. Delamination/thinning of sub-continental lithospheric mantle under eastern china: The role of water and multiple subduction. *Am. J. Sci.* **2010**, *310*, 1250–1293. [CrossRef]
90. Zhu, R.X.; Chen, L.; Wu, F.Y.; Liu, J.L. Timing, scale and mechanism of the destruction of the North China Craton. *Sci. China Earth Sci.* **2011**, *54*, 789–797. [CrossRef]
91. Deng, J.; Yang, L.Q.; Groves, D.I.; Zhang, L.; Qiu, K.F.; Wang, Q.F. An integrated mineral system model for the gold deposits of the giant Jiaodong province, eastern China. *Earth-Sci. Rev.* **2020**, *208*, 103274. [CrossRef]
92. Zhang, Z.L.; Zhang, C.; Li, Y.; Wang, L.Y.; Gao, J.L.; Ma, M.; Li, Y.D. Petrogenesis and Geological Significance of the Quartz Monzonites in the Jinling Area, Western Shandong Province. *Minerals* **2022**, *12*, 771. [CrossRef]
93. Ye, G.; Mao, G.; Xu, Q.; Ding, Z.; Han, Y.; Zhao, H.; Shen, Y. Petrogenesis of the Early Cretaceous Tietonggou Diorite and Its Geological Implications. *Minerals* **2024**, *14*, 390. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Tectonic Evolution of the Hainan Island, South China: Geochronological and Geochemical Constraints from Late Permian to Early Triassic Basalts

Jieting Ouyang ^{1,2}, Guoyu Chen ^{1,2}, Liya Yang ^{1,2}, Wenqian Lu ^{1,2} and Yun Zhou ^{1,2,*}

¹ Guangxi Key Laboratory of Hidden Metallic Ore Deposits Exploration, Guilin University of Technology, Guilin 541004, China; ouyangjt2000@163.com (J.O.); chenguoyu2117@163.com (G.C.); yangliya0701@163.com (L.Y.); 13666087671@163.com (W.L.)

² Collaborative Innovation Center for Exploration of Nonferrous Metal Deposits and Efficient Utilization of Resources, Guilin University of Technology, Guilin 541006, China

* Correspondence: zhouyun@glut.edu.cn

Abstract: The tectonic evolution of Hainan Island during the Late Permian–Early Triassic period is still unclear. This study identified two types of basalts on the island and presented detailed geochronology, whole-rock geochemistry, and Hf isotope data of the Late Permian–Early Triassic basalts. U–Pb dating results indicated that baddeleyites and zircons of one sample from Group 1 basalts had formation ages of 256 ± 3 Ma and 255 ± 3 Ma, respectively, and two samples from Group 2 gave formation ages of 241 ± 2 Ma and 240 ± 3 Ma, respectively. Both groups are characterized by negative anomalies of Nb, Ta, and Ti, and enrichment in Ba, Th, U, and K. Group 1 belongs to sub-alkaline basalt and exhibited SiO₂ contents ranging from 50.50% to 51.05%, with Σ REE concentration of 136–148 ppm. Hf isotope analysis showed that the $\epsilon_{\text{Hf}}(t)$ values of baddeleyites and zircons were -10.56 to -4.70 and -14.94 to -6.95 , respectively. Group 2 belongs to alkaline basalt and had a higher SiO₂ content of 52.48%–55.49% and Σ REE concentration of 168–298 ppm. They showed more depleted Hf isotopic composition with $\epsilon_{\text{Hf}}(t)$ values ranging from -2.82 to $+4.74$. These data indicate that the source area of Group 1 was an enriched mantle, likely derived from partial melting of spinel lherzolite mantle, and was modified by subduction-derived fluids. Group 2 was derived from depleted mantle, most likely originating from partial melting of garnet + spinel lherzolite mantle. They were contaminated by crustal materials and metasomatized by subduction-derived fluids with a certain degree of fractional crystallization. Comprehensive analysis suggests that Group 1 samples likely formed in an island arc tectonic setting, while Group 2 formed in a continental intraplate extensional (or initial rift) tectonic setting. Their formation was mainly controlled by the Paleo-Tethys tectonic domain. Group 1 basalts implied that subduction of the Paleo-Tethys oceanic crust lasted at least in the late Permian (ca. 255 Ma). Group 2 basalts revealed that the intra-plate extensional (or initial rift) stage occurred in the middle Triassic (ca. 240 Ma).

Keywords: basalt; U–Pb dating; Hf isotopes; geochemistry; Paleo-Tethys; Hainan Island

1. Introduction

The Southeast Asian region is composed of multiple microcontinental blocks, which began to drift northward from the northern margin of the Gondwana continent under the influence of the expansion of the Paleo-Tethys Ocean to the east [1–4]. During the Late Paleozoic to Early Mesozoic period, Indosinian Orogeny, a continental collision event,

occurred between the North China, South China, Indochina, and Siberian blocks [5,6]. This orogeny event led to the closure of the Paleo-Tethys Ocean, marking the basic formation of the geological structural pattern in Southeast Asia [3,7–11].

Hainan Island, a continental island located on the southern margin of China, is separated from the South China Block by the Qiongzhou Strait and is connected to the Indochina Block by the Beibu Gulf. It has been subjected to the dual influences of the Paleo-Tethys and Paleo-Pacific tectonic domains, experiencing a complex multi-stage crustal evolutionary history. The unique tectonic position of Hainan Island makes it an important region for studying the evolution of the South China continental margin, the formation of the South China Sea, and the timing of the transition between the Paleo-Tethys and Paleo-Pacific tectonic domains, which are key scientific issues [12–16].

In recent years, the origin and tectonic evolution of Hainan Island have attracted widespread attention. Although some studies have been conducted on the widely distributed Late Permian–Early Triassic granites on Hainan Island and some important results have been achieved, the study of mafic volcanic rocks, which are closely related to the concurrent tectonic evolution, is relatively poor. Mafic volcanic rocks, as a key rock type from the mantle, play an important role in constraining petrogenesis, tectonic background, and dynamic mechanisms. This study presents detailed petrological, geochemical, U–Pb geochronological, and Hf isotopic data for Late Permian to Early Triassic basalts on Hainan Island. The aims were to (1) analyze the formation age of the basalts, (2) reveal the petrogenesis and tectonic background of the basalts, and (3) discuss the tectonic evolution of the South China Block during the Late Permian–Early Triassic period.

2. Geological Background and Petrography

2.1. Geological Background

Hainan Island is located on the northwestern side of the South China Sea (Figure 1a). In terms of tectonic position, it is located at the junction of the Indochina Block, South China Block, and Pacific (Philippine) Plate, representing an overlapping area of the Paleo-Tethys and Paleo-Pacific tectonic domains. The academic community generally considers Hainan Island to be part of the South China Block [17]. However, some studies have also suggested that Hainan Island has geotectonic affinity with the Indochina Block [12,14]. Within Hainan Island, a series of SW-trending faults have developed, including the Wangwu-Wenjiao, Changjiang-Qionghai, Jianfeng-Diaoluo, and Jiusuo-Lingshui faults (Figure 1b) [18].

The stratigraphy of Hainan Island mainly consists of Cambrian quartz sandstone, siliceous rocks, carbonate rocks, Ordovician carbonate rocks, shale, siltstone, phyllite, carbonaceous slate interlayered with volcanic rocks, and Silurian clastic rocks, limestone, slate, and shallow-sea sandstone. The Mesozoic–Cenozoic strata consist of Lower Triassic coarse clastic rocks, mud shale, and Cretaceous coarse clastic rocks, mudstone, and shale interlayered with volcanic rocks, and Paleogene and Neogene terrestrial sedimentary rocks, volcanic rocks, and marine sedimentary rocks. In addition, a small number of Mesoproterozoic strata (such as the Baoban Group) and Neoproterozoic strata (such as the Shilu Group) outcrop on the island. The Baoban Group underwent regional metamorphism from high greenschist to high amphibolite facies, including the lower Gezhecun Group, which is mainly composed of plagioclase gneiss, and the upper Ewenling Group, which is composed of flysch-like sedimentary assemblages. The Shilu Group consists mainly of a volcanic-sedimentary-carbonate sequence [19,20].

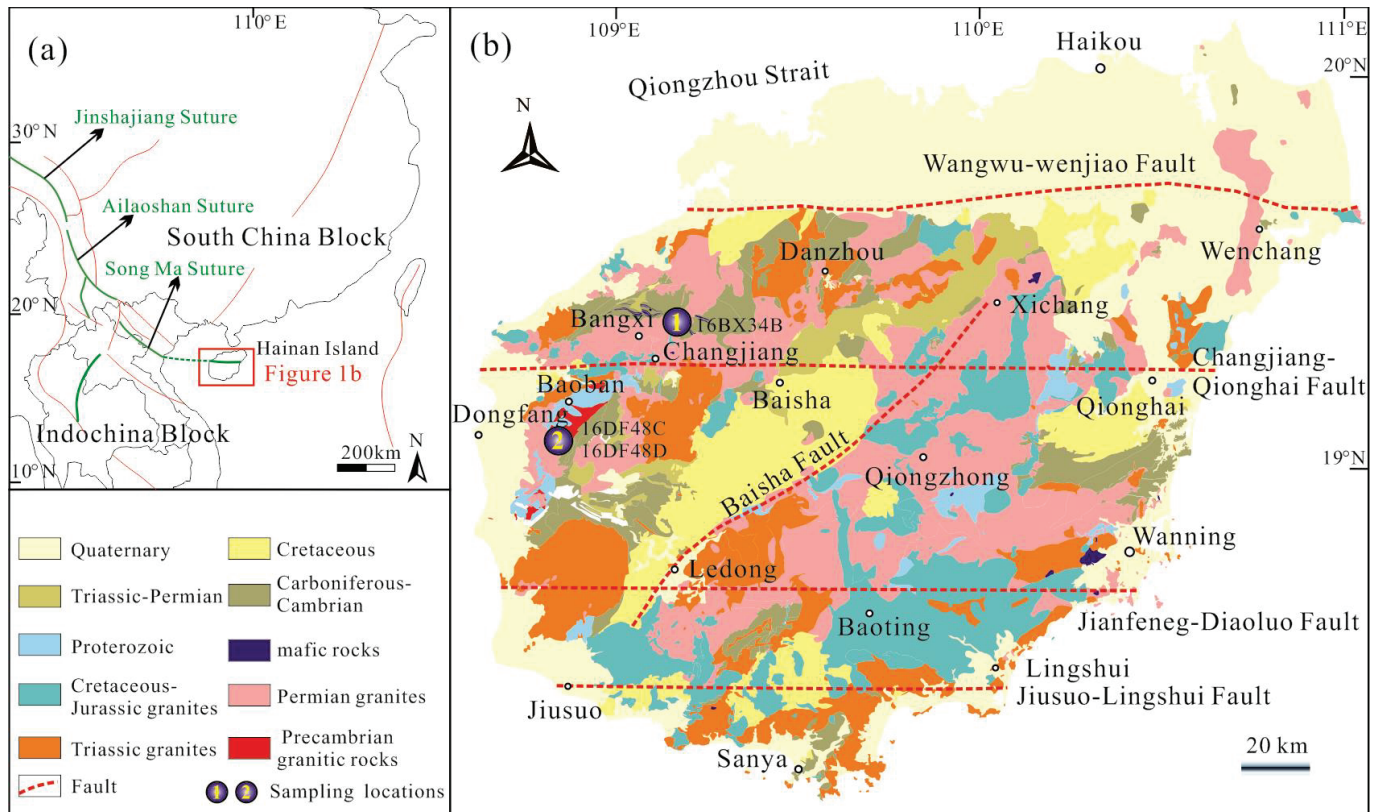


Figure 1. (a) Tectonic outline of Southeast Asia, and (b) regional geological map of Hainan Island.

Hainan Island is characterized by intense magmatic activity, with granite being the most widely distributed rock type, covering approximately 40% of the island's area (Figure 1b) [21–24]. In addition, some Mesoproterozoic metabasic rocks, Late Paleozoic to Early Mesozoic basalts, gabbros, diorites, and Cenozoic basalts outcrop along the Changjiang-Qionghai Fault Zone [22,25].

2.2. Sampling and Petrography

In this study, two groups of basalts were identified in the western part of Hainan Island, specifically in the Bangxi area along the north of the Changjiang-Qionghai Fault Zone (Group 1) and in the Dongfang area to the south of the fault zone (Group 2). Group 1 basalt samples interbedded with granite in the Ordovician Nanbigou Formation present a gray to dark gray color, porphyritic texture, and massive structure (Figure 2a,d). The main minerals include plagioclase and pyroxene, with plagioclase predominantly occurring as short prismatic crystals, most of which underwent saussuritization. The matrix contained randomly distributed tabular plagioclase filled with fine-grained pyroxene and magnetite, forming an intergranular texture (Figure 2g,j). Accessory minerals included zircon, apatite, and magnetite. Group 2 basalts outcrop within the epizonal metamorphic rock series, interlayered between phyllite and metamorphic sandstone, presenting a light gray color, porphyritic texture, and massive structure (Figure 2b,c,e,f). The main minerals are plagioclase, pyroxene, and amphibole, with plagioclase predominantly occurring as prismatic to long-prismatic crystals and pyroxene as short prismatic crystals, uniformly distributed in the fine-grained matrix, displaying an intergranular texture. The matrix consists of volcanic glass and microcrystals of amphibole and plagioclase, with accessory minerals including apatite, zircon, and magnetite (Figure 2h,i,k,l).

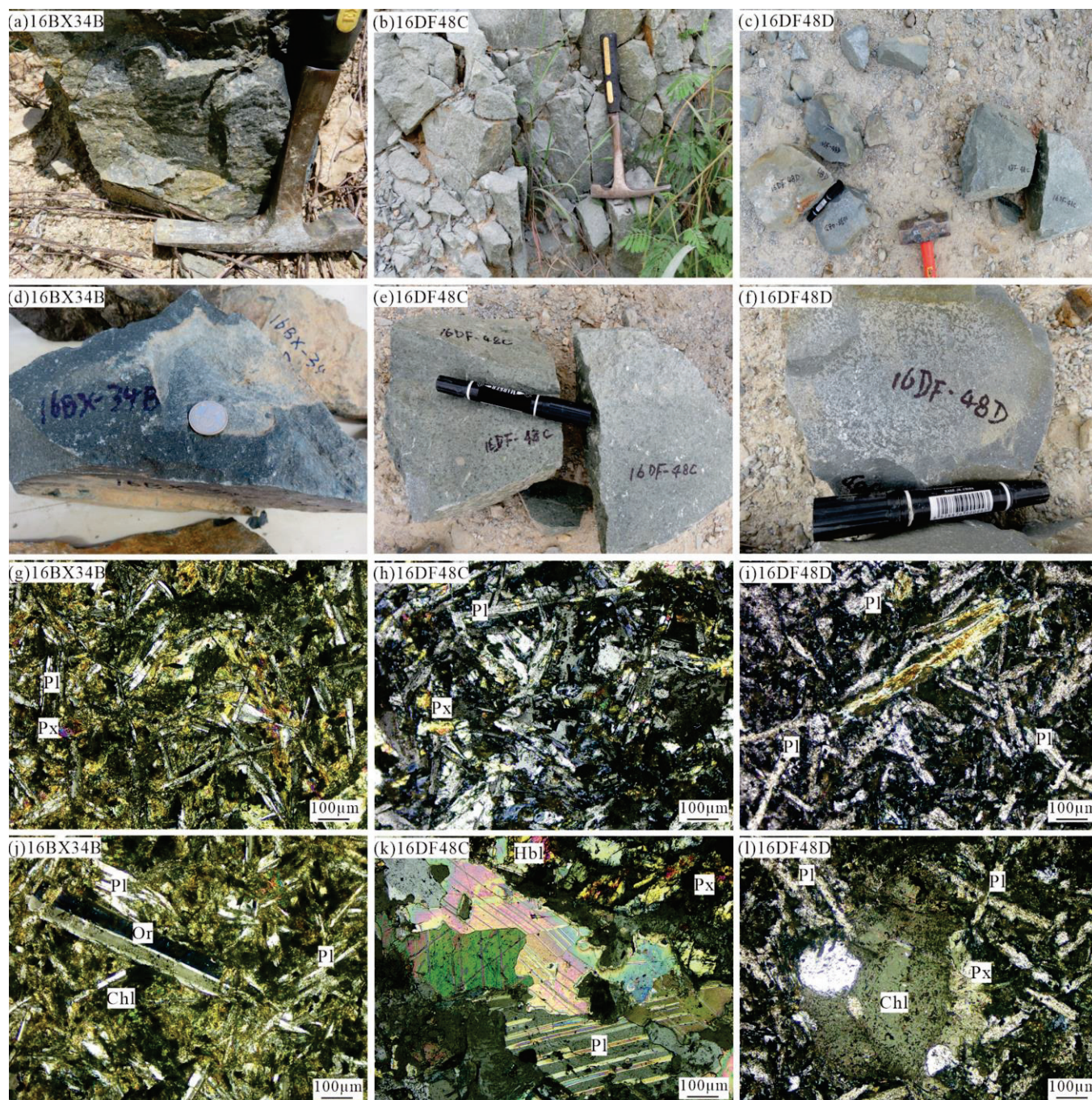


Figure 2. Basalt samples (a–f) and microscopic images (g–l) from the Bangxi and Dongfang areas of Hainan Island; (a–c) massive texture; (d–f) porphyritic basalt with uniformly distributed dark phenocrysts; (g–i) intergranular texture with randomly distributed plagioclase microlites in the matrix; (j) Carlsbad twinning of orthoclase; (k) polysynthetic twinning in plagioclase; (l) alteration and saussuritization of garnet. Pl—plagioclase; Px—pyroxene; Chl—chlorite; Hbl—hornblende; Or—orthoclase.

3. Analytical Methods

3.1. Analysis and Testing of Major, Trace, and Rare Earth Elements

We completed the major, trace, and rare earth element testing at the Guangxi Key Laboratory of Hidden Metallic Ore Deposits Exploration, Guilin University of Technology (GUT), and all were conducted in a pollution-free environment. The test of the major oxide was completed by using X-ray fluorescence spectroscopy (XRF), with a precision of better

than 5%. The analysis of the trace and rare earth elements is carried out using the acid dissolution method and tested using an inductively coupled plasma mass spectrometer (ICP-MS), with an analysis precision generally better than 5%.

3.2. Geochronological Analysis

The selection of zircon and baddeleyite was conducted using conventional heavy liquid and magnetic techniques. Zircon and baddeleyite with large grains and perfect crystallization were selected under a binocular microscope. The picked zircon and baddeleyite grains, together with the standard sample (Temora), were mounted in epoxy resin. Subsequently, it was polished to expose the center of the zircon and baddeleyite.

The photography of transmitted light, reflected light, cathodoluminescence (CL) images, and U-Pb geochronology testing of zircon and baddeleyite were completed at the Guangxi Key Laboratory of Hidden Metallic Ore Deposits Exploration, GUT. The CL image was captured using an electron microprobe. By observing the CL image of zircon and baddeleyite, the internal structural and crystal morphology characteristics can be identified, providing a basis for selecting age testing points and determining the genetic type of zircon.

Zircon and baddeleyite U-Pb isotope dating analysis was conducted using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The testing was conducted using the NWR-193 laser ablation sampling system from ESI (Elemental Scientific, Inc., Omaha, NA, USA) and the 7500 laser ablation inductively coupled plasma mass spectrometry from Agilent (Agilent Technologies, Santa Clara, CA, USA). The laser spot diameter used in this experiment is 32 μm . The calculation of zircon and baddeleyite age uses standard zircon TEM (the standard age is 416.75 ± 0.24 Ma) as the external standard, and the element content uses the artificially synthesized silicate NIST610 from the National Bureau of Standards and Materials of the United States as the external standard. The processing of analytical data, U-Th-Pb isotope ratios, and age calculations were all performed using ICPMSDataCal 7.2 software, while Andersen was used for the correction of common-Pb. The plotting of the U-Pb age concordia plots and the calculation of average weight used the international standard program Isoplot3, with an analysis and calculation error of 1σ ; the confidence level of the weighted average age is 95%.

3.3. Zircon and Baddeleyite Hf Isotope Analysis

The Hf isotopic analysis of zircons was conducted at the Guangxi Key Laboratory of Hidden Metallic Ore Deposits Exploration, GUT. Zircon and baddeleyite grains that had undergone U-Pb isotopic dating were selected for Hf isotopic analysis, with measurement points positioned as close as possible to the U-Pb testing points or at symmetrical positions within the same growth ring or in larger zircon and baddeleyite grains. The analysis was performed using a laser ablation multi-collector inductively coupled plasma mass spectrometer (LA-MS-ICP-MS) and a resolution M-50 laser ablation system, with a laser ablation spot diameter of 44 μm . The specific experimental procedures followed those described by Griffin et al. (2002) and Wu et al. (2006) [26,27]. The calculation of ϵ_{Hf} used the ^{176}Lu decay constant of $1.867 \times 10^{-10}/\text{a}$ [28]. For the calculation of $\epsilon_{\text{Hf}}(t)$ and Hf model ages, the $^{176}\text{Hf}/^{177}\text{Hf}$ ratios for chondritic and depleted mantle were adopted as 0.282772 [29] and 0.28325 [26], respectively. For the calculation of the single-stage Hf model age (t_{DM1}), the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio for the depleted mantle was 0.28325, and the $^{176}\text{Lu}/^{177}\text{Hf}$ ratio was 0.0384. For the two-stage model age calculation, the average crustal $^{176}\text{Lu}/^{177}\text{Hf}$ ratio was 0.015, and the f_{cc} was -0.55 [26].

4. Results

4.1. Zircon and Baddeleyite Geochronology

The U-Pb dating results of zircon and baddeleyite grains from Group 1 and 2 basalts are presented in Table 1. The zircon grains are light brown to brown, subhedral to euhedral, prismatic, and semi-transparent to transparent, with a length of 40–120 μm . The majority of the zircons are morphologically intact, with significant oscillatory zoning developed within the crystal interiors (Figure 3), and their Th/U ratios are generally >0.1 (Table 1), which is consistent with the typical characteristics of magmatic zircons [30,31]. The baddeleyite grains are dark gray and prismatic, with a length of 30–100 μm (Figure 3a).

Table 1. LA-ICP-MS zircon and baddeleyite U-Pb isotopic dating results of the basalts from the Bangxi-Dongfang in Hainan Island.

NO.	Th/U	Isotope Ratio						Age (Ma)					
		²⁰⁷ Pb/ ²⁰⁶ Pb	1σ	²⁰⁷ Pb/ ²³⁵ U	1σ	²⁰⁶ Pb/ ²³⁸ U	1σ	²⁰⁷ Pb/ ²⁰⁶ Pb	1σ	²⁰⁷ Pb/ ²³⁵ U	1σ	²⁰⁶ Pb/ ²³⁸ U	1σ
Sample 16BX34B, baddeleyite													
1	3.41	0.0512	0.0035	0.2817	0.0182	0.0401	0.0007	250	157	252	14	254	4
2	1.07	0.0513	0.0039	0.2862	0.0209	0.0404	0.0009	257	174	256	16	255	6
3	6.55	0.0508	0.0016	0.2849	0.0094	0.0406	0.0004	235	69	255	7	256	2
4	13.13	0.0520	0.0029	0.2895	0.0158	0.0406	0.0006	287	128	258	12	257	4
5	10.79	0.0515	0.0014	0.2861	0.0078	0.0403	0.0004	265	56	255	6	255	2
6	8.81	0.0515	0.0020	0.2883	0.0133	0.0404	0.0008	265	89	257	10	255	5
Sample 16BX34B, zircon													
1	1.50	0.0501	0.0030	0.2909	0.0159	0.0406	0.0008	198	139	259	13	257	5
2	3.91	0.0627	0.0025	0.1211	0.0048	0.0141	0.0002	698	88	116	4	90	1
3	5.20	0.0632	0.0051	0.1322	0.0105	0.0147	0.0002	715	138	126	9	94	1
4	3.04	0.0633	0.0084	0.1469	0.0192	0.0168	0.0004	720	290	139	17	107	3
5	0.89	0.0505	0.0009	0.2817	0.0062	0.0403	0.0005	220	36	252	5	255	3
6	5.57	0.0574	0.0044	0.1388	0.0084	0.0154	0.0003	506	203	132	7	98	2
7	5.19	0.0553	0.0060	0.1334	0.0095	0.0151	0.0003	433	242	127	8	97	2
8	6.95	0.0665	0.0080	0.1237	0.0156	0.0137	0.0004	833	254	118	14	88	3
9	2.82	0.0521	0.0013	0.2898	0.0078	0.0401	0.0004	300	56	258	6	254	3
10	8.48	0.0632	0.0077	0.1117	0.0151	0.0128	0.0005	717	259	108	14	82	3
11	5.64	0.0538	0.0014	0.4734	0.0145	0.0634	0.0010	365	59	394	10	396	6
12	8.51	0.0511	0.0022	0.2811	0.0117	0.0405	0.0006	256	98	252	9	256	3
13	18.84	0.0616	0.0098	0.1316	0.0211	0.0154	0.0006	661	344	126	19	99	4
14	17.05	0.0551	0.0057	0.1563	0.0120	0.0171	0.0004	417	233	147	11	109	3
15	20.03	0.0677	0.0078	0.1280	0.0114	0.0141	0.0004	861	243	122	10	91	2
16	20.39	0.0622	0.0123	0.1273	0.0258	0.0146	0.0006	680	432	122	23	94	4
17	25.85	0.0600	0.0050	0.3336	0.0282	0.0405	0.0014	606	181	292	21	256	9
18	27.27	0.0653	0.0030	0.1296	0.0062	0.0144	0.0002	783	95	124	6	92	1
19	22.46	0.0657	0.0038	0.1471	0.0089	0.0159	0.0002	798	92	139	8	102	1
20	42.37	0.0651	0.0031	0.1376	0.0062	0.0149	0.0002	789	100	131	6	95	1
21	24.05	0.0672	0.0079	0.1233	0.0146	0.0135	0.0006	843	241	118	13	86	4
22	6.28	0.0608	0.0023	0.5361	0.0292	0.0633	0.0020	632	86	436	19	395	12
Sample 16DF48C, zircon													
1	0.82	0.0530	0.0040	0.1360	0.0071	0.0149	0.0003	332	175	129	6	95	2
2	0.85	0.0630	0.0035	0.1076	0.0062	0.0124	0.0003	706	119	104	6	79	2
3	0.03	0.0531	0.0013	0.2804	0.0074	0.0383	0.0004	332	57	251	6	242	3
4	0.90	0.0492	0.0064	0.2015	0.0109	0.0179	0.0005	167	272	186	9	114	3
5	0.16	0.0599	0.0054	0.6966	0.0635	0.0841	0.0021	598	196	537	38	520	13
6	1.14	0.0654	0.0029	0.1126	0.0047	0.0125	0.0002	787	88	108	4	80	1
7	0.87	0.0529	0.0021	0.2800	0.0112	0.0382	0.0004	324	89	251	9	242	3
8	0.20	0.0492	0.0017	0.2561	0.0093	0.0378	0.0006	154	80	231	8	239	3
9	0.02	0.0515	0.0018	0.2695	0.0099	0.0378	0.0004	265	77	242	8	239	3
10	0.02	0.0514	0.0010	0.2713	0.0055	0.0382	0.0004	257	43	244	4	242	2
11	0.09	0.0736	0.0042	0.6267	0.0382	0.0614	0.0010	1031	110	494	24	384	11
12	0.27	0.0494	0.0039	0.2546	0.0174	0.0378	0.0009	165	174	230	14	239	5
13	0.09	0.0520	0.0009	0.2749	0.0055	0.0383	0.0004	283	41	247	4	242	2
14	0.03	0.0728	0.0042	0.3834	0.0217	0.0381	0.0008	1009	117	330	16	241	14
15	0.81	0.0519	0.0012	0.2712	0.0075	0.0378	0.0006	280	52	244	6	239	4
16	0.12	0.0526	0.0014	0.2743	0.0075	0.0378	0.0004	309	59	246	6	239	2
17	0.17	0.0856	0.0017	2.5732	0.0566	0.2173	0.0024	1329	34	1293	16	1268	17
18	0.36	0.0507	0.0013	0.2664	0.0066	0.0380	0.0004	228	57	240	5	240	2
19	0.55	0.0931	0.0021	3.2022	0.0720	0.2489	0.0027	1500	42	1458	17	1433	14
20	0.19	0.0937	0.0040	3.4848	0.1380	0.2704	0.0067	1502	82	1524	31	1543	34
Sample 16DF48D, zircon													
1	1.98	0.0543	0.0058	0.4464	0.0258	0.0379	0.0011	383	244	375	18	240	7
2	1.49	0.0522	0.0092	0.4051	0.0370	0.0383	0.0013	295	359	345	27	243	8
3	1.59	0.0477	0.0066	0.3166	0.0303	0.0376	0.0012	87	313	279	23	238	8
4	0.20	0.0488	0.0044	0.2497	0.0214	0.0376	0.0010	139	200	226	17	238	6
5	1.76	0.0489	0.0068	0.4024	0.0265	0.0379	0.0013	143	296	343	19	240	8
6	0.42	0.0556	0.0027	0.2873	0.0141	0.0379	0.0008	435	106	256	11	240	5
7	0.29	0.0551	0.0018	0.4574	0.0150	0.0608	0.0006	417	74	382	10	381	4
8	2.02	0.0543	0.0101	0.3690	0.0408	0.0384	0.0023	383	370	319	30	243	14
9	0.29	0.0487	0.0046	0.1882	0.0116	0.0172	0.0004	200	139	175	10	110	3
10	1.04	0.0547	0.0043	0.3616	0.0177	0.0382	0.0007	467	176	313	13	242	4
11	1.34	0.0573	0.0119	0.3790	0.0371	0.0388	0.0016	506	400	326	27	245	10
12	1.78	0.0513	0.0206	0.3710	0.0805	0.0377	0.0022	257	726	320	60	239	14
13	0.25	0.0537	0.0021	0.4469	0.0205	0.0602	0.0012	367	95	375	14	377	7
14	1.27	0.0564	0.0042	0.3925	0.0188	0.0381	0.0007	478	164	336	14	241	4
15	1.23	0.0523	0.0091	0.3364	0.0390	0.0385	0.0015	298	356	294	30	244	9
16	1.29	0.0473	0.0042	0.3502	0.0190	0.0377	0.0008	65	200	305	14	239	5
17	0.84	0.0545	0.0059	0.1307	0.0109	0.0159	0.0004	394	243	125	10	102	3
18	1.33	0.0931	0.0296	0.3781	0.0739	0.0361	0.0038	1500	637	326	54	228	23

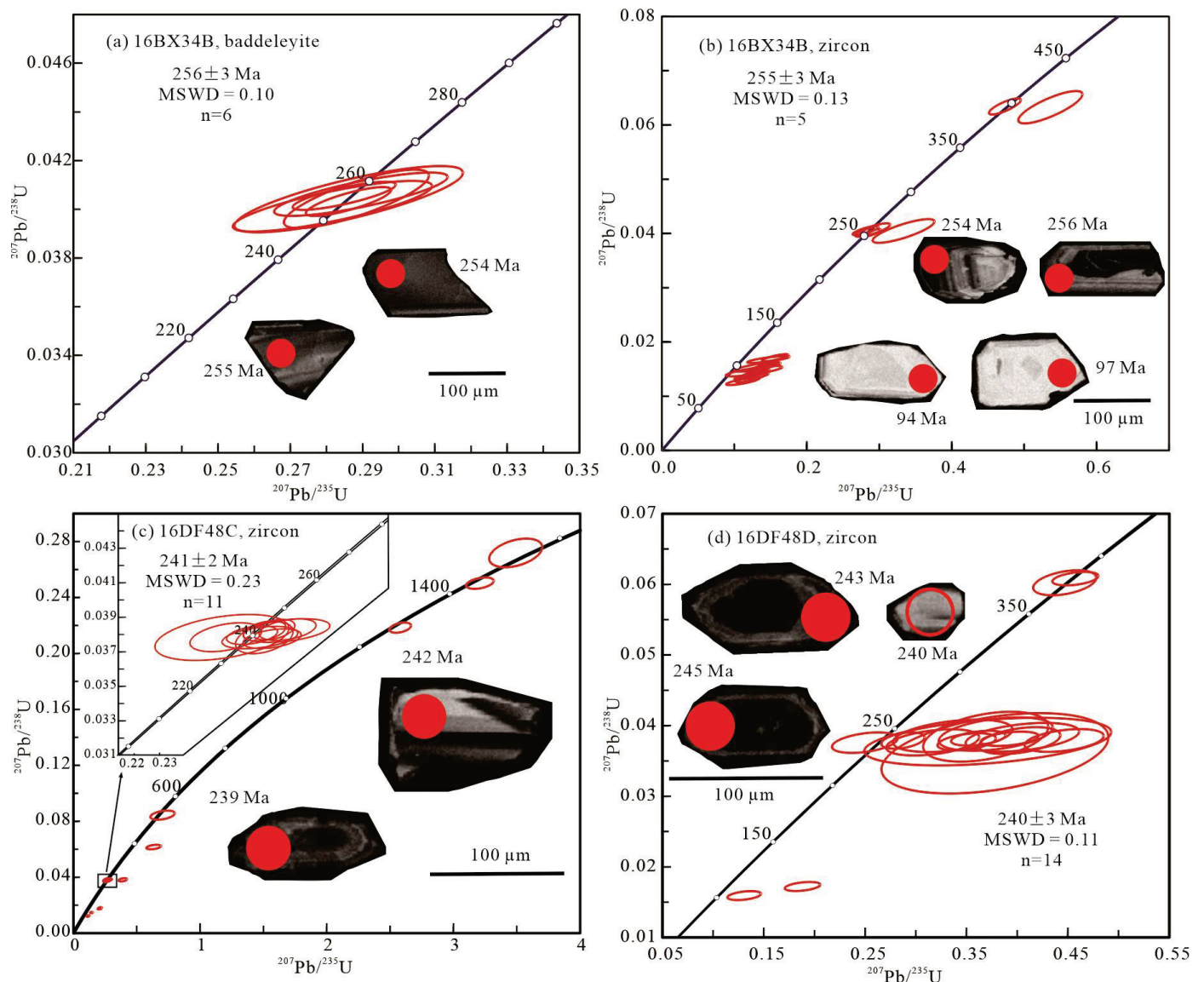


Figure 3. Concordia diagrams of the LA-ICP-MS zircon and baddeleyite analyses and representative cathodoluminescence (CL) images of the Late Permian to Early Triassic basalts from Hainan Island. (a) 16BX34B, baddeleyite; (b) 16BX34B, zircon; (c) 16DF48C, zircon; (d) 16DF48D, zircon.

Group 1: Six baddeleyite grains and twenty-two zircon grains were obtained from basalt sample 16BX34B. The results showed that the Th/U ratios of the six baddeleyite grains are 1.07–13.13 (Table 1). They yielded a coherent group with a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age of 256 ± 3 Ma (MSWD = 0.10) (Figure 3a), interpreted to represent the eruption age of the sample. The Th/U ratios of the twenty-two zircon grains are mainly 0.89–25.85 (Table 1). Five of the grains had $^{206}\text{Pb}/^{238}\text{U}$ ages of 257–254 Ma with a weighted mean age of 255 ± 3 Ma (MSWD = 0.13) (Figure 3b), representing its formation age. A few ~95 Ma zircons were obtained, and they likely reflect a regional metamorphic thermal event during the Late Cretaceous, as evidenced by their bright morphology (Figure 3b). Some of them showed high Th/U ratios (>20), similar to zircon modified by fluid [30,32].

Group 2: Twenty zircons from sample 16DF48C were analyzed. Their Th/U ratios are mainly 0.02–1.14 (Table 1). Eleven of the spots yielded a coherent group with a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age of 241 ± 2 Ma (MSWD = 0.23) (Figure 3c), interpreted to represent the eruption age of the sample. Eighteen grains from sample 16DF48D were analyzed. Their Th/U ratios are 0.20–2.02 (Table 1). Fourteen of the grains had $^{206}\text{Pb}/^{238}\text{U}$ ages

of 245–228 Ma with a weighted mean age of 240 ± 3 Ma (MSWD = 0.11) (Figure 3d), representing its formation age.

4.2. Zircon and Baddeleyite Hf Isotopes

Baddeleyite from the Group 1 basalt samples had $^{176}\text{Lu}/^{177}\text{Hf}$ values of 0.005814–0.043853 and $^{176}\text{Hf}/^{177}\text{Hf}$ values of 0.282425–0.282580 (Table 2). Their $\varepsilon_{\text{Hf}}(t)$ values (t is the formation age based on $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age, i.e., $t = 256$ Ma) were -10.56 to -4.70 with two-stage model age (t_{DM2}) of 1579–1291 Ma (Figure 4). Zircon from the Group 1 basalt samples had $^{176}\text{Lu}/^{177}\text{Hf}$ values of 0.016649–0.052749 and $^{176}\text{Hf}/^{177}\text{Hf}$ values of 0.282432–0.282525 (Table 2). Their $\varepsilon_{\text{Hf}}(t)$ values (t is the formation age based on $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age, i.e., $t = 255$ Ma) were -14.94 to -6.95 with a two-stage model age (t_{DM2}) of 1794–1402 Ma (Figure 4).

Table 2. Analyzed results of zircon and baddeleyite in situ Hf isotopic compositions of the basalts from the Bangxi-Dongfang in Hainan Island.

No.	$^{176}\text{Hf}/^{177}\text{Hf}$	2 σ	$^{176}\text{Lu}/^{177}\text{Hf}$	2 σ	$^{176}\text{Yb}/^{177}\text{Hf}$	2 σ	Age/Ma	$\varepsilon_{\text{Hf}}(t)$	2 σ	T_{DM2}/Ma
Sample 16BX34B, baddeleyite										
1	0.282575	0.000020	0.035205	0.001083	0.001151	0.299921	254	−7.32	0.71	1420
2	0.282425	0.000019	0.023103	0.000796	0.001289	0.458691	255	−10.56	0.67	1579
3	0.282486	0.000024	0.029539	0.001022	0.001062	0.293931	256	−9.49	0.84	1527
4	0.282547	0.000024	0.022946	0.000760	0.000877	0.325695	257	−6.25	0.83	1367
5	0.282580	0.000025	0.043853	0.001545	0.001499	0.274112	255	−8.57	0.87	1482
6	0.282508	0.000025	0.005814	0.000239	0.000256	0.302946	255	−4.70	0.87	1291
Sample 16BX34B, zircon										
1	0.282525	0.000025	0.022620	0.000714	0.000703	0.276865	257	−6.95	0.87	1402
5	0.282432	0.000025	0.038154	0.001304	0.001527	0.331220	255	−12.85	0.86	1692
6	0.282606	0.000024	0.015710	0.000550	0.000531	0.273169	98	−2.91	0.85	1202
9	0.282443	0.000021	0.052749	0.001865	0.002204	0.333836	254	−14.94	0.74	1794
10	0.282632	0.000022	0.022198	0.000921	0.001133	0.347385	82	−3.09	0.76	1211
12	0.282443	0.000022	0.016649	0.000574	0.000624	0.307513	256	−8.85	0.76	1495
13	0.282674	0.000027	0.025916	0.000842	0.000834	0.279887	99	−2.23	0.93	1169
16	0.282598	0.000025	0.026890	0.000955	0.000878	0.258730	94	−5.10	0.89	1310
Sample 16DF48C, zircon										
1	0.282635	0.000036	0.001830	0.000079	0.060482	0.002213	95	0.12	1.27	1040
2	0.282633	0.000029	0.001537	0.000009	0.053666	0.000268	79	0.12	1.03	1040
3	0.282653	0.000028	0.000528	0.000007	0.019168	0.000279	242	0.99	0.98	997
8	0.282546	0.000028	0.000619	0.000013	0.021246	0.000363	239	−2.82	0.97	1186
9	0.282685	0.000028	0.001785	0.000062	0.044342	0.001863	239	1.92	0.97	950
10	0.282716	0.000026	0.001748	0.000008	0.051723	0.000243	242	3.00	0.92	896
13	0.282768	0.000020	0.002392	0.000065	0.055243	0.001746	242	4.74	0.70	810
15	0.282588	0.000043	0.002559	0.000020	0.056763	0.000656	239	−1.63	1.50	1126
16	0.282620	0.000034	0.000337	0.000033	0.011051	0.000932	239	−0.16	1.21	1054
17	0.282121	0.000022	0.001179	0.000062	0.029418	0.001299	1329	−17.96	0.77	1929
18	0.282716	0.000042	0.001719	0.000069	0.042785	0.002074	240	3.02	1.48	896

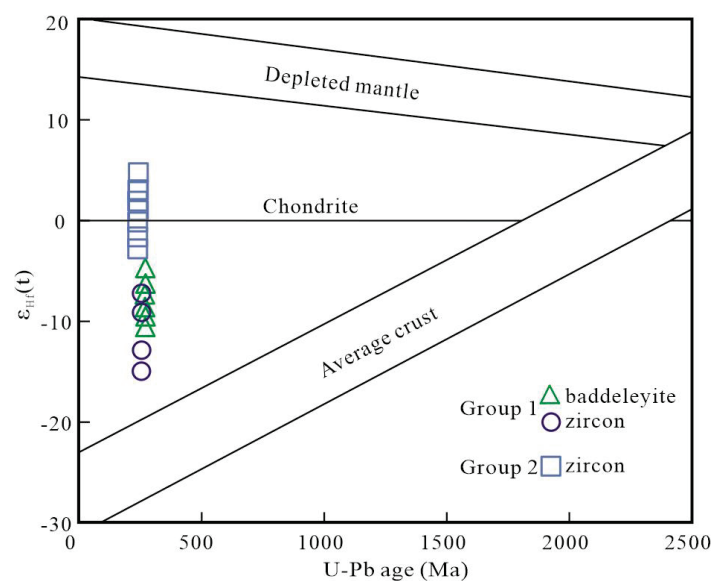


Figure 4. Plot of zircon and baddeleyite U-Pb age (Ma) versus $\varepsilon_{\text{Hf}}(t)$ of the Late Permian to Early Triassic basalts from Hainan Island.

The Group 2 basalt samples had $^{176}\text{Lu}/^{177}\text{Hf}$ ratios of 0.000337–0.002559, with the majority being <0.002, indicating an extremely low accumulation of radiogenic Hf in the zircons after their formation. Their $^{176}\text{Hf}/^{177}\text{Hf}$ ratios were 0.282121–0.282768. The $\varepsilon_{\text{Hf}}(t)$ values (t is the formation age based on $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age, i.e., $t = 240$ Ma) were -2.82 to $+4.74$ (Figure 4), with a two-stage model age (t_{DM2}) of 1186–810 Ma.

4.3. Major and Trace Elements

The chemical composition data of the Late Permian–Early Triassic basalt samples are presented in Table 3. The Group 1 samples were similar to those of the sub-alkaline basalts (Figure 5). They have SiO_2 contents of 50.50%–51.05% (average = 50.83%), MgO contents of 5.72%–5.77% (average = 5.76%), $\text{Fe}_2\text{O}_3^{\text{T}}$ contents of 11.47%–11.73% (average = 11.66%), TiO_2 contents of 1.43%–1.47% (average = 1.45%), Al_2O_3 contents of 15.87%–16.14% (average = 16.00%), total alkali ($\text{K}_2\text{O} + \text{Na}_2\text{O}$) contents of 4.90%–5.01% (average = 4.95%), $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios of 0.76–0.82 (average = 0.80), Ni contents of 25.67–28.42 ppm (average = 27.36 ppm), Cr contents of 40.0–48.5 ppm (average = 44.2 ppm), and $\text{Mg}^\#$ values of 53–54 (average = 54).

Table 3. Major elements (in wt.%), trace elements, and REEs (in ppm) compositions of the basalts from the Bangxi-Dongfang in Hainan Island.

Sample	Group1					Group2				
	16BX34B	16BX34B1	16BX34B2	16BX34B3	16DF48C	16DF48C1	16DF48C2	16DF48C3	16DF48D	16DF48D1
SiO_2	51.05	50.81	50.97	50.50	52.48	52.73	52.84	52.73	55.49	55.31
TiO_2	1.43	1.47	1.47	1.44	1.04	1.10	1.10	1.10	1.44	1.52
Al_2O_3	16.14	15.96	16.02	15.87	15.60	15.60	15.66	15.67	15.77	15.71
$\text{Fe}_2\text{O}_3^{\text{T}}$	11.47	11.73	11.69	11.73	8.01	8.43	8.45	8.45	6.84	7.10
MgO	5.72	5.77	5.77	5.77	5.19	5.26	5.27	5.24	3.46	3.60
CaO	7.76	7.83	7.87	7.90	7.37	7.54	7.53	7.53	4.27	4.31
K_2O	2.14	2.23	2.23	2.18	0.78	0.82	0.82	0.82	3.51	3.68
Na_2O	2.80	2.73	2.78	2.71	3.49	3.33	3.36	3.38	4.20	4.01
MnO	0.20	0.20	0.20	0.20	0.11	0.12	0.12	0.12	0.10	0.11
P_2O_5	0.24	0.25	0.25	0.25	0.39	0.39	0.39	0.39	0.70	0.69
LOI	0.94	0.77	0.8	0.71	4.38	4.47	4.48	4.58	3.33	3.41
Total	99.89	99.76	100.05	99.26	98.84	99.78	100.02	100.02	99.11	99.46
$\text{Mg}^\#$	54	53	54	53	60	59	59	59	54	54
V	214	179	192	203	163	126	138	142	135	114
Cr	40.0	43.7	44.8	48.5	150	145	157	160	60	78.1
Ga	22.3	3.43	3.74	3.85	20.8	3.36	3.65	3.77	19	13.5
Rb	267	260	278	291	28.5	25.7	27.8	29.1	113	111
Sr	321	278	295	312	997	833	888	919	657	604
Y	39.7	33.2	36.1	36.8	21.8	17.2	18.7	19.4	26.6	23.1
Zr	241	217	232	244	212	186	203	203	360	359
Nb	9.7	8.97	9.37	9.95	13.8	12.9	14.1	13.9	25.7	27.3
Cs	52.6	51.5	54	56.6	1.02	0.98	1.06	1.06	2.1	2.18
Ba	186	180	197	204	232	214	231	223	1040	999
La	25.7	25.1	25.6	27.3	40.8	36.1	39.7	38.1	64.1	61.1
Ce	55.6	52.9	53.8	58.4	83.9	73.7	81.4	77.3	134	130
Pr	6.48	6.39	6.67	7.04	9.68	8.74	9.48	9.14	14.7	15
Nd	25.4	20.1	20.6	21.8	36.4	26.3	28.1	27.1	54.2	44
Sm	5.81	6.04	6.08	6.47	6.6	6.35	6.84	6.43	9.51	10.3
Eu	1.74	1.6	1.64	1.75	1.83	1.54	1.68	1.58	2.49	2.56
Gd	6.6	5.83	5.89	6.21	5.42	5.04	5.49	5.2	7.3	7.97
Tb	1.05	1.09	1.1	1.15	0.79	0.79	0.87	0.8	1	1.16
Dy	6.77	6.46	6.43	6.85	4.18	3.96	4.4	3.95	5.06	5.31
Ho	1.46	1.36	1.34	1.45	0.86	0.76	0.83	0.77	0.95	0.99
Er	4.13	3.61	3.54	3.86	2.33	1.91	2.08	1.94	2.51	2.42
Tm	0.61	0.61	0.62	0.65	0.31	0.31	0.34	0.31	0.34	0.37
Yb	4.01	3.94	3.98	4.26	1.92	1.99	2.2	1.96	2.03	2.4
Lu	0.58	0.57	0.59	0.63	0.29	0.29	0.32	0.3	0.29	0.35
Hf	5.8	6.13	6.21	6.47	5.4	5.55	6.06	5.42	8.2	10.3
Ta	0.6	0.61	0.58	0.64	0.7	0.81	0.89	0.77	1.3	1.65
Th	7.54	8.65	8.45	8.72	6.89	7.98	8.54	7.56	9.54	12.2
U	1.4	1.5	1.47	1.58	1.45	1.59	1.72	1.48	3.87	5.04
W	4	3.39	3.11	3.65	1	0.5	0.58	0.49	1	0.89
ΣHREE	25.2	23.5	23.5	25.1	16.1	15.1	16.5	15.2	19.5	21
ΣLREE	121	112	114	123	179	153	167	160	279	263
ΣREE	146	136	138	148	195	168	184	175	298	284
δEu	0.86	0.81	0.83	0.83	0.91	0.8	0.81	0.81	0.88	0.83

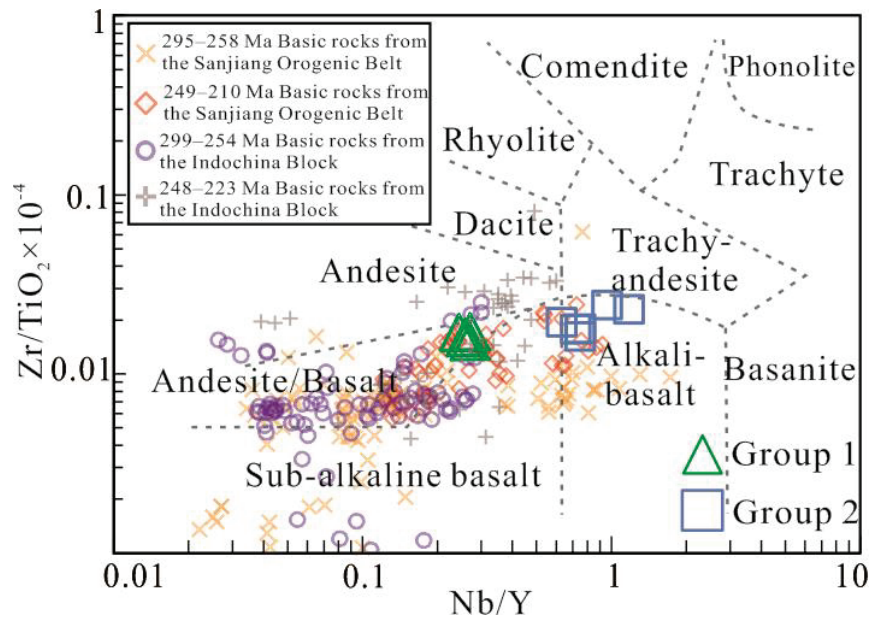


Figure 5. Plot of $\text{Zr}/\text{TiO}_2 \times 10^{-4}$ versus Nb/Y of the Late Permian to Early Triassic basalts from Hainan Island. Data sources are listed in Table S1.

In contrast to Group 1, the Group 2 samples were alkaline basalts (Figure 5). They have higher SiO_2 contents (52.48%–55.49%, average = 53.60%), Al_2O_3 contents (15.60%–15.77%, average = 15.67%), and total alkali ($\text{K}_2\text{O} + \text{Na}_2\text{O}$) contents (4.14%–7.71%, average = 5.37%), but lower MgO contents (3.46%–5.27%, average = 4.67%), $\text{Fe}_2\text{O}_3^{\text{T}}$ contents (6.84%–8.45%, average = 7.88%), TiO_2 contents (1.04%–1.52%, average = 1.22%), and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios (0.22–0.92, average = 0.45). Moreover, their Ni contents (26.84–48.80 ppm, average = 42.24 ppm), Cr contents (60–160.07 ppm, average = 125.06 ppm), and $\text{Mg}^\#$ values (54–60, average = 58) are higher than those of Group 1.

The total rare earth element content (ΣREE) of Group 1 ranged from 136 to 148 ppm (average = 142 ppm). The total light rare earth element (ΣLREE) contents (112–123 ppm) were relatively enriched compared to the total heavy rare earth element (ΣHREE) contents (23.5–25.2 ppm), with $\Sigma\text{LREE}/\Sigma\text{HREE}$ ratios ranging from 1.60 to 1.64. Their $(\text{La}/\text{Yb})_{\text{N}}$ and $(\text{Gd}/\text{Yb})_{\text{N}}$ were 4.56–4.61 and 1.21–1.36, respectively, with a slightly negative Eu anomaly ($\delta\text{Eu} = 0.81$ –0.86). The chondrite-normalized REE pattern diagrams (Figure 6a) exhibited a right-leaning REE-normalized pattern. In the trace element spider diagrams (Figure 6b), there are negative anomalies of Nb, Ta, and Ti, and enrichments in Ba, Th, U, and K. Compared to Group 1, Group 2 had higher ΣREE contents (168–298 ppm), with ΣLREE of 153–279 ppm, ΣHREE of 15.1–21.0 ppm, and $\Sigma\text{LREE}/\Sigma\text{HREE}$ ratios of 10.11–14.32. They had higher $(\text{La}/\text{Yb})_{\text{N}}$ (12.91–22.65) and $(\text{Gd}/\text{Yb})_{\text{N}}$ (2.06–2.97) ratios and a slight negative Eu anomaly ($\delta\text{Eu} = 0.80$ –0.91) (Figure 6c). They showed obviously negative anomalies of Nb, Ta, and Ti and enrichment in Ba, Th, U, and K (Figure 6d).

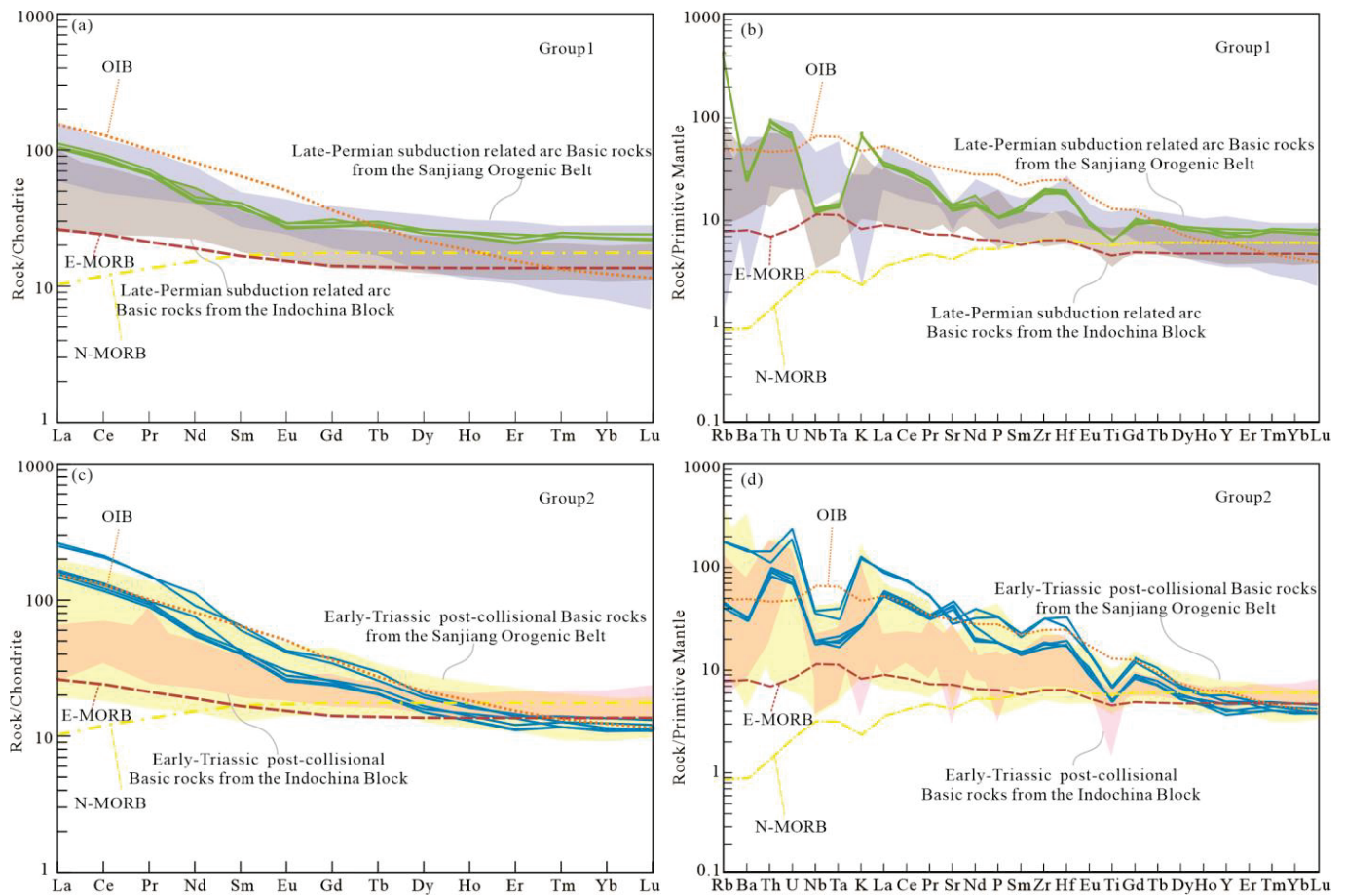


Figure 6. Chondrite-normalized REE pattern (a,c) and primitive mantle-normalized incompatible element spider diagrams (b,d) of the Late Permian to Early Triassic basalts from Hainan Island. Chondrite- and primitive mantle-normalized values are from [33]. The Late-Permian subduction-related mafic rocks from the Sanjiang Orogenic Belt and the Indochina Block are from [34] and [35], respectively; the Early Triassic post-collisional mafic rocks from the Sanjiang Orogenic Belt and the Indochina Block are from [36] and [37], respectively.

5. Discussion

5.1. Petrogenesis of the Basalts

5.1.1. Group 1 Basalts

$\epsilon_{\text{Hf}}(t)$ values are a key indicator to reveal the nature of the magma source area. Specifically, positive $\epsilon_{\text{Hf}}(t)$ values suggest that the magma source area may originate from depleted mantle or newly formed crust derived from depleted mantle, while negative values imply that the source area is primarily enriched mantle or mainly composed of ancient crustal materials [26,38]. The $\epsilon_{\text{Hf}}(t)$ values of baddeleyites and zircons from Group 1 samples range from -10.56 to -4.70 and -14.94 to -6.95 , respectively, located below the chondritic evolution line, indicating an enriched mantle source (Figure 4).

The Nb/La (average = 0.37) and Ce/Pb (average = 9.2) ratios of Group 1 were significantly lower than the typical values for MORB and OIB, which were unaffected by crustal contamination (Nb/La = 1.0, Ce/Pb = 25 ± 5) [39]. The Th/La (average = 0.32) ratios were higher than that of N-MORB (0.05) but lower than that of the crust (0.3) [40]. These characteristics are similar to those of a mantle source modified by slab-derived fluids and melts [41–43]. In terms of trace elements, they are characterized by enrichment in LILEs and LREEs and depletion in Nb, Ta, and Ti (Figure 6a,b), which is consistent with the characteristics of typical arc volcanic rocks and is also similar to the mafic rocks from Hainan Island

that have been modified by subduction-related fluids or melts [22]. Furthermore, Group 1 samples show high Ba/Y ratios but low Nb/Y ratios (Figure 7a), indicating fluid-related enrichment. The plot of Nb/Zr versus Th/Zr (Figure 7b) shows a fluid enrichment trend, suggesting that the mantle source may have experienced metasomatic events caused by fluids derived from the subducting slab.

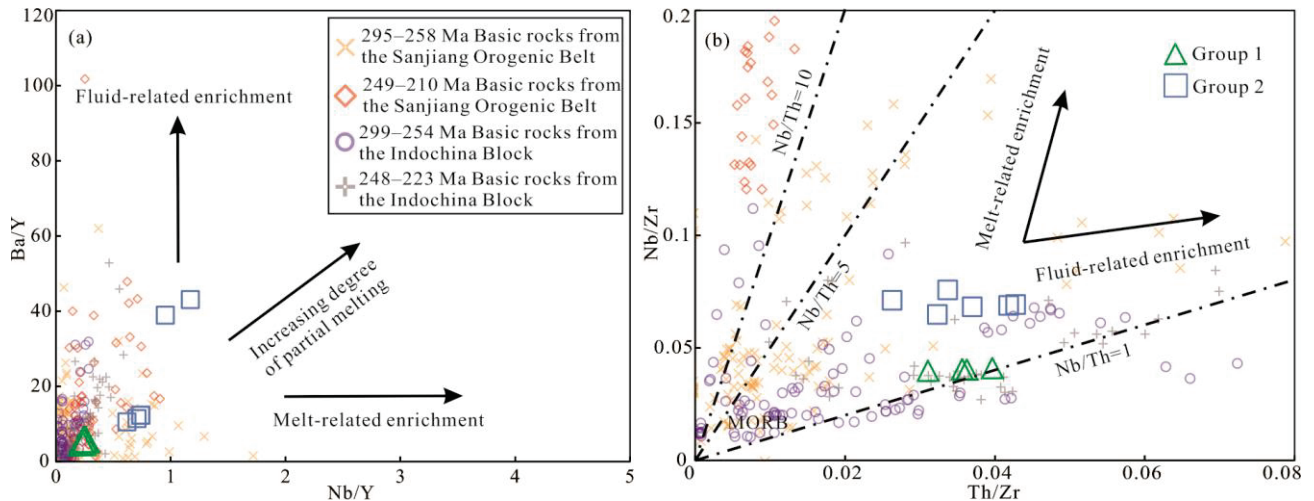


Figure 7. Plots of (a) Ba/Y versus Nb/Y and (b) Nb/Zr versus Th/Zr of the Late Permian to Early Triassic basalts from Hainan Island. Data sources are the same as in Figure 5.

The REE compositions of mafic rocks can reveal the nature of the magma source area and the degree of partial melting. When $(\text{Gd}/\text{Yb})_N < 2$ and $(\text{Tb}/\text{Yb})_N < 1.8$, it indicates that the magma source area is likely derived from spinel lherzolite mantle; conversely, higher ratios suggest that the source area is more likely to be garnet lherzolite mantle [44,45]. The $(\text{Gd}/\text{Yb})_N$ (1.21–1.36) and $(\text{Tb}/\text{Yb})_N$ (1.19–1.26) ratios of Group 1 are less than 2 and 1.8, respectively, indicating that its source area is from the spinel lherzolite mantle. In the plots of Sm/Yb versus Sm and Dy/Yb versus Yb (Figure 8a,b), the Group 1 samples are close to the melting curve of spinel lherzolite, further indicating that the magma source area is spinel lherzolite mantle, with a partial melting degree of approximately 3% to 5%.

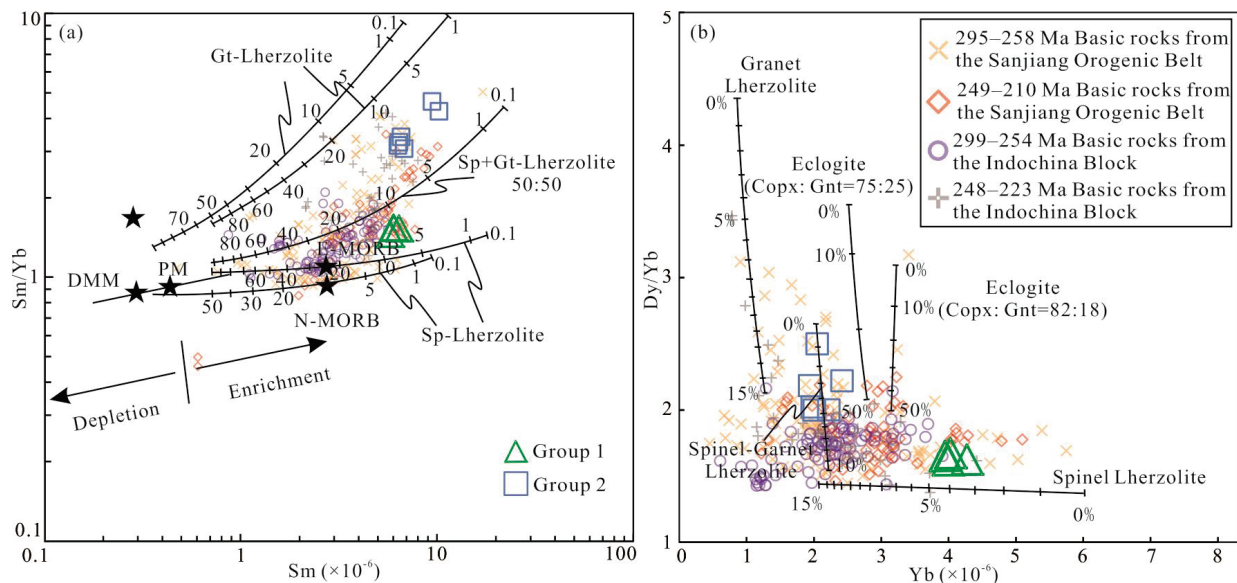


Figure 8. Plots of (a) Sm/Yb versus Sm and (b) Dy/Yb versus Yb of the Late Permian to Early Triassic basalts from Hainan Island. Data sources are the same as in Figure 5.

Additionally, the average $Mg^\#$ of Group 1 is 54, with average Cr and Ni contents of 44.2 ppm and 27.39 ppm, respectively, which are significantly lower than those of the primitive mantle ($Mg^\# = 68\text{--}72$; Cr = 300–500 ppm; Ni = 300–400 ppm) [46]. This indicates that the Group 1 magma underwent fractional crystallization of olivine and pyroxene during its evolution. The weak negative anomalies of Eu and Sr (Figure 6a,b) suggest fractional crystallization of plagioclase during the formation and evolution of the magma [47].

In summary, the source area of the Group 1 samples was enriched mantle. They were derived from the partial melting of the spinel lherzolite mantle and modified by subduction-derived fluids with a certain degree of fractional crystallization.

5.1.2. Group 2 Basalts

Group 2 samples exhibit predominantly positive $\epsilon_{Hf}(t)$ values (Figure 4), indicating that the magma source area was primarily a depleted mantle. The Nb/U (average = 7.9), Nb/La (average = 0.38), and Ce/Pb (average = 5.2) ratios were significantly different from the typical values for MORB and OIB (Nb/U = 47 ± 10 , Nb/La = 1.0, Ce/Pb = 25 ± 5) [39], suggesting that the magma was metasomatized by subduction-derived fluids during its formation. They showed high Ba/Y and low Nb/Y ratios (Figure 7a), indicating fluid-related elemental enrichment. In the Nb/Zr versus Th/Zr diagram (Figure 7b), they are also characterized by fluid enrichment, suggesting that they may have experienced interactions between fluids released from the subducting slab and the mantle wedge. Additionally, their Nb/Ta (average = 17.64) and Zr/Hf (average = 37.12) ratios were similar to that of primitive mantle (Nb/Ta = 17.5 ± 2.0 , Zr/Hf = 36.27 ± 2.0) [48]. However, their Th/Ta (7.34–9.85) ratios are significantly higher than those of the primitive mantle (Th/Ta = 2.3) [49] but similar to that of the continental crust (Th/Ta = 10) [49]. Zircon Hf isotopic data show that some zircons have negative $\epsilon_{Hf}(t)$ values (Figure 4). These data suggest that the mantle source was contaminated with crustal material. In the plots of Sm/Yb versus Sm and Dy/Yb versus Yb (Figure 8a,b), Group 2 samples are located within the distribution range of garnet + spinel lherzolite, indicating their magma source is garnet + spinel lherzolite mantle, with an estimated partial melting degree of 1%–5%.

The average $Mg^\#$ of Group 2 is 58, with average Cr and Ni contents of 125 ppm and 27.2 ppm, respectively, which are significantly lower than those of the primitive mantle ($Mg^\# = 68\text{--}72$; Cr = 300–500 ppm; Ni = 300–400 ppm). This indicates that they underwent a certain degree of fractional crystallization of olivine and pyroxene. The weak negative Eu anomaly (Figure 6c,d) indicates that crystallization of plagioclase occurred during magma evolution.

In conclusion, the source area of Group 2 basalts is a depleted mantle contaminated by crustal materials. It is a product of the partial melting of garnet + spinel lherzolite mantle and has experienced metasomatism due to subduction-derived fluids, with a certain degree of fractional crystallization.

5.2. Tectonic Setting

The Chondrite-normalized REE pattern of Group 1 samples displays a rightward-inclined distribution pattern (Figure 6a,c), with a negative Eu anomaly. On the primitive mantle-normalized incompatible element spider diagrams (Figure 6b,d), they are characterized by enrichment in large ion lithophile elements (LILEs, such as Rb and Ba) and depletion in high field strength elements (HFSEs, such as Th and U), with distinctly negative Nb and Ta anomalies. These characteristics are similar to that of island arc volcanic rocks [50]. Group 1 samples had low Nb/Zr (average = 0.04) and Ta/Hf (average = 0.09) ratios, and high Th/Ta ratios (average = 13.7), similar to that of island arc basalts (Nb/Zr < 0.04,

$\text{Ta}/\text{Hf} < 0.1$, $\text{Th}/\text{Ta} > 1.6$) [51,52]. As shown in Figure 9a, Group 1 exhibits characteristics of continental arc basalts (CAB). This evidence indicates that the Group 1 samples were formed in an island arc tectonic setting.

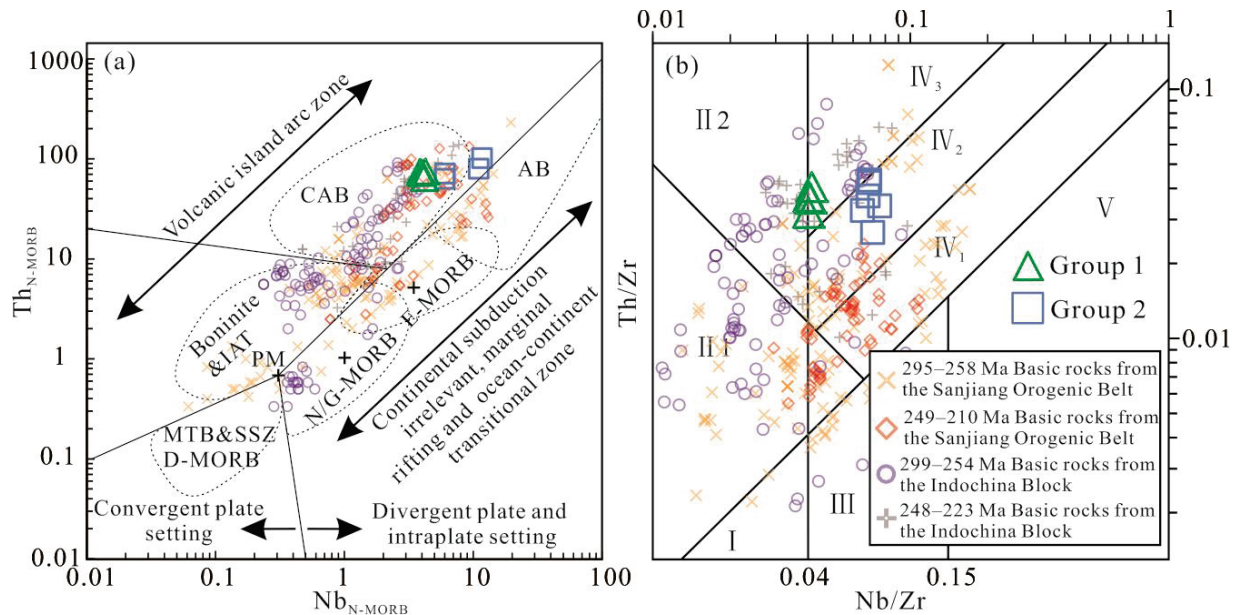


Figure 9. Plots of (a) $\text{Th}_{\text{N-MORB}}$ versus $\text{Nb}_{\text{N-MORB}}$ (N-MORB normalize values are from [33]) and (b) Th/Zr versus Nb/Zr of the Late Permian to Early Triassic basalts from Hainan Island. Abbreviations: AB: alkaline ocean-island basalt; CAB: calc-alkaline basalt; D-MORB: depleted-type MORB; E-MORB: enriched-type MORB; G-MORB: garnet-influenced MORB; N-MORB: normal-type MORB; IAT: island arc tholeiite; MTB: medium-Ti basalt; SSZ: supra-subduction zone; I. N-MORB Zone; II. Plate Convergence Boundaries (II₁. Oceanic Island Arc Basalts, II₂. Continental Margin Arc Basalts); III. Oceanic Plate Interior; IV. Continental Plate Interior (IV₁. Continental Initial Rift and Continental Margin Rift Tholeiitic Basalts, IV₂. Continental Extensional Zone Basalts, IV₃. Continent–Continent Collision Zone Basalts); V. Mantle Plume Basalts. Data sources are the same as in Figure 5.

Group 2 samples generally show geochemical features similar to those of the OIB (Figure 6c,d). Their Nb/Zr ratios (average = 0.07) are similar to those of continental intraplate basalts ($\text{Nb}/\text{Zr} > 0.04$) [51]. Previous studies have shown that typical rift basalts have Th/Ta ratio of 1.6–4, basalts from intra-continental extensional zones (or initial rifts) have Th/Ta ratios greater than 4 (generally 4–10), and basalts from orogenic belts formed by continent–continent collision have Th/Ta ratios greater than 10 [52]. Group 2 samples have Th/Ta ratios (average = 9.0) greater than 4 but less than 10, similar to basalts from intra-continental extensional zones (or initial rifts). In the plot of Th/Zr - Nb/Zr (Figure 9b), Group 2 samples fall within the area of the continental extensional zone (or initial rift). The above evidence indicates that Group 2 basalts formed in a continental intraplate extensional (or initial rift) tectonic setting.

6. Geological Significance

Late Paleozoic to Early Mesozoic igneous rocks are widespread along the Jinshajiang, Ailaoshan, and Song Ma suture zones in the southwestern South China Block (Figure 1a), and their formation is related to subduction-collision events of Paleo-Tethys Ocean, as evidenced by the Carboniferous ophiolites or ophiolitic mélangé in the Jinshajiang, Ailaoshan, and Song Ma areas. These ophiolites or ophiolitic mélangé represent remnants of the Paleo-Tethys Ocean between the South China and Indochina blocks [53–57]. In addition, within the Ailaoshan suture zone, 287 Ma MORB-type basalts and 265 Ma subduction-related

basalts have been identified, indicating that the Ailaoshan area was in an arc setting during the Late Permian [58]. The formation of 252 Ma and 248 Ma granites indicates the closure of the branch ocean basin [59]. In the Jinshajiang suture zone, there are 271 Ma granites [60] and 254–247 Ma tuffs [61], indicating the persistence of arc magmatic activity during the Late Permian to Early Triassic. The identification of 247–246 Ma rhyolites is considered a geological record of the initial collision between the Indochina and Yangtze blocks [62]. The 234–231 Ma granites formed in a post-collisional setting [63]. The development of ca. 275 Ma igneous rocks in the Song Ma suture zone indicates the presence of a branch ocean or back-arc basin of the Paleo-Tethys Ocean [64]. Late Permian (272–253 Ma) calc-alkaline, volcanic-plutonic, and peraluminous granite assemblages reflect the tectonic setting of an active continental margin [65,66]. The formation of the Early Triassic (ca. 250 Ma) S-type granites indicates that the branch ocean or back-arc basin of the Paleo-Tethys Ocean was closed, followed by a collision with the South China Block [67,68].

Previous studies have shown that Hainan Island records a large number of 345–245 Ma magmatic rocks, including basalts, andesites, mafic intrusive rocks, gabbro-diorites, and I-type granites, which are generally considered to have formed in an island arc setting [14,22,25,69–76]. This study identified 255 Ma basalts (Group 1) on Hainan Island that formed in an island arc tectonic setting, as discussed above. The widespread 272–262 Ma I-type granites along the Jiusuo-Lingshui and Changjiang-Qionghai faults were considered to have resulted from arc magmatism caused by the subduction of the Paleo-Tethys oceanic crust [69,75], further supporting an island arc tectonic setting during the Late Paleozoic. In addition, ca. 240 Ma basalts (Group 2), which formed in an intraplate extensional or initial rift tectonic setting, were also identified in this study. It is worth noting that the Carboniferous (ca. 330 Ma) Bangxi-Chenxing ophiolite outcrops in northwestern Hainan Island [14,73] indicate that the Late Paleozoic to Early Mesozoic tectonic evolution of Hainan Island was mainly controlled by the Paleo-Tethys tectonic domain. Taking the above data into consideration, the evolution of Paleo-Tethys recorded on Hainan Island can be summarized as follows. The opening of the Paleo-Tethys Ocean Basin occurred at least earlier than the Late Carboniferous, as evidenced by the ca. 330 Ma Bangxi-Chenxing ophiolite [14,73]. The subduction of the Paleo-Tethys oceanic crust lasted at least in the late Permian, as demonstrated by Group 1 ca. 255 Ma basalts in this study. The initial rift or intra-plate extensional stage occurred in the middle Triassic, as evidenced by Group 2 ca. 240 Ma basalts (this study) and 244–230 Ma A-type granites and bimodal volcanic rocks on the island [22,71,77]. The closure of the Paleo-Tethys Ocean Basin can be inferred at 255–244 Ma.

7. Conclusions

1. Hainan Island recorded two different types of basalts. Group 1 basalts formed at ca. 255 Ma and are sub-alkaline basalts. Their $\varepsilon_{\text{Hf}}(t)$ values of baddeleyites and zircons were -10.56 to -4.70 and -14.94 to -6.95 , respectively. Two samples from Group 2 basalts dated to 241 ± 2 Ma and 240 ± 4 Ma, respectively. They belong to alkaline basalts, and their $\varepsilon_{\text{Hf}}(t)$ values were -2.82 to $+4.74$, with t_{DM2} of 1186–810 Ma.
2. Group 1 basalts were derived from enriched mantle, likely from partial melting of the spinel lherzolite mantle, and modified by subduction-derived fluids, with a certain degree of fractional crystallization. They were formed in an island arc tectonic setting. Group 2 basalts originated from depleted mantle and were contaminated by crustal material. They were likely produced by partial melting of the garnet + spinel lherzolite mantle and were metasomatized by subduction-derived fluids. They likely formed in a continental intraplate extensional (or initial rift) tectonic setting.

3. The formation of the two groups of basalt is related to the evolution of the Paleo-Tethys. Group 1 basalts revealed that subduction of the Paleo-Tethys oceanic crust lasted at least in the late Permian. Group 2 basalts indicate that the initial rift or intra-plate extensional stage occurred during the Middle Triassic.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/min15030293/s1>, Table S1: Tectonic Evolution of the Hainan Island, South China: Geochronological and Geochemical Constraints from Late Permian to Early Triassic Basalts.

Author Contributions: Conceptualization, J.O. and Y.Z.; methodology, G.C., L.Y. and W.L.; software, J.O. and W.L.; validation, Y.Z.; formal analysis, G.C.; investigation, J.O., L.Y. and Y.Z.; resources, Y.Z.; data curation, Y.Z.; writing—original draft preparation, J.O.; writing—review and editing, Y.Z.; visualization, Y.Z.; supervision, Y.Z.; project administration, Y.Z.; funding acquisition, Y.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Grant No. 42372102) and the Guangxi Key R&D Program (Grant No. Guike AB22035045).

Data Availability Statement: The original contributions presented in this study are included in the article/supplementary material. Further inquiries can be directed to the corresponding author(s).

Acknowledgments: We sincerely appreciate the insightful comments and constructive suggestions from the reviewers and editorial team, which have significantly improved the quality of this manuscript.

Conflicts of Interest: The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Metcalfe, I. Permian tectonic framework and palaeogeography of SE Asia. *J. Asian Earth Sci.* **2002**, *20*, 551–566. [CrossRef]
2. Metcalfe, I. Tectonic framework and Phanerozoic evolution of Sundaland. *Gondwana Res.* **2011**, *19*, 3–21. [CrossRef]
3. Metcalfe, I. Gondwana dispersion and Asian accretion: Tectonic and palaeogeographic evolution of eastern Tethys. *J. Asian Earth Sci.* **2013**, *66*, 1–33. [CrossRef]
4. Qian, X.; Feng, Q.L.; Wang, Y.J.; Chonglakmani, C.; Monjai, D. Geochronological and geochemical constraints on the mafic rocks along the Luang Prabang zone: Carboniferous back-arc setting in northwest Laos. *Lithos* **2016**, *245*, 60–75. [CrossRef]
5. Hathaichanok, V.; Keith, C.M.; Sopon, P. The hydrocarbon source potential of Permo-Triassic rocks of the Indochina Block adjacent to the Paleo-Tethys suture in Thailand. *J. Asian Earth Sci.* **2024**, *259*, 105915.
6. Wang, D.; Kang, H.; Chen, Y.L.; Li, D.P.; Hu, X.S.; Yu, T.; Liang, Q.K. Timeframe of eastern Paleo-Tethys closure: Constraint on the Songpan-Ganzi Complex by big data-based multiproxy provenance analysis. *Lithos* **2024**, *466–467*, 107457. [CrossRef]
7. Metcalfe, I. 1996. Gondwanaland dispersion, Asian accretion and evolution of eastern Tethys. *Aust. J. Earth Sci.* **1996**, *43*, 605–623. [CrossRef]
8. Wang, Y.J.; Fan, W.M.; Zhang, G.W.; Zhang, Y.L. Phanerozoic tectonics of the South China Block: Key observations and controversies. *Gondwana Res.* **2013**, *23*, 1273–1305. [CrossRef]
9. Wang, Y.J.; Qian, X.; Cawood, P.A.; Liu, H.C.; Feng, Q.L.; Zhao, G.C.; Zhang, Y.H.; He, H.Y.; Zhang, P.Z. Closure of the East Paleotethyan Ocean and amalgamation of the Eastern Cimmerian and Southeast Asia continental fragments. *Earth-Sci. Rev.* **2018**, *186*, 195–230. [CrossRef]
10. Cui, Y.; Wang, Y.J.; Zhou, R.J.; Wang, Y.; Ubide, T.; Qian, X.; Wang, C.; Wang, X. Spatio-temporal evolution of the Paleo-Tethys in western Yunnan: Insights from mafic rocks in the Lancang tectonic belt. *Lithos* **2024**, *488–489*, 107830. [CrossRef]
11. Qin, Y.; Zhou, Y.; Liu, X.J.; Zhao, Y.S.; Li, Z.L.; Yang, L.Y.; Li, C.; Cai, Y.F. Geochronology and geochemistry of igneous rocks in the Qinfang belt: Implications for spatio-temporal framework of Paleo-Tethys. *Lithos* **2025**, *949–945*, 107900. [CrossRef]
12. Hsu, K.J.; Li, J.L.; Chen, H.H.; Wang, Q.C.; Sun, S.; Şengör, A.M.C. Tectonics of South China: Key to understanding West Pacific geology. *Tectonophysics* **1990**, *183*, 9–39. [CrossRef]
13. Metcalfe, I.; Shergold, H.; Li, Z.X. IGCP 321 Gondwana dispersion and Asian accretion: Fieldwork on Hainan Island. *Episodes* **1993**, *16*, 443–447.

14. Li, X.H.; Zhou, H.W.; Chung, S.L.; Ding, S.J.; Liu, Y.; Lee, C.Y.; Ge, W.C.; Zhang, Y.M.; Zhang, R.J. Geochemical and Sm–Nd isotopic characteristics of metabasites from central Hainan Island, South China and their tectonic significance. *Isl. Arc* **2002**, *11*, 193–205. [CrossRef]
15. Zhang, H.C.; Xu, Y.J.; Cawood, P.A.; Zi, J.W.; Zhou, J.B.; Du, Y.S. Linking the Paleozoic evolution of Hainan Island to Indochina and Australia: Implication for the paleogeography of the eastern Tethys Ocean. *Tectonophysics* **2023**, *858*, 229882. [CrossRef]
16. Song, Q.Q.; Hu, J.; Lei, D.; Li, Z.W.; Tang, R.; Hu, S.B. Provenance evolution of the Fushan Sag (Hainan Island, southern China): Constraints from U–Pb geochronology on detrital zircons. *Mar. Pet. Geol.* **2024**, *168*, 107037. [CrossRef]
17. Li, S.B.; He, H.Y.; Qian, X.; Wang, Y.J.; Zhang, A.M. Carboniferous arc setting in Central Hainan: Geochronological and geochemical evidences on the andesitic and dacitic rocks. *J. Earth Sci.* **2018**, *29*, 265–279. [CrossRef]
18. Zhou, Y.; Sun, S.Y.; Feng, Z.H.; Xu, C.; Cai, Y.F.; Liang, X.Q.; Liu, X.J.; Du, Y.J. A new insight into the eastern extension of the Proto-Tethyan margin of Gondwana by Early Paleozoic volcanic rocks in South China. *Lithos* **2021**, *338–339*, 106328. [CrossRef]
19. Li, Z.X.; Li, X.H.; Li, W.X.; Ding, S.I. Was Cathaysia part of Proterozoic Laurentia?—New data from Hainan Island, south China. *Terra Nova* **2008**, *20*, 154–164. [CrossRef]
20. Yao, W.H.; Li, Z.X.; Li, W.X.; Li, X.H. Proterozoic tectonics of Hainan Island in supercontinent cycles: New insights from geochronological and isotopic results. *Precambrian Res.* **2017**, *290*, 86–100. [CrossRef]
21. Wang, X.F.; Ma, D.Q.; Jiang, D.H. *Geology of Hainan Island: Structural Geology*; Geological Publish House: Beijing, China, 1991.
22. Cao, G.Y.; Li, X.; Xie, G.G.; Zhang, Z.Y.; Wang, L.; Tong, Y. Petrogenesis of late Permian to Middle Triassic magmatic rocks on northern Hainan Island, South China: Implications for crust–mantle interaction and the tectonic evolution of the Paleo-Tethys. *J. Asian Earth Sci.* **2002**, *234*, 105238. [CrossRef]
23. Xie, C.F.; Zhu, J.C.; Ding, S.J.; Zhang, Y.M.; Fu, T.A.; Li, Z.H. Identification of Hercynian shoshonitic intrusive rocks in central Hainan Island and its geotectonic implications. *Chin. Sci. Bull.* **2006**, *51*, 2507–2519. [CrossRef]
24. Zhou, Y.; Liang, X.Q.; Kröner, A.; Cai, Y.F.; Shao, T.B.; Wen, S.N.; Jiang, Y.; Fu, J.G.; Wang, C.; Dong, C.G. Late Cretaceous lithospheric extension in SE China: Constraints from volcanic rocks in Hainan Island. *Lithos* **2015**, *23*, 100–110. [CrossRef]
25. He, H.Y.; Wang, Y.J.; Qian, X.; Zhang, Y.Z. The Bangxi–Chenxing tectonic zone in Hainan Island (South China) as the eastern extension of the Song Ma–Ailaoshan zone: Evidence of late Paleozoic and Triassic igneous rocks. *J. Asian Earth Sci.* **2018**, *164*, 274–291. [CrossRef]
26. Griffin, W.L.; Wang, X.; Jackson, S.E.; Pearson, N.J.; O'Reilly, S.Y.; Xu, X.S.; Zhou, X.M. Zircon chemistry and magma mixing, SE China: In-situ analysis of Hf isotopes, Tonglu and Pingtan igneous complexes. *Lithos* **2002**, *61*, 237–269. [CrossRef]
27. Wu, F.Y.; Yang, Y.H.; Xie, L.W.; Yang, J.H.; Xu, P. Hf isotopic compositions of the standard zircons and baddeleyites used in u–pb geochronology. *Chem. Geol.* **2006**, *234*, 105–126. [CrossRef]
28. Scherer, E.; Munker, C.; Mezger, K. Calibration of the lutetium–hafnium clock. *Science* **2001**, *293*, 683–687. [CrossRef]
29. Blichert, T.J.; Albarède, F. The Lu–Hf isotope geo-chemistry of chondrites and the evolution of the mantle–crust system. *Earth Planet. Sci. Lett.* **1997**, *148*, 243–258. [CrossRef]
30. Hoskin, P.W.O.; Schaltegger, U. The composition of zircon and igneous and metamorphic petrogenesis. *Rev. Mineral. Geochem.* **2003**, *53*, 27–62. [CrossRef]
31. Rubatto, D. Zircon trace element geochemistry: Partitioning with garnet and the link between U–Pb ages and metamorphism. *Chem. Geol.* **2002**, *184*, 123–138. [CrossRef]
32. Tsygankov, A.A.; Khubanov, V.B.; Burmakina, G.N.; Buyantuev, M.D. Periodicity of Endogenic Events of West Transbaikalia and North Mongolia (Eastern Segment of the Central Asian Foldbelt): U–Pb Age of Detrital Zircon from the Present-Day River Sediments. *Stratigr. Geol. Correl.* **2023**, *31*, 355–375. [CrossRef]
33. Sun, S.S.; McDonough, W.F. Chemical and isotopic systematics of oceanic basalts: Implication for mantle composition and processes. *Geol. Soc. Lond. Spec. Publ.* **1989**, *42*, 313–345. [CrossRef]
34. Qian, X.; Feng, Q.L.; Wang, Y.J.; Zhang, Z.B. Geochemical and Geochronological Constraints on the Origin of the Meta-basic Volcanic Rocks in the Tengtaohe Zone, Southeast Yunnan. *Acta Geol. Sin. (Engl. Ed.)* **2016**, *90*, 669–683.
35. Zhang, Y.Z.; Yang, X.; Wang, Y.J.; Qian, X.; Wang, Y.K.; Gou, Q.Y.; Senebottalath, V.; Zhang, A.M. Rifting and subduction records of the Paleo–Tethys in North Laos: Constraints from Late Paleozoic mafic and plagiogranitic magmatism along the Song Ma tectonic zone. *Geol. Soc. Am. Bull.* **2020**, *133*, 212–232. [CrossRef]
36. Wang, Y.J.; Zhang, A.M.; Fan, W.M.; Peng, T.P.; Zhang, F.F.; Zhang, Y.Z.; Bi, X.W. Petrogenesis of late Triassic post-collisional basaltic rocks of the Lancangjiang tectonic zone, southwest China, and tectonic implications for the evolution of the eastern Paleotethys: Geochronological and geochemical constraints. *Lithos* **2010**, *120*, 529–546. [CrossRef]
37. Srichan, W.; Crawford, A.J.; Berry, R.F. Geochemistry and geochronology of Late Triassic volcanic rocks in the Chiang Khong region, northern Thailand. *Isl. Arc* **2009**, *18*, 32–51. [CrossRef]
38. Vervoort, J.D.; Pachelt, P.J.; Albarède, F.; Blichert-Toft, J.; Rudnick, R.; Downes, H. Hf–Nd isotopic evolution of the lower crust. *Earth Planet. Sci. Lett.* **2000**, *181*, 115–129. [CrossRef]

39. Hoffman, A.W.; Jochum, K.P.; Seufert, M.; White, W.M. Nd and Pb in Oceanic Basalts: New Constraints on Mantle Evolution. *Earth Planet. Sci. Lett.* **1986**, *79*, 33–45. [CrossRef]
40. Hoffman, P.F.; Ranalli, G. Archean Oceanic plate tectonics. *Geophys. Res. Lett.* **1998**, *15*, 1077–1080. [CrossRef]
41. Boniface, N.; Schenk, V.; Appel, P. Paleoproterozoic eclogites of MORB-type chemistry and three Proterozoic orogenic cycles in the Ubendian Belt (Tanzania): Evidence from monazite and zircon geochronology, and geochemistry. *Precambrian Res.* **2012**, *192–195*, 16–33. [CrossRef]
42. Kay, S.M.; Ramos, V.A.; Marquez, M. Evidence in cerro pampa volcanic rocks for slab-melting prior to ridge-trench collision in Southern South America. *J. Geol.* **1993**, *101*, 703–714. [CrossRef]
43. Pearce, J.A.; and Peate, D.W. Tectonic implications of the composition of volcanic arc magmas. *Annu. Rev. Earth Planet. Sci. Lett.* **1995**, *23*, 251–286. [CrossRef]
44. Xu, Y.G.; Chung, S.L.; Jahn, B.N.; Wu, G. Petrologic and geochemical constraints on the petrogenesis of Permian–Triassic Emeishan flood basalts in southwestern China. *Lithos* **2001**, *58*, 145–168. [CrossRef]
45. Rooney, T.O. Geochemical evidence of lithospheric thinning in the southern Main Ethiopian Rift. *Lithos* **2010**, *117*, 33–48. [CrossRef]
46. Wilson, M. *Igneous Petrogenesis: A Global Tectonic Approach*; Unwin Hyman: London, UK, 1989; pp. 1–466.
47. Yoder, H.S. *Evolution of the Igneous Rocks*; Princeton University Press: Princeton, NJ, USA, 1979.
48. Stolz, A.J.; Jochum, K.P.; Spettel, B.; Hofmann, A.W. Fluid and melt-related enrichment in the subarc mantle: Evidence from Nb/Ta variations in island-arc basalts. *Geology* **1996**, *24*, 587–590. [CrossRef]
49. Rudnick, R.L.; Fountain, D.M. Nature and composition of the continental crust: A lower crustal perspective. *Rev. Geophys.* **1995**, *33*, 267–309. [CrossRef]
50. Pearce, J.A.; Harris, N.B.W.; Tindle, A.G. Trace element discrimination diagrams for the tectonic interpretation of granitic rocks. *J. Petrol.* **1984**, *25*, 956–983. [CrossRef]
51. Sun, S.Q.; Wang, Y.L.; Zhang, C.J. Discrimination of the tectonic setting of basalts by Th, Nb and Zr. *Geol. Rev.* **2003**, *49*, 40–47. (In Chinese with English abstract)
52. Wang, Y.L.; Zhang, C.J.; Xiu, S.Z. Th/Hf-Ta/Hf identification of tectonic setting of basalts. *Acta Petrol. Sin.* **2001**, *17*, 413–421. (In Chinese with English abstract)
53. Jian, P.; Liu, D.Y.; Sun, X.M. SHRIMP dating of the Permo-Carboniferous Jishajiang ophiolite, southwestern China: Geochronological constraints for the evolution of Paleo-Tethys. *J. Asian Earth Sci.* **2008**, *32*, 371–384. [CrossRef]
54. Jian, P.; Liu, D.Y.; Kröner, A.; Zhang, Q.; Wang, Y.Z.; Sun, X.M.; Zhang, W. Devonian to Permian plate tectonic cycle of the Paleo-Tethys Orogen in southwest China (I): Geochemistry of ophiolites, arc/back-arc assemblages and within-plate igneous rocks. *Lithos* **2009**, *113*, 748–766. [CrossRef]
55. Jian, P.; Liu, D.Y.; Kröner, A.; Zhang, Q.; Wang, Y.Z.; Sun, X.M.; Zhang, W. Devonian to Permian plate tectonic cycle of the Paleo-Tethys Orogen in southwest China (II): Insights from zircon ages of ophiolites, arc/back-arc assemblages and within-plate igneous rocks and generation of the Emeishan CFB province. *Lithos* **2009**, *113*, 767–784. [CrossRef]
56. Lepvrier, C.; Vuong, N.V.; Maluski, H.; Thi, P.T.; Vu, T.V. Indosinian tectonics in Vietnam. *Comptes Rendus—Géosci.* **2008**, *340*, 94–111. [CrossRef]
57. Wang, X.F.; Metcalfe, I.; Jian, P.; He, L.Q.; Wang, C.S. The Jishajiang-Ailaoshan suture zone, China: Tectonostratigraphy, age and evolution. *J. Asian Earth Sci.* **2000**, *18*, 675–690. [CrossRef]
58. Fan, W.M.; Wang, Y.J.; Zhang, A.M.; Zhang, F.F.; Yuzhi Zhang, Y.Z. Permian arc–back-arc basin development along the Ailaoshan tectonic zone: Geochemical, isotopic and geochronological evidence from the Mojiang volcanic rocks, Southwest China. *Lithos* **2010**, *119*, 553–568. [CrossRef]
59. Liu, H.C.; Wang, Y.J.; Cawood, P.A.; Fan, W.M.; Cai, Y.F.; Xing, X.W. Record of Tethyan ocean closure and Indosinian collision along the Ailaoshan suture zone (SW China). *Gondwana Res.* **2015**, *27*, 1292–1306. [CrossRef]
60. Hu, F.Y.; Wu, F.Y.; Wang, J.G.; Ducea, M.N.; Chapman, J.B.; Zaw, K.; Lin, W.; Sein, K.; Meffre, S. Newly discovered Early Carboniferous and Late Permian magmatic rocks in eastern Myanmar: Implications for the tectonic evolution of the eastern Paleo-Tethys. *J. Asian Earth Sci.* **2022**, *227*, 105093. [CrossRef]
61. Chuan, M.S.; Hu, L.; Lin, R.X.; Mao, C.Z.; Li, S.Z.; Li, S.M.; Yuan, Y.S. Origin and tectonic implications of early Mesozoic “mung bean rock” in the western margin of the Yangtze Platform: Zircon U-Pb age, trace elements and Hf isotope constraints. *Earth Sci. Front.* **2024**, *31*, 204–223. (In Chinese with English abstract)
62. Zi, J.W.; Cawood, P.A.; Fan, W.M.; Tohver, E.; Wang, Y.J.; McCuaig, C.T. Generation of Early Indosinian enriched mantle-derived granitoid pluton in the Sanjiang Orogen (SW China) in response to closure of the Paleo-Tethys. *Lithos* **2012**, *140*, 166–182. [CrossRef]
63. Zhu, J.J.; Hu, R.Z.; Bi, X.W.; Zhong, H.; Chen, H. Zircon U-Pb Ages, Hf-O Isotopes and Whole-Rock Sr-Nd-Pb Isotopic Geochemistry of Granitoids in the Jinshajiang Suture Zone, SW China: Constraints on Petrogenesis and Tectonic Evolution of the Paleo-Tethys Ocean. *Lithos* **2011**, *126*, 248–264. [CrossRef]

64. Qian, X.; Li, H.L.; Yu, X.Q.; Zhang, Y.Z.; Wang, Y.J. Permian-Triassic Magmatism Along the Truong Son Zone in SE Asia and its Paleotethyan Tectonic Implications. *Geotecton. Metallog.* **2022**, *46*, 585–604. (In Chinese with English abstract)
65. Hoa, T.T.; Anh, T.T.; Phuong, N.T.; Dung, P.T.; Anh, T.V.; Izokh, A.E.; Borisenko, A.S.; Lan, C.Y.; Chung, S.L.; Lo, C.H. Permo-Triassic intermediate-felsic magmatism of the Truong Son belt, eastern margin of Indochina. *Comptes Rendus Geosci.* **2008**, *340*, 112–126. [CrossRef]
66. Shi, M.F.; Zhu, H.P.; Lin, F.C.; Fan, W.Y.; Wang, h.; Deng, Q.; Cong, F. Geochemical characteristic, zircon U-Pb age and Hf isotopic compositions of monzogranites from the Thack Khe Iron deposit, Vietnam. *Acta Geol. Sin.* **2015**, *89*, 1683–1695. (In Chinese with English abstract)
67. Halpin, J.A.; Tran, H.T.; Lai, C.K.; Meffre, S.; Zaw, K. U-Pb zircon geochronology and geochemistry from NE Vietnam: A 'tectonically disputed' territory between the Indochina and South China Blocks. *Gondwana Res.* **2016**, *34*, 254–273. [CrossRef]
68. Huang, C.W.; Li, H.; Lai, C.K. Genesis of the Binh do Pb-Zn deposit in northern Vietnam: Evidence from H-O-S-Pb isotope geochemistry. *J. Earth Sci.* **2019**, *30*, 679–688. [CrossRef]
69. Li, X.H.; Li, Z.X.; Li, W.X.; Wang, Y.J. Initiation of the Indosinian Orogeny in South China: Evidence for a Permian magmatic arc on Hainan Island. *J. Geol.* **2006**, *114*, 341–353. [CrossRef]
70. Xu, D.R.; Xia, B.; Li, P.C.; CHEN, G.H.; MA, C.; ZHANG, Y.Q. Protolith natures and U-Pb sensitive high mass-resolution ion microprobe (SHRIMP) zircon ages of the metabasites in Hainan Island, South China: Implications for geodynamic evolution since the late Precambrian. *Isl. Arc* **2007**, *16*, 575–597. [CrossRef]
71. Yan, Q.S.; Metcalfe, I.; Shi, X.F. U-Pb isotope geochronology and geochemistry of granites from Hainan Island (northern South China Sea margin): Constraints on late Paleozoic-Mesozoic tectonic evolution. *Gondwana Res.* **2017**, *49*, 333–349. [CrossRef]
72. Shen, L.W.; Yu, J.H.; O'Reilly, S.Y.; Griffin, W.L.; Xueyao Zhou, X.Y. Subduction-related middle Permian to early Triassic magmatism in central Hainan Island, South China. *Lithos* **2018**, *318–319*, 158–175. [CrossRef]
73. He, H.Y.; Wang, Y.J.; Zhang, Y.H.; Qian, X.; Zhang, Y.Z. Fingerprints of the Paleotethyan back-arc basin in Central Hainan, South China: Geochronological and geochemical constraints on the Carboniferous metabasites. *Int. J. Earth Sci.* **2018**, *107*, 553–570. [CrossRef]
74. He, H.Y.; Wang, Y.J.; Cawood, P.A.; Qian, X.; Zhang, Y.Z.; Zhao, G.F. Permo-Triassic granitoids, Hainan Island, link to Paleotethyan not Paleopacific tectonics. *Geol. Soc. Am. Bull.* **2020**, *132*, 2067–2083. [CrossRef]
75. Zhou, Y.; Yan, Y.; Liu, H.L.; Cai, J.X.; Zhou, M.F.; Zhang, X.C.; Wang, Y.; Shen, B.Y. U-Pb isotope geochronology of syntectonic granites from Hainan Island, South China: Constraints on tectonic evolution of the eastern Paleo-Tethys Ocean. *J. Ocean Univ. China* **2020**, *19*, 1315–1330. [CrossRef]
76. Ouyang, J.T.; Zhou, Y.; Liu, X.J.; Li, Z.L.; Xie, Y.H.; Cai, Y.F. Petrogenesis of Late Permian granites from West Hainan Island and its geotectonic implications. *Chin. J. Geol.* **2025**, *60*, 212–228. (In Chinese with English abstract)
77. Tang, L.M.; Chen, H.L.; Dong, C.W.; Yang, S.F.; Shen, Z.Y.; Cheng, X.G.; Fu, L.L. Middle Triassic post-orogenic extension on Hainan Island: Chronology and geochemistry constraints of bimodal intrusive rocks. *Sci. China Earth Sci.* **2013**, *56*, 783–793. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Formation Mechanism of Plagioclase–Amphibole and Amphibole–Spinel Symplectites in the Bijigou Layered Intrusion: Insights from Mineralogical and Crystallographic Constraints

Baoqun Sun ^{1,2}, Xinyu Wei ² and Huan Dong ^{1,2,*}

¹ Key Laboratory of Exploration Technologies for Oil and Gas Resources (Yangtze University), Ministry of Education, Wuhan 430100, China; sunbaoqun9928@163.com

² School of Geosciences, Yangtze University, Wuhan 430100, China; 2023710487@yangtzeu.edu.cn

* Correspondence: donghuan@yangtzeu.edu.cn

Abstract

The Bijigou layered intrusion is located in the northern margin of the Yangtze block. Based on cumulus mineral assemblages, the intrusion is divided into three major units from the base upwards: the lower zone (LZ), dominated by olivine gabbro; the middle zone (MZ), composed of gabbro and Fe-Ti oxide ore layers; and the upper zone (UZ), characterized by (quartz) diorite. Previous studies reported various vermicular symplectite textures in layered intrusions, which are thought to be related to the magmatic evolution of the layered intrusions and the mineralization of vanadium–titanium magnetite. However, detailed studies on the specific reaction mechanism of those symplectites are lacking. In this study, the characteristics, mineral compositions, and crystal orientation relationships of minerals in symplectites from Fe-Ti oxide Fe-Ti oxide-rich gabbro in the Bijigou layered intrusion investigated by an Electron Probe Microanalyzer (EPMA) and Electron Backscattered Diffraction (EBSD) to reveal the formation process of symplectites in gabbros. In the Fe-Ti oxide-rich gabbro, abundant amphibole + spinel (Amp₁ + Spl) symplectite and amphibole + plagioclase (Pl₂ + Amp₂) symplectite are developed between the primocryst plagioclase (Pl₁) and Fe-Ti oxide; Pl₂ had significantly higher An contents (An_{92–97}) relative to Pl₁. The Mg # for Amp₁ and Amp₂ was 0.78–1 and 0.6–0.84, respectively. Amphibole geothermometer calculations show Amp₁ and Amp₂ at 934–953 °C and 834–914 °C, suggesting that these symplectites crystallized at a late stage of magmatic evolution. The crystallographic orientation relationship between Amp₁ and Spl varies in different areas, and Spl has a particular orientation relationship with the external Ilm. Pl₂ and Amp₂ inherit the crystallographic orientation of Amp₁ and Pl₁, respectively. We speculate that in the Bijigou layered intrusions, Amp₁ + Spl and Pl₂ + Amp₂ were formed in two stages: Amp₁ + Spl symplectite due to Ilm epitaxial growth as a result of supersaturation and rapid nucleation; and Pl₂ + Amp₂ symplectite due to dissolution–precipitation.

Keywords: Bijigou layered intrusion; vanadium–titanium magnetite; symplectite; formation mechanism

1. Introduction

Symplectite is a microstructure characterized by the fine-grained worm-like intergrowth of two or more minerals, which usually coexist in lamellae [1,2]. Symplectites and

other microstructures in igneous rocks are vital records of magmatic transport, evolution, and solidification processes [3–10]. In recent years, significant progress has been made in studying the origin of symplectites. Baldwin proposed that changes in chemical potential gradient between minerals drive the formation of symplectites [11]; Keevil's study of the Sept Iles intrusion revealed the influence of fluid activity on the microstructural evolution of symplectite through microzonation compositional analysis [7]. In terms of experimental simulation, Dharmapriya and Spruzeniece showed through experimental simulations that Na-K-rich fluids accelerate the formation of symplectite and microstructural adjustments through a dissolution–precipitation mechanism [12,13]; Yudovskaya showed through high-temperature and high-pressure experiments and numerical simulations that reactive melts led to the formation of spinel–clinopyroxene symplectite [14]; and Ashworth and Chambers proposed a new theory of symplectite formation in olivine based on the relationship between the spacing between crystals and the dynamics of the reactive interface [15]. However, there is still controversy about the formation mechanism of symplectite in layered intrusions. This study combined crystal orientation relationship analysis with mineralogical investigations on the Bijigou layered intrusion to unravel the formation mechanism of symplectites.

The Bijigou layered intrusion, hosting a large vanadium–titanium magnetite deposit, is located at the northern margin of the Yangtze block. It is the largest known basal-ultramafic layered intrusion in this area and the entire Qinling Orogenic Belt. Abundant symplectites are developed in the layered intrusions, including amphibole + plagioclase and amphibole + spinel symplectite developed between Fe-Ti oxides and plagioclase, and amphibole + plagioclase and clinopyroxene + magnetite symplectite developed between olivine and plagioclase. These symplectites are thought to be a result of reactions between Fe-rich melts and cumulus minerals formed by the immiscibility of the melts during magmatic evolution [8]. However, the mineral assemblages and developmental characteristics of these symplectites are distinctly different from those of typical structures formed by the reaction of immiscible Fe-rich melts with cumulus minerals [5–7,9]. On the other hand, the formation process and genesis of these symplectites have been studied mainly by analyzing the petrographic features and mineral microzonation compositions. However, there have been no mineralogical and crystallographic studies, so the detailed formation process and reaction mechanism of the symplectites are not yet clear. This study will address the information mechanism of symplectites in the Bijigou layered intrusion and provide insights into the magmatic evolution of layered intrusions and the genesis of vanadium–titanium magnetite deposits.

2. Geological Background and Petrography

The Yangtze block is adjacent to the Huaxia block in the southeast, the Songpan-Ganzi Orogenic Belt in the west, and the Qinling–Dabie Orogenic Belt and the southern margin of the North China Craton form the Central Orogenic Belt along the northern margin (Figure 1a). The Yangtze block has an expansive Archaean–Middle Proterozoic basement overlain by a Neoproterozoic–Cenozoic cover [16]. The Proterozoic–Mesoproterozoic basement mainly comprises metamorphic sedimentary strata and Granodioritic gneiss of the Kongling and Kangdian areas [17,18]. Late Sinian–Jurassic strata consist of carbonate rocks, terrestrial clastic rocks, and glacial deposits [16,19]. The long-term subduction of Neoarchean and the thickening of the crust along the northeastern Han-Nan Arc on the northern edge of the Yangtze block has resulted in the remelting of mafic–ultramafic layered intrusions and felsic intrusions [19–22]. Magnetite layered intrusions mainly include Bijigou, Wangjiangshan, Liushudian, and Luojiaba (Figure 1b). The Bijigou layered intrusion is the most considerable known basic–ultrabasic layered intrusion in the northern

Yangtze block and even the entire Qinling Orogenic Belt, and it has an occurrence of sizeable vanadium–titanium magnetite deposits [20,23].

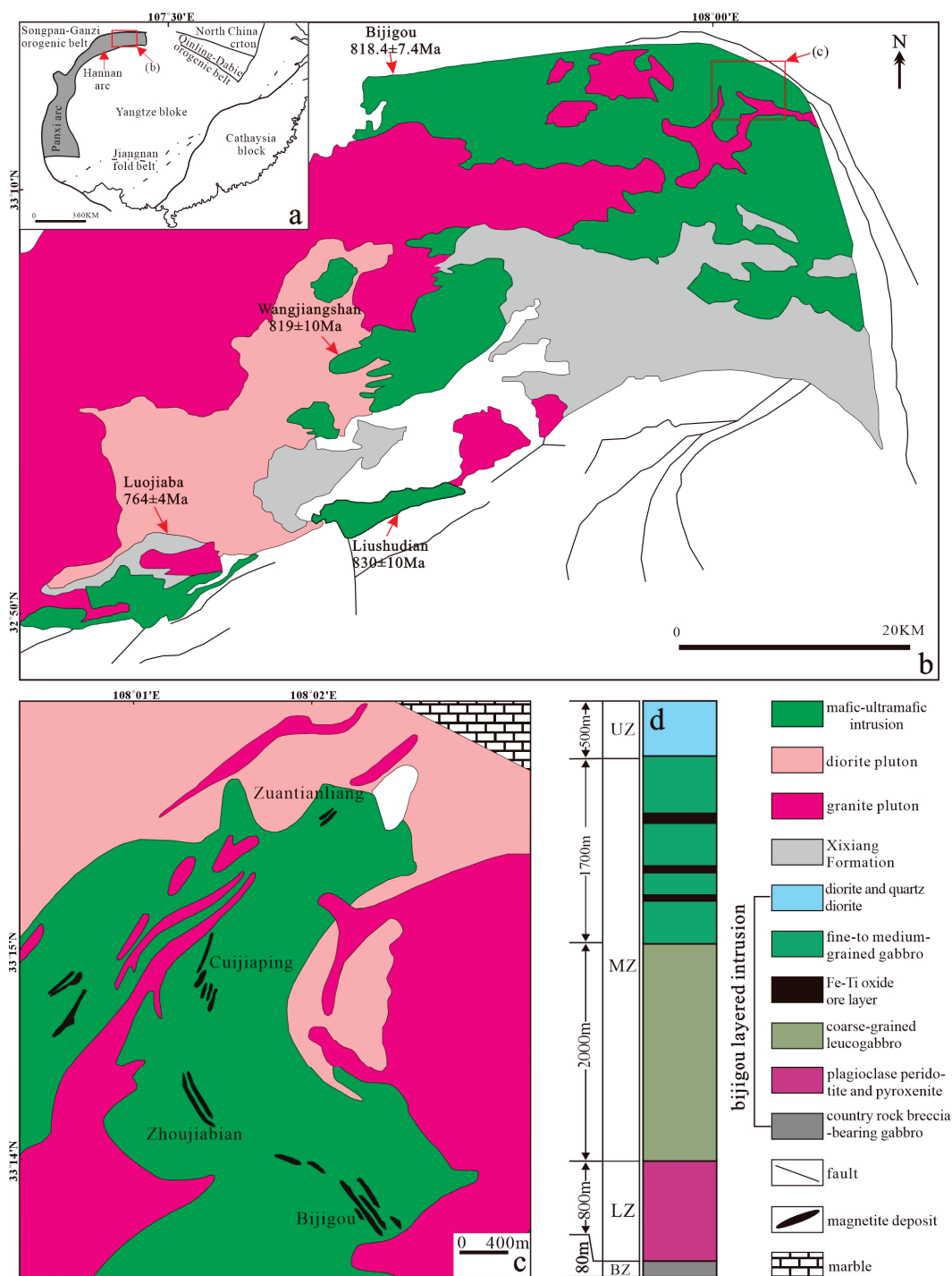


Figure 1. (a) Schematic diagram of the Neoproterozoic Hannan-Panxi Arc at the northern and western margins of the Yangtze block; (b) simplified geological map of the Neoproterozoic basic–ultrabasic and felsic rocks in the Hannan Arc at the northern margin of the Yangtze block; (c) plan view of the main iron-rich titan oxide section of the Bijigou layered intrusion. (d) Main rock composition of the Bijigou layered intrusion.

The Bijigou layered intrusion is about 50 km long, 6–12 km wide, and covers an area of about 500 km². It is about 5 km thick (Figure 1b) [19,24]. The layered medium-sized and small-scale vanadium–titanium magnetite deposits form a curved mineralized zone with a total length of 5400 m. It can be divided into four mining sections from south to north: Bijigou, Zhoujiaban, Cuijiaping, and Zhantianliang (Figure 1c). The layered rock is divided into four lithofacies zones based on the mineral composition: from bottom to top, the bottom zone (BZ) is composed of brecciated gabbro; the lower zone (LZ) is mainly composed of olivine gabbro and troctolite; the middle zone (MZ) is mainly composed of gabbro and an Fe–Ti oxide ore layer; and the upper zone (UZ) is mainly composed of (quartz) diorite. The vanadium–titanium magnetite ore layer is mainly found in the central zone’s medium- to fine-grained gabbro (Figure 1d). The ore body is mainly found in a laminated, layered, or lens-like manner.

This paper mainly selects samples from the central part of the middle and upper parts of the medium-fine-grained gabbro and Fe–Ti oxide-rich gabbro for analysis. The gabbro is mainly composed of plagioclase (55–65%), clinopyroxene (15–35%), intergranular Fe–Ti oxides (<10%), and amphibole (<5%). Plagioclase and clinopyroxene are highly self-shaped, both in slabs, with a typical gabbroic texture. The size of the plagioclase grains is 0.2–3 mm (Figure 2a), and the self-shaped to semi-self-shaped clinopyroxene grains are 0.2–2.2 mm (Figure 2a). The Fe–Ti oxides are mainly distributed irregularly among the grains, and the amphiboles are irregularly distributed around the Fe–Ti oxides (Figure 2b). The Fe–Ti oxide-rich gabbro is mainly composed of plagioclase (10%–15%), clinopyroxene (10%–15%), Fe–Ti oxides (40%–55%), and a small amount of amphibole (<5%) (Figure 2b). Plagioclase is distributed in granular form, with sizes ranging from 0.2 to 2 mm. The size of clinopyroxene grains is 0.2 to 0.5 mm. Fe–Ti oxides are distributed irregularly among the cumulus plagioclase grains. Symplectite can be seen at the edge of the contact between plagioclase and Fe–Ti oxides (Figure 2b).

In the middle of the layered rock, the upper cumulus plagioclase can develop into symplectites at the contact edge with the intergranular mineral Fe–Ti oxides, especially in ore-rich areas. According to mineral composition, these symplectites can be divided into two categories: amphibole (Amp) + spinel (Spl) symplectite and plagioclase (Pl) + amphibole (Amp) symplectite (Figure 2c–f). In Amp + Spl, the spinel is distributed in the amphibole in the form of irregular, excellent particles, with the Spl measuring 1–20 µm; in Pl + Amp, on the other hand, the amphibole is 1–30 µm in size and is worm-like in shape, surrounded by plagioclase. These two types of symplectite can develop either independently or in symbiosis (Figure 2c,f). When they are adjacent to each other, Amp + Spl are close to ilmenite, and Pl + Amp are close to plagioclase (Figure 2c–e). Sometimes, the edges of Pl + Amp are connected to fishhook-like structures (Figure 2e).

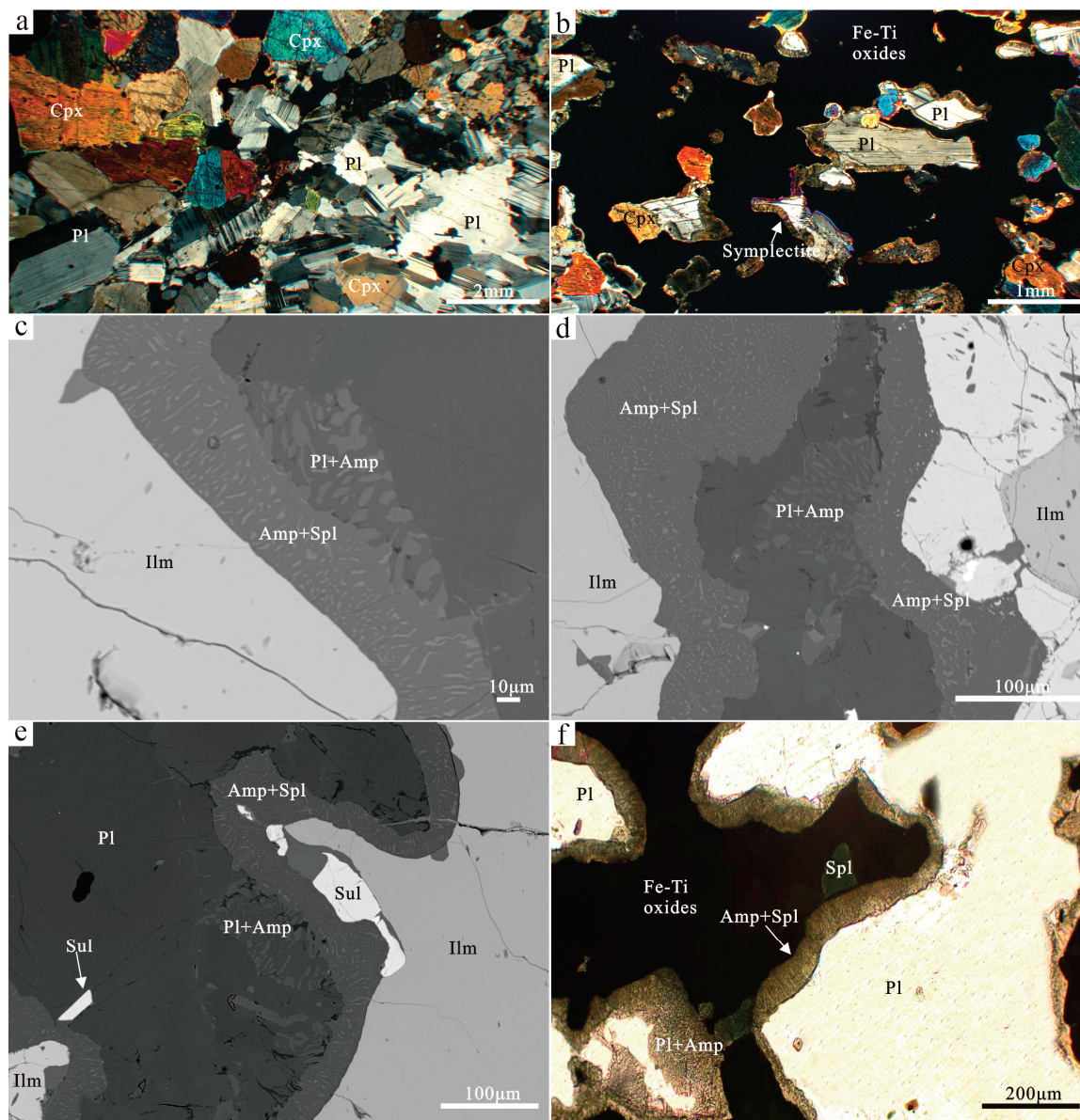


Figure 2. Representative rocks and symplectites in the upper ore-bearing layer in the middle of the Bijigou layered complex. (a) Gabbro, orthopolarized, sample BJG-1515. (b) Fe-Ti oxide-rich gabbro, orthopolarized, sample BJG-1580. (c) Amp + Spl symplectite adjacent to Pl + Amp symplectite, BSE, Sample BJG-1579. (d) Visible Amp + Spl symplectite develops independently, partially symplastically with Pl + Amp symplectite, BSE, Sample BJG-1579. (e) Amp + Spl outer edge with fishhook-like structure connected to fishhook-like structure, BSE, Sample BJG-1579. (f) Uniaxial development in the plagioclase–amphibole and amphibole–spinel symplectites between Pl and Mt. Uniaxial, sample BJG-1579. Pl—plagioclase; Cpx—clinopyroxene; Amp—amphibole; Spl—spinel; Ilm—ilmenite; Sul—sulfide.

3. Materials and Methods

3.1. Electron Probe Microanalyzer

The main components of amphibole, plagioclase, and spinel were tested using a JEOL JXA-8230 electron microprobe at the Key Laboratory of Mineralogy and Metallogeny of the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The experimental conditions were an accelerating voltage of 15 kV, a test current of 20 nA, and a beam spot diameter of 1 μm . The reference materials used for amphibole analysis were Diopside (Si, Mg, and Ca), Magnetite (Fe), Potassium Feldspar (K), Sodium Feldspar (Na), Grossular

(Al), Rutile (Ti), and Clinopyroxene (Mn). The plagioclase reference standards used for analysis are as follows: plagioclase (Si, Al, and Ca), Albite (Na), Potassium Feldspar (K), Rutile (Ti), Garnet (Fe and Mg), and Clinopyroxene (Mn). The reference materials used for the analysis of spinel are Diopside (Si and Ca), Olivine (Mg), Magnetite (Fe), Nickel metal (Ni), Garnet (Al), Rutile (Ti), Rose Clinopyroxene (Mn), Cr_2O_3 (Cr), and Vanadium metal (V). The analytical error is 2% for Si, Fe, and Mg and 5% for the other elements.

3.2. Electron Backscattered Diffraction

Electron Backscattered Diffraction (EBSD) analysis was performed using an FEI Quanta 450 FEG environmental scanning electron microscope (Thermo Fisher Scientific, Hillsboro, OR, USA) from the State Key Laboratory of Geological Processes and Mineral Resources at China University of Geosciences. The experimental conditions were as follows: low vacuum mode (30 pa), accelerating voltage 20 kV, spot size 6, working distance 23–25 mm, sample tilt 70° , and scanning step 50 μm . All samples were calibrated automatically and processed using the CHANNEL5.0 software from Oxford Instruments HKL Technology. All measurements were performed with the exclusion of erroneous, poorly oriented, and more than 5° misaligned data.

4. Results

4.1. Mineral Chemistry

This paper analyzes the composition of Fe-Ti oxides, plagioclase (Pl_1), and the symplectite minerals Amp (Amp_1) + Spl-Pl (Pl_2) + Amp (Amp_2) that develop between them, as well as intergranular amphiboles (Amp_3) in Fe-Ti oxide-rich gabbro. The composition of the plagioclase is shown in Table 1. Primocryst plagioclase (Pl_1) has the following composition: 51.32–52.12 wt% SiO_2 , 30.20–30.98 wt% Al_2O_3 , 0.20–0.98 wt% FeO, and 0–0.08 wt% TiO_2 . Its anorthite content (An = molar $\text{Ca}/(\text{Ca} + \text{Na})$) ranges from 68 to 71. The Pl_2 in the symplectite is different from primocryst plagioclase (Pl_1). Pl_2 has a higher An content (An_{92-97}) and FeO (0.21–4.03 wt%) and a lower TiO_2 content (Figure 3).

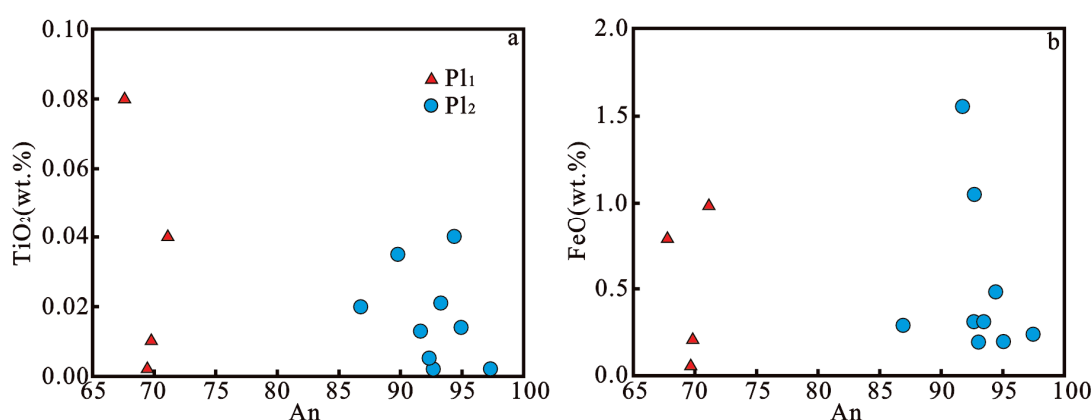


Figure 3. Plagioclase composition of the Bijigou layered intrusion. A comparison between An and (a) TiO_2 and (b) FeO is shown. Pl_1 (blue circles); Pl_2 (red triangles).

The amphibole components are shown in Table 2. Amp_1 contains 38.83–41.99 wt% SiO_2 , 15.46–18.03 wt% Al_2O_3 , 13.23–14.52 wt% FeO, 11.67–13.49 wt% MgO , 10.92–11.83 wt% CaO , 0.24–0.78 wt% TiO_2 , and $\text{Mg \#}$ ($[\text{Mg}/(\text{Mg} + \text{Fe}^{2+})]$) is 0.78–1. Compared with Amp_1 , Amp_2 has a lower $\text{Mg \#}$ ($\text{Mg \#}$ 0.6–0.84) and TiO_2 and higher SiO_2 and CaO content (Figure 4). Amp_3 , compared with Amp_1 , has a lower $\text{Mg \#}$ (0.79–0.83) and Al_2O_3 (12.36–13.85) and higher TiO_2 (0.18–2.7 wt%) (Figure 4).

Table 1. Representative microanalyses of plagioclase in primocryst (Pl₁) and plagioclase in symplectite (Pl₂) (wt.%).

Sample	1579-1	1579-2	1579-9	1579-10	1579-3	1579-4	1579-5	1579-6	1579-7	1579-8	1579-11	1579-12	1579-13
SiO ₂	51.32	52.12	51.61	52.02	46.21	45.60	46.17	45.43	45.20	45.54	44.84	44.86	45.86
TiO ₂	0.04	0.08	0.01	b.d	b.d	0.01	0.01	0.02	0.01	0.04	b.d	0.04	b.d
Al ₂ O ₃	30.21	30.61	30.99	30.84	34.70	35.01	34.33	34.59	33.24	34.96	35.40	28.98	33.17
FeO	0.99	0.80	0.21	0.07	0.21	0.21	0.33	0.32	1.57	0.49	0.26	4.03	1.07
MnO	b.d	0.01	b.d	0.01	0.06	b.d	0.12	0.23	1.72	0.07	0.03	3.87	0.90
MgO	0.44	0.01	0.03	b.d	b.d	b.d	0.02	0.01	0.03	b.d	0.01	0.02	0.01
CaO	14.07	13.54	13.92	14.00	17.96	18.93	17.92	18.15	17.54	18.30	19.09	16.21	17.58
Na ₂ O	3.14	3.58	3.31	3.38	0.75	0.55	0.79	0.70	0.88	0.59	0.28	0.93	0.76
K ₂ O	0.02	0.01	0.02	0.03	0.01	0.01	0.03	0.02	0.01	0.01	0.01	0.14	0.03
total	100.22	100.75	100.09	100.34	99.90	100.32	99.69	99.47	100.19	10b.d	99.91	99.06	99.39
Si	2.34	2.36	2.35	2.36	2.14	2.10	2.14	2.11	2.08	2.11	2.08	2.09	2.13
Ti	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d
Al	1.62	1.63	1.66	1.65	1.89	1.90	1.88	1.89	1.80	1.91	1.93	1.59	1.82
Cr	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d
Fe ³⁺	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d
Fe ²⁺	0.04	0.03	0.01	b.d	0.01	0.01	0.01	0.01	0.06	0.02	0.01	0.16	0.04
Mn	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d
Mg	0.03	b.d	b.d	b.d	b.d	b.d	0.01	0.02	0.12	b.d	b.d	0.27	0.06
Ca	0.69	0.66	0.68	0.68	0.89	0.94	0.89	0.90	0.86	0.91	0.95	0.81	0.88
Ba	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d
Na	0.28	0.31	0.29	0.30	0.07	0.05	0.07	0.06	0.08	0.05	0.02	0.08	0.07
K	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	0.01	b.d
An	71.14	67.64	69.81	69.51	92.93	94.97	92.56	93.32	91.66	94.38	97.40	89.81	92.55
Ab	28.77	32.32	30.06	30.33	7.02	4.97	7.28	6.54	8.29	5.54	2.57	9.30	7.25
Or	0.09	0.04	0.14	0.16	0.05	0.06	0.15	0.14	0.05	0.07	0.04	0.89	0.20

Note: Sample 1579-1, 1579-2, 1579-9, 1579-10 for Pl₁; Sample 1579-3~1579-13 for Pl₂.**Table 2.** Representative microanalyses of the Amp₁ in Amp₁ + Spl symplectite and Amp₂ in the Amp₂ + Pl₂ symplectite in the Fe-Ti oxide-rich gabbro (wt.%).

Sample	BJG1579-6	BJG1579-7	BJG1579-8	BJG1579-9	BJG1579-1	BJG1579-2	BJG1579-3	BJG1579-4	BJG1579-5
SiO ₂	41.53	39.81	41.69	41.35	46.28	43.18	42.27	43.17	43.14
TiO ₂	0.25	0.42	0.67	0.79	0.06	0.13	0.18	0.08	0.11
Al ₂ O ₃	16.58	17.65	15.46	15.74	12.12	14.83	16.05	14.52	15.92
FeO	13.09	13.85	13.28	13.59	11.91	13.49	13.09	13.04	12.24
MnO	0.22	0.22	0.22	0.21	0.22	0.21	0.24	0.21	0.23
MgO	13.13	13.04	13.31	13.47	14.09	12.67	12.38	12.85	13.36
CaO	11.54	10.92	11.56	11.40	11.91	11.80	11.82	11.91	11.72
Na ₂ O	2.27	2.13	2.26	2.23	1.36	1.98	2.11	1.93	2.04
K ₂ O	0.16	0.16	0.20	0.18	0.10	0.17	0.13	0.15	0.12
Cl	b.d	b.d	b.d	b.d	0.01	b.d	0.01	b.d	0.01
Total	102.10	101.87	101.94	102.43	100.95	101.47	101.24	100.80	102.03
Si	5.87	5.64	5.92	5.84	6.56	6.16	6.04	6.20	6.07
Aliv	2.13	2.36	2.08	2.16	1.44	1.84	1.96	1.80	1.93
Alvi	0.63	0.59	0.51	0.45	0.58	0.66	0.75	0.65	0.71
Ti	0.03	0.04	0.07	0.08	0.01	0.01	0.02	0.01	0.01
Cr	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d
Fe ³⁺	1.30	1.64	1.25	1.46	0.84	0.97	0.94	0.91	1.07
Fe ²⁺	0.25	b.d	0.32	0.15	0.57	0.64	0.62	0.66	0.37
Mn	0.03	0.03	0.03	0.02	0.03	0.03	0.03	0.03	0.03
Mg	2.77	2.75	2.82	2.83	2.98	2.69	2.64	2.75	2.80
Ca	1.75	1.66	1.76	1.72	1.81	1.80	1.81	1.83	1.77
Na	0.62	0.59	0.62	0.61	0.37	0.55	0.58	0.54	0.56
K	0.03	0.03	0.04	0.03	0.02	0.03	0.02	0.03	0.02
Mg #	0.92	1.00	0.90	0.95	0.84	0.81	0.81	0.81	0.88

Note: Sample 1579-6~1579-9 for Amp₁; BJG1579-1~BJG1539-5 for Amp₂.

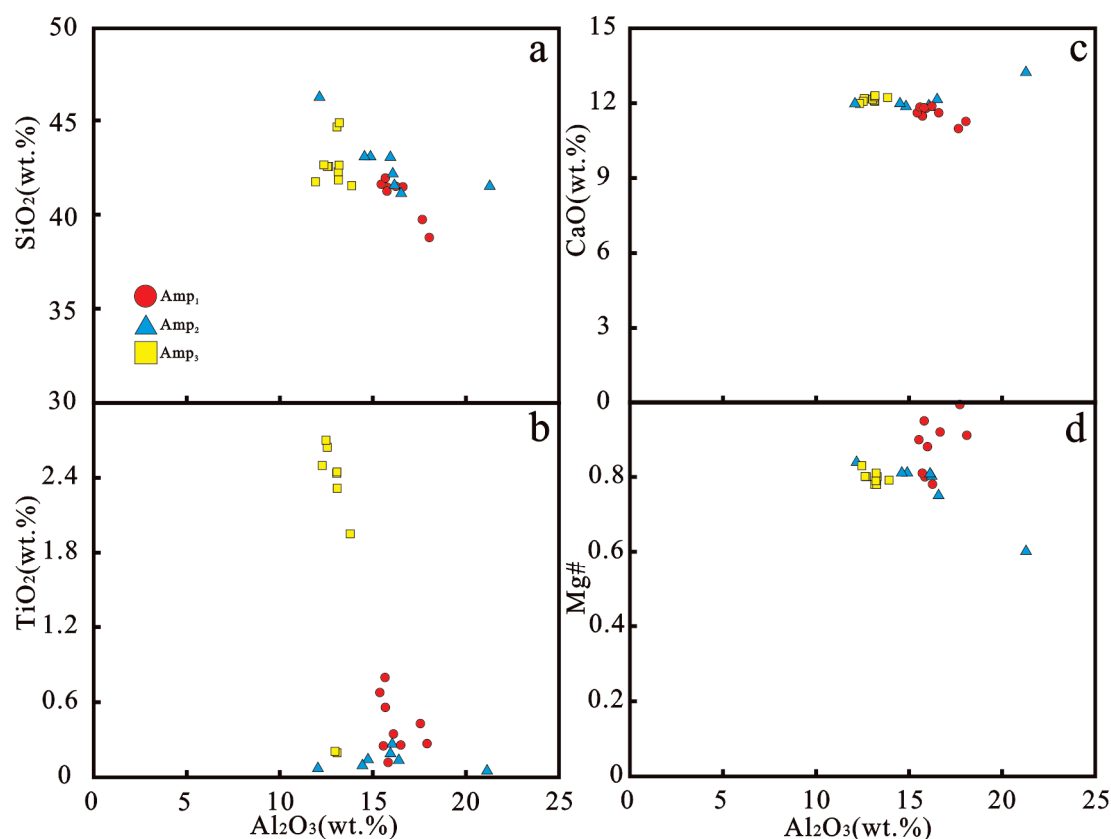


Figure 4. Binaric diagram of amphibole components in the Bijigou layered intrusion. (a) Plots of Al_2O_3 versus SiO_2 , (b) plots of Al_2O_3 versus TiO_2 , (c) plots of Al_2O_3 versus CaO , (d) plots of Al_2O_3 versus $\text{Mg\#}$. Amp_1 (red circles); Amp_2 (blue triangles); Amp_3 (yellow squares).

The spinel in the $\text{Amp} + \text{Spl}$ symplectite contains 0.05–9.58 wt% SiO_2 , 47.17–57.91 wt% Al_2O_3 , 26.54–31.49 wt% FeO , and 8.59–9.34 wt% MgO (Table 3).

Table 3. Representative microanalyses of spinel (Spl) in a symplectite (wt.%).

Sample	TiO_2	FeO	MnO	NiO	Cr_2O_3	CaO	V_2O_5	SiO_2	Al_2O_3	MgO	Total
Spl-BJG1579-1	0.11	26.54	0.20	0.02	b.d	3.07	0.01	9.58	47.17	9.34	96.03
Spl-BJG1579-2	b.d	29.89	0.22	0.02	b.d	0.07	0.01	0.05	57.91	8.88	97.04
Spl-BJG1579-3	0.07	31.49	0.21	0.01	b.d	0.05	b.d	0.12	55.82	8.59	96.36

4.2. Crystal Orientation Relationship

This study uses AZtecCrystal EBSD data analysis software to analyze the orientation of the symplectite structure formed by $\text{Amp}_1 + \text{Spl-Pl}_2 + \text{Amp}_2$ and the surrounding paramount crystals of Fe-Ti oxide and plagioclase (Pl_1). The study area was divided into seven areas (Pl_1 for area 1; $\text{Amp}_2 + \text{Pl}_2$ for area 2; $\text{Amp}_1 + \text{Spl}$ for areas 3–6; and Ilm for area 7) based on the difference in Euler angles of the EBSD results. In the sample, the plagioclase exhibits a consistent crystal orientation in a single area ((Figures 5a and 6). The amphibole also shows a consistent crystal orientation in a single area except for area 2 (Figure 5a); however, the amphibole in area 2 shows significant differences in crystallographic orientation (Figure 5b). In addition, the orientation between Amp_2 grains and Amp_1 grains overlaps in some areas (Figure 6), indicating that Amp_2 inherits the crystal orientation of Amp_1 in some cases. The orientation of the spinel is more complicated than amphibole, with the spinel showing a variety of orientations within the same region (Figure 7). There are significant differences in the orientation distribution of spinel between different areas.

However, in all pole figures, the spinel grains consistently rotate around a common axis that is sub-parallel to the normal of the Spl {110} plane (Figure 7), nearly perpendicular to the thin section surface. Ilmenite maintains the same orientation relationship in area 7 (Figure 8a).

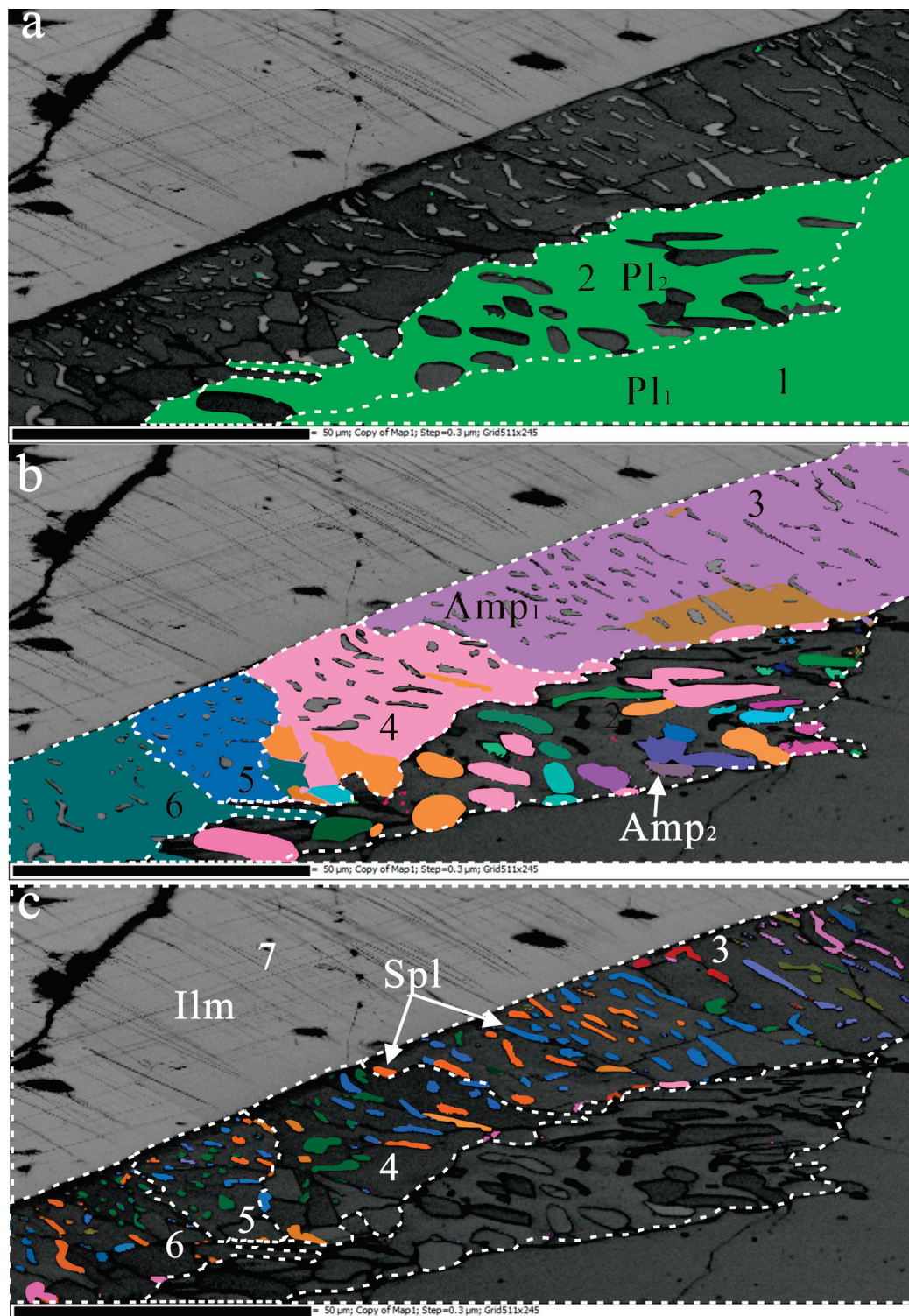


Figure 5. Crystal orientation distribution maps of minerals in the symplectite area. (a) Plagioclase orientation distribution map, (b) amphibole orientation distribution map, and (c) spinel orientation distribution map. According to the distribution of positions and differences in orientation, the symplectite is divided into 7 areas: Pl—plagioclase, Amp—amphibole, Spl—spinel, Ilm—ilmenite.

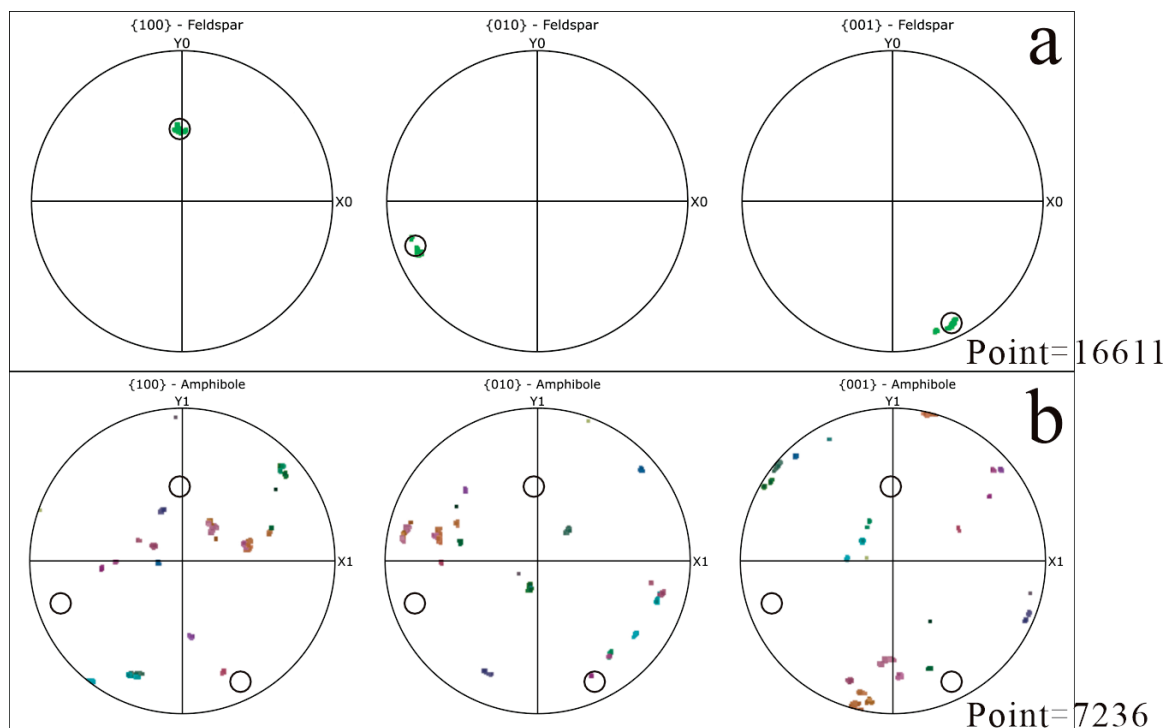


Figure 6. Orientations of plagioclase and amphibole in the Fe-Ti oxide-rich gabbro obtained by EBSD. (a) Pl₁ and Pl₂ pole figures and (b) Amp₂ pole figures in area 2, divided according to the areas outlined in Figure 5. Each color in the pole figure corresponds to the Euler angle coloring in each area, as shown in Figure 5.

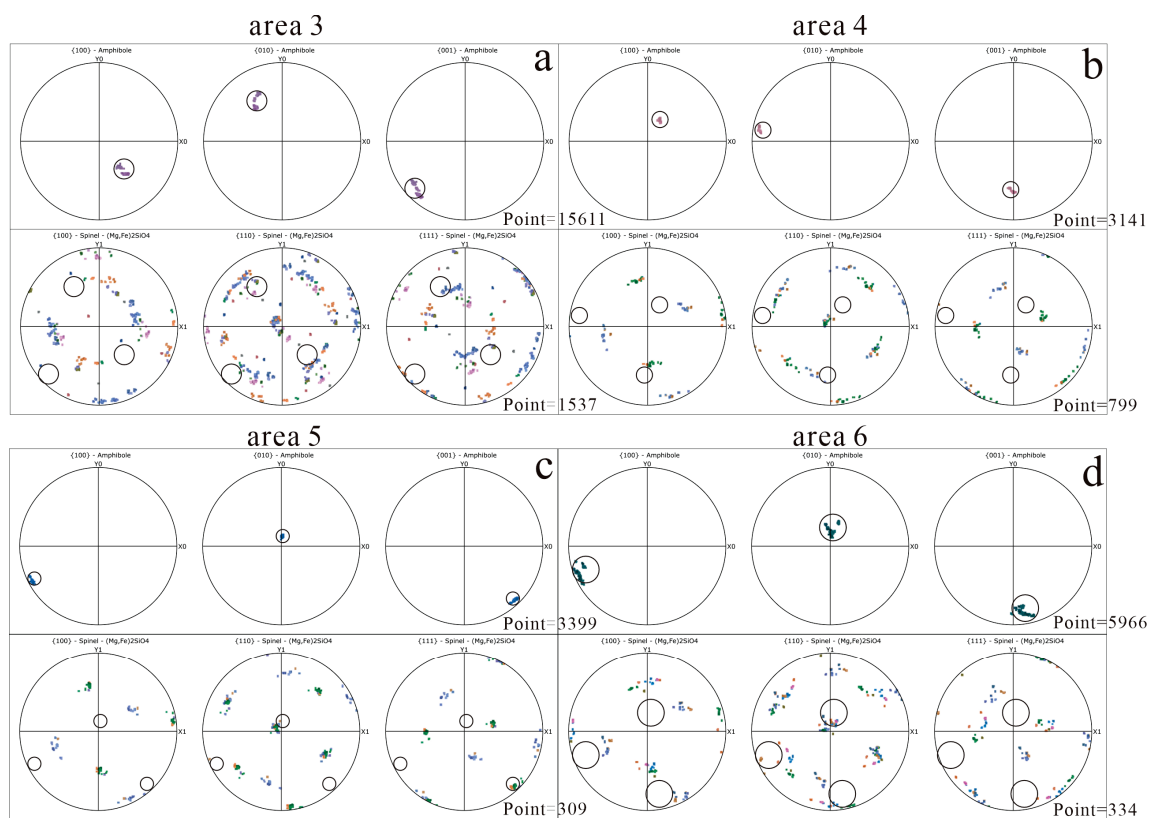


Figure 7. Comparison of amphibole and spinel pole figures (a) in area 3, (b) in area 4, (c) in area 5, and (d) in area 6. The areas are defined according to Figure 5. Each color in the polar plot corresponds to a color in the Euler angle coloring of each area, as shown in Figure 5.

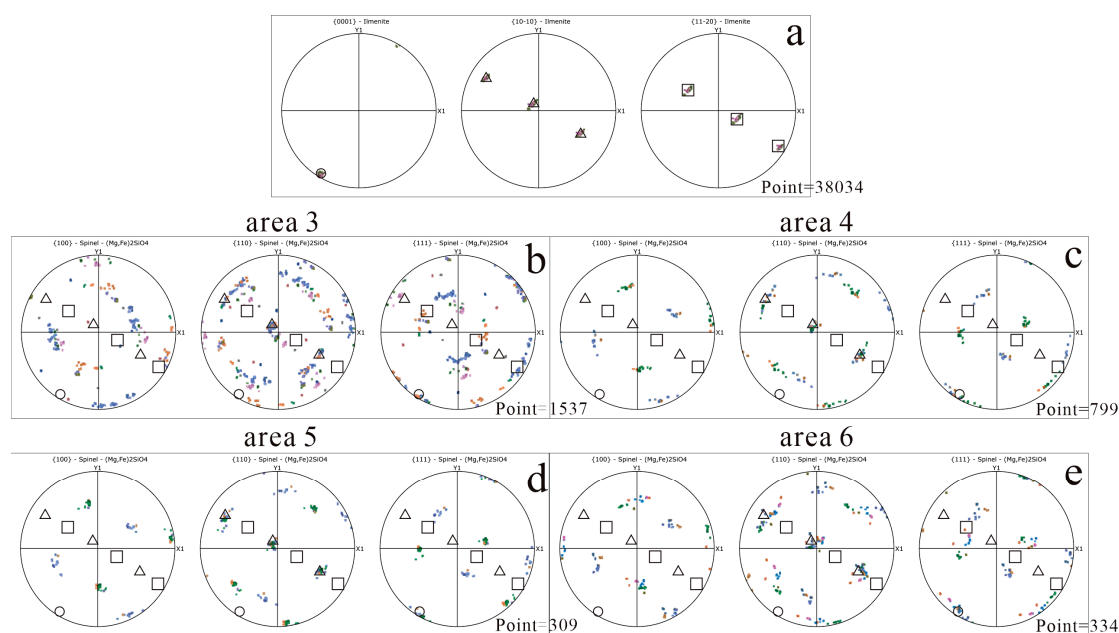


Figure 8. (a) Ilmenite pole figure in area 7. Comparison of ilmenite and Spl pole figure (b) in area 3, (c) in area 4, (d) in area 5, and (e) in area 6. The areas are defined according to Figure 5. Each color in the polar plot corresponds to a color in the Euler angle coloring of each area, as shown in Figure 5.

Regarding crystallographic orientation, EBSD analysis shows that for the symplectites $Pl_2 + Amp_2$, there is no reasonable orientation relationship between Pl_2 and Amp_2 on the pole Figure (Figure 6). For the symplectite $Amp_1 + Spl$, the orientation relationship in each area is more complex (as shown in Figure 5). Amphiboles show different orientation relationships with spinels colored according to their Euler angles. In area 3, spinel sections of different orientations show orientation relationships with host amphibole (i.e., $Amp\{100\}$ overlaps with $Spl\{111\}$ and $\{110\}$; $Amp\{010\}$ overlaps with $Spl\{110\}$); however, area 4 shows only partial overlap of spinel $\{100\}$ with host $Amp\{001\}$ and no overlap with spinel $\{110\}$ or $\{111\}$ (Figure 7). In areas 5 and 6, $Spl\{110\}$ also approximately overlaps with $Amp\{010\}$.

The crystallographic orientation analysis of spinel was conducted by coloring different Euler angles using external ilmenite as a reference phase. In Figure 8, it can be seen that almost all of the spinel and ilmenite have the following crystallographic orientation relationship: $Ilm\{1000\}$ coincides with $Spl\{111\}$, $Ilm\{10-10\}$ coincides with $Spl\{110\}$. This specific crystallographic relationship may be the cause of the generation of spinel. The origin of these differences will be analyzed in this study.

5. Discussion

5.1. Symplectite Formation Temperature

The microstructure of the layered intrusions in Bijigou was used to estimate the formation temperatures of the minerals using amphibole and plagioclase thermometers, respectively. The formation temperature of amphibole was estimated using the amphibole thermometer of Putirka, as follows:

$$T (^{\circ}C) = 1781 - 132.74 \times Si_{Amp} + 116.6 \times Ti_{Amp} + 69.41 \times Fet_{Amp} + 101.62 \times Na_{Amp} \quad (1)$$

where Si_{Amp} , Ti_{Amp} , and Na_{Amp} are the calculated number of cations in 23 O atoms in amphibole; and Fet_{Amp} represents the total number of Fe cations, calculated as FeO [25].

The formation temperatures (T) of Amp₁ and Amp₂ are 934–953 °C and 834–914 °C, respectively.

The temperature data provide critical constraints on the physicochemical conditions governing symplectite formation. Temperature data provide key kinetic and thermodynamic constraints on the origin of the symplectites. We show that amphibole (Amp₁ and Amp₂) crystallized at temperatures in the 934–953 °C interval, respectively, revealing a gradual cooling process during the late stages of magma evolution [5]. This temperature constrains the cause of the stage formation of symplectites.

5.2. Amphibole + Spinel Symplectite Formation Mechanism

From the kinetic point of view, the amount of nucleation is closely related to the rate of nucleation, which is essentially a function of the degree of supersaturation. Under thermodynamic equilibrium conditions ($\Delta G = 0$), the nucleation rate is zero. As the pressure decreases or the supersaturation increases, the nucleation rate gradually increases. In the study by Obata, two different orientation relationships were observed between spinel and host clinopyroxene: in one area, the {100} of clinopyroxene perfectly coincided with the {111} of spinel, while in the other area, no clear crystallographic orientation relationship was observed [26]. During mantle peridotite decompression, low temperatures or rapid pressure drops drive the system far from thermodynamic equilibrium (i.e., the degree of supersaturation will increase). According to classical nucleation theory, an increase in supersaturation (ΔC) directly enhances the driving force for phase transformation (ΔG), resulting in an exponential increase in the nucleation rate (J) ($J \propto \exp(-\Delta G^2)$). Under these conditions, new phases, such as spinel, form in large quantities due to rapid nucleation. However, due to the rapid nucleation rate, lattice orientation adjustment via interface diffusion to inherit the original arrangement of clinopyroxene is not possible, and a disordered topotaxial structure is ultimately formed.

The study analysis of the crystallographic orientation relationship between amphibole and spinel shows that no perfect orientation correlation feature is formed between them, but there is a specific crystallographic orientation relationship between spinel and external ilmenite. In contrast to Sept Iles layered intrusions, the same Amp + Spl symplectite forms at similar temperatures but shows an ordered topology due to its slow diffusion in melts with high Si content [7]. This result can be attributed to delayed spinel nucleation during ilmenite epitaxial growth caused by a rapid pressure drop and sluggish diffusion kinetics that result in high supersaturation. This phenomenon may be attributed to a nucleation delay effect caused by a rapid decrease in phase transformation pressure and a slow diffusion kinetics rate, resulting in a rather large degree of supersaturation. At such a high degree of supersaturation, it is so rapid that the spinel in each area may not form the perfect orientation relationship with its host amphibole when nucleation occurs. Therefore, we speculate that the observed amphibole + spinel symplectites in the Bijigou layered intrusions are due to the epitaxial growth of spinel, the oversaturation of amphibole, and rapid nucleation.

5.3. Plagioclase + Amphibole (Pl₂ + Amp₂) Symplectite Formation Mechanism

The plagioclase + amphibole (Pl₂ + Amp₂) symplectite is adjacent to Pl₁ (Figure 2c), where the crystal orientation of Pl₂ inherits the crystal orientation of Pl₁. The maximum orientation difference is 2° (Figure 6), indicating that the precipitation of Pl₂ on Pl₁ is the growth of pseudocrystals (maintaining the size and shape of pre-existing phases), which is often observed during the dissolution–precipitation process [27–30]. The slight (usually <2°) and local differences in the crystal orientation of Pl₁ and Pl₂ may be due to slightly different unit cell parameters [31]. The An content of Pl₂ is significantly higher than that of

Pl₁, and the Ca content has increased significantly (Figure 9). The formation of high An in plagioclase is due to the reactive dissolution of plagioclase protoplasts by an evolved iron-rich unmixed melt [5,9], which was then precipitated. The fluid-rich melt penetrates along the grain boundary, causing the dissolution of the reaction interface along which Pl₁ moves inward. The melt introduces Al ions, and the components in Pl₁ release Na and Si, which combine with Ca²⁺ in the fluid to form Pl₂ by reaction precipitation.

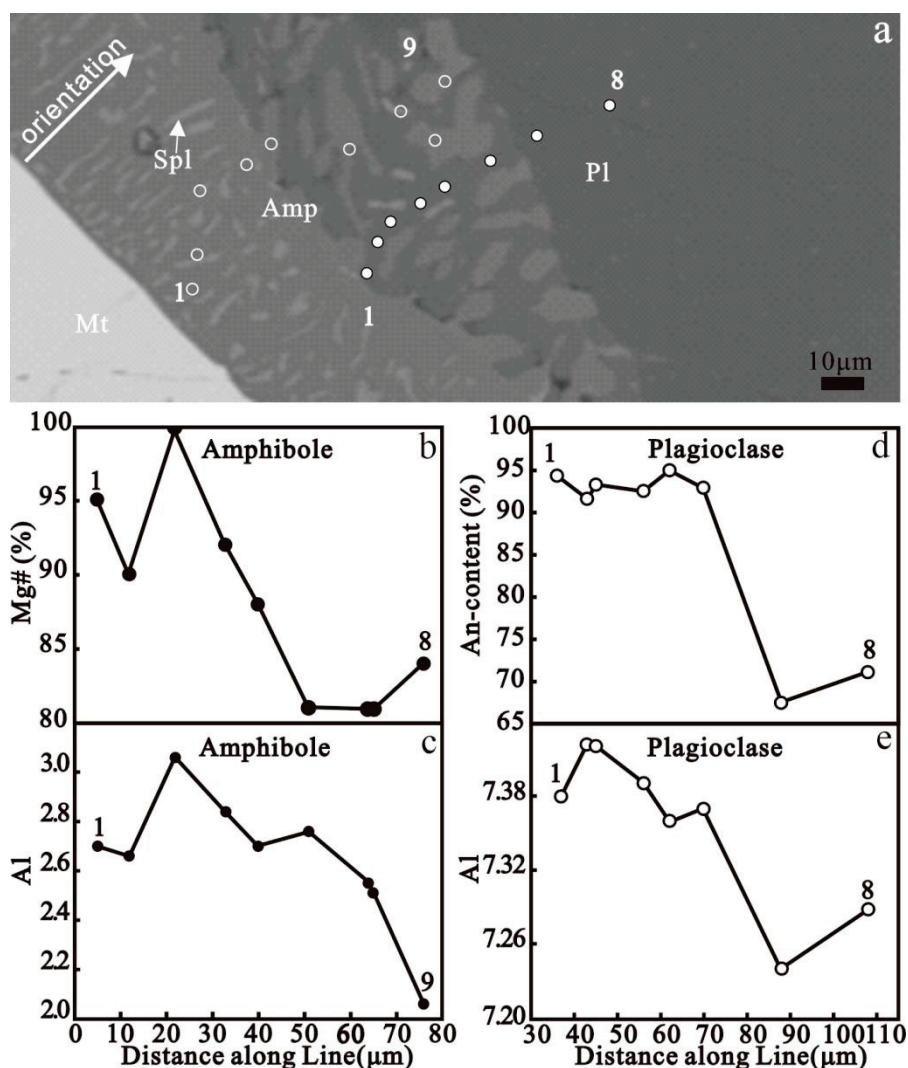


Figure 9. Sample BJG-1579: Changes in the composition of symplectites. (a) BSE images of amphibole and spinel symplectite and amphibole and plagioclase symplectite. The points in the images indicate electron microprobe analysis points. The solid circles are plagioclase, and the hollow circles are amphibole. (b) Graph of the variation of amphibole Mg # content with distance. (c) Graph of the variation of amphibole Al content with distance. (d) Graph of the variation of plagioclase An content with distance. (e) Graph of the variation of plagioclase Al content with distance. Al is the elemental content of Al.

The orientation characteristics of amphibole indicate that its reaction history is similar to that of plagioclase. Although the Mg # of amphibole generally decreases in the direction indicated by the arrow in Figure 9a,b, the Mg content of Amp₂ decreases significantly during the transition from Amp₁ to Amp₂, and in Amp₁, the contact area between the two appears concave (Figure 8a). In the samples studied, the preferred orientation exhibited by Amp₂ in area 2 is mainly inherited from Amp₁ in area 4 (Figures 6b and 7b). These features indicate that Amp₁ has dissolved and Amp₂ has precipitated [32–35].

If plagioclase is involved in forming amphibole, it will release Al during the reaction. Thus, the amphibole formed by reacting with plagioclase should be enriched in Al. As shown in Figure 9c, along the direction indicated in Figure 9a, the Al content of amphibole decreases with distance and does not increase. A comparison of the Al content of amphibole in symplectite with that of marginal amphibole (Figure 10) shows there is no regularity of increasing or decreasing Al content in amphibole and marginal amphibole in symplectite, and the Al content of plagioclase also does not decrease due to the increase in Al content in amphibole (Figure 9e). Plagioclase is not involved in amphibole growth, and the amphibole in the symplectite is formed by the epitaxial growth of marginal amphibole.

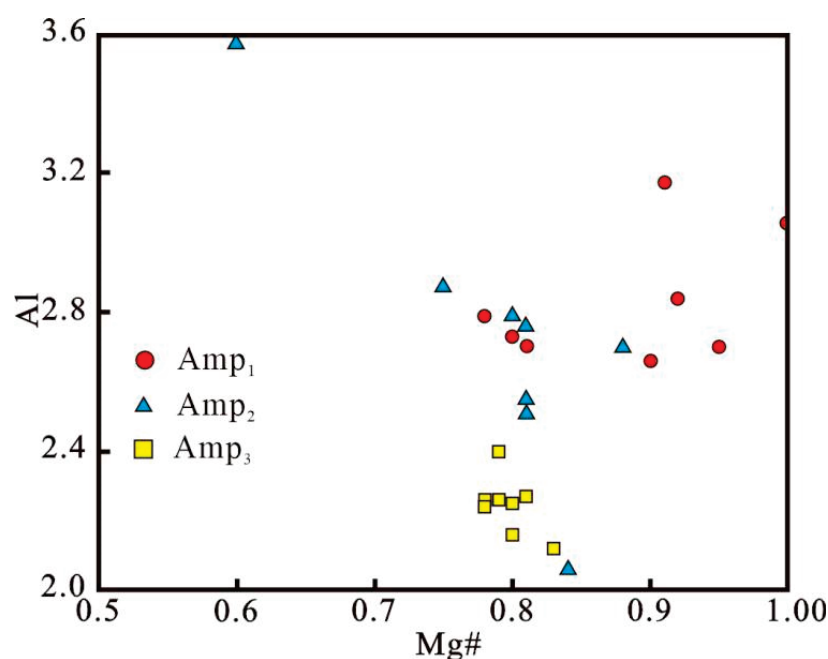


Figure 10. Comparison of the Mg #–Al content. Amp₁ (red circles); Amp₂ (blue triangles); Amp₃ (yellow squares).

Our research has found that during magmatic evolution, as the temperature decreases, Pl₁ is first formed, followed by the Amp₁ boundary. As the temperature continues to decrease, Spl in Amp₁, due to low saturation, quickly nucleates Amp₁ + Spl to form symplectite; due to the dissolution of Pl₁ by the melt, the melt replaces Pl₁ and continues to precipitate to form Pl₂. Amp₂ is formed by the melt replacing Amp₁ during the epitaxial growth of Amp₁ and the melt replacing Pl₂. From a temperature perspective, there is not much of a temperature difference between Pl₂ and Amp₂, and they have formed at the same time, thus forming the worm structure Pl₂ + Amp₂.

6. Conclusions

Based on our detailed investigation, we strongly conclude the following regarding the formation mechanisms of symplectites in the Bijigou layered intrusion:

We find that amphiboles crystallized during the late magmatic stage. Their formation temperatures range from 934 °C to 953 °C, revealing a gradual cooling process during the late stages of magma evolution.

In the amphibole–spinel symplectites, the crystallographic orientations vary significantly among different areas. Spinel often does not develop a perfect toptotaxial relationship with its amphibole. Moreover, the epitaxial growth of spinel on ilmenite reinforces the notion that kinetic factors dominate the formation process. The combined toptotaxial anomaly

and the strong ilmenite–spinel relationship provide robust evidence for kinetic control during symplectite formation.

The plagioclase–amphibole symplectites are formed via a dissolution–precipitation mechanism. We observed that Pl₂ inherits the crystallographic orientation of Pl₁, with an angular deviation of less than 2°. Similarly, Amp₂ partially retains the orientation of Amp₁. These findings indicate that melt infiltration replaces Pl₁ with Pl₂ and replaces Amp₁ with Amp₂ through epitaxial growth.

Since symplectite is a common feature of layered igneous rocks, a study of the similar petrology and composition of symplectite in different bare igneous rocks can further refine the hypothesis proposed in this study.

Author Contributions: Conceptualization, B.S.; methodology, B.S.; software, B.S.; validation, B.S. and X.W.; formal analysis, B.S.; investigation, H.D.; data curation, H.D.; writing—original draft preparation, B.S.; writing—review and editing, H.D.; supervision, H.D.; project administration, H.D.; funding acquisition, H.D. All authors have read and agreed to the published version of the manuscript.

Funding: This study is supported by the National Natural Science Foundation of China (Grant No. 41802085) and the open fund of the Key Laboratory of Exploration Technologies for Oil and Gas Resources (Yangtze University), Ministry of Education (No. PI2023-04). Three reviewers are gratefully acknowledged for their constructive comments.

Data Availability Statement: All data and materials are available on request from the corresponding author. The data are not publicly available due to ongoing research using part of the data.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Mongkoltip, P.; Ashworth, J.R. Quantitative estimation of an open-system symplectite-forming reaction: Restricted diffusion of Al and Si in coronas around olivine. *J. Pet.* **1983**, *24*, 635–661. [CrossRef]
2. Haselton, J.D.; Nash, W.P. Observations on Titanium in Lunar Oxides and Silicates. *Abstr. Lunar Planet. Sci. Conf.* **1975**, *6*, 343.
3. Ambler, E.P.; Ashley, P.M.; McSween, H.Y. Mineralogy and petrology of the Dutchmans Creek gabbroic intrusion, South Carolina: Discussion and reply. *Am. Mineral.* **1980**, *65*, 1302–1306.
4. Holness, M.B.; Stripp, G.; Humphreys, M.C.S. Silicate liquid Immiscibility within the crystal mush: Late-stage magmatic microstructures in the skaergaard Intrusion, east greenland. *J. Pet.* **2011**, *52*, 175–222. [CrossRef]
5. Namur, O.; Charlier, B.; Holness, M.B. Dual origin of Fe-Ti-P gabbros by immiscibility and fractional crystallization of evolved tholeiitic basalts in the Sept Iles layered intrusion. *Lithos* **2012**, *154*, 100–114. [CrossRef]
6. Keevil, H.A.; Namur, O.; Holness, M.B. Microstructures and late-stage magmatic processes in layered mafic intrusions: Symplectites from the sept iles intrusion, quebec, canada. *J. Pet.* **2020**, *61*, egaa071. [CrossRef]
7. Wang, M.; Wang, C.Y.; Tan, W. Compositional evolution of interstitial liquid after onset of abundant Fe-Ti oxide crystallization in crystal mush: Insights from late-stage microstructures and mineral compositions of the bijigou layered intrusion, central china. *J. Pet.* **2022**, *63*, egac025. [CrossRef]
8. Dong, H.; Wang, C.Y. Microstructures in the Baima layered intrusion, SW China: Constraints on the late-stage magmatic processes during solidification of a crystal mush. *J. Asian Earth Sci.* **2023**, *255*, 105774. [CrossRef]
9. Xie, Q.; Zhang, Z.; Cheng, Z. Interstitial microstructures in Ji’nan mafic intrusion, North China Craton: Magmatic or hydrothermal origin? *Eur. J. Mineral.* **2017**, *29*, 839–850. [CrossRef]
10. Baldwin, J.A.; Powell, R.; White, R.W.; Štípská, P. Ussing calculated chemical potential relationships to account for replacement of kyanite by symplectite in high pressure granulites. *J. Metamorph. Geol.* **2015**, *33*, 311–330. [CrossRef]
11. Dharmapriya, P.L.; Malaviarachchi, S.P.K.; Kriegsmann, L.M.; Galli, A.; Dyck, B.; Sajeev, K.; Su, B.-X.; Pitawala, A. Symplectite growth in the presence of alkaline fluids: Evidence from high-aluminous metasediments of the Highland Complex, Sri Lanka. *Mineral. Petrol.* **2020**, *114*, 515–538. [CrossRef]
12. Spruzeniec, L.; Piazzolo, S.; Daczko, N.R.; Kilburn, M.R.; Putnis, A. Symplectite formation in the presence of a reactive fluid: Insights from hydrothermal experiments. *J. Metamorph. Geol.* **2017**, *35*, 281–299. [CrossRef]

13. Yudovskaya, M.A.; Kinnaird, J.A.; Costin, G.; McCreesh, M.; Shilovskikh, V.; Kovalchuk, E.; Kuzmin, D. Formation of spinel-orthopyroxene symplectites by reactive melt flow: Examples from the northern Bushveld Complex and implications for mineralization in layered intrusions. *Econ. Geol.* **2022**, *117*, 1935–1960. [CrossRef]
14. Ashworth, J.R.; Chambers, A.D. Symplectic reaction in olivine and the controls of intergrowth spacing in symplectites. *J. Pet.* **2000**, *41*, 285–304. [CrossRef]
15. Yan, D.P.; Zhou, M.F.; Song, H.L. Origin and tectonic significance of a Mesozoic multi-layer over-thrust system within the Yangtze Block (South China). *Tectonophysics* **2003**, *361*, 239–254. [CrossRef]
16. Gao, S.; Ling, W.; Qiu, Y. Contrasting geochemical and Sm-Nd isotopic compositions of Archean metasediments from the Kongling high-grade terrain of the Yangtze craton: Evidence for cratonic evolution and redistribution of REE during crustal anatexis. *Geochim. Cosmochim. Acta* **1999**, *63*, 2071–2088. [CrossRef]
17. Qiu, Y.M.; Gao, S.; McNaughton, N.J.; Groves, D.I.; Ling, W. First evidence of >3.2 Ga continental crust in the Yangtze craton of south China and its implications for Archean crustal evolution and Phanerozoic tectonics. *Geology* **2000**, *28*, 11–14. [CrossRef]
18. Zhou, M.F.; Kennedy, A.K.; Sun, M. Neoproterozoic arc-related mafic Intrusions along the northern, margin of South China: Implications for the accretion of rodonia. *J. Geol.* **2002**, *110*, 611–618. [CrossRef]
19. Zhao, J.H.; Zhou, M.F. Secular evolution of the Neoproterozoic lithospheric mantle underneath the northern margin of the Yangtze Block, South China. *Lithos* **2009**, *107*, 152–168. [CrossRef]
20. Zhao, J.H.; Zhou, M.F. Neoproterozoic adakitic plutons in the northern margin the Yangtze Block, China: Partial melting of a thickened lower crust and implications for secular crustal evolution. *Lithos* **2008**, *104*, 231–248. [CrossRef]
21. Ao, W.H.; Zhang, Y.K.; Zhang, R.Y.; Zhao, Y.; Sun, Y. Neoproterozoic Crustal Accretion of the Northern Margin of Yangtze Plate: Constrains from Geochemical Characteristics, LA-ICP-MS Zircon U-Pb Chronology and Hf Isotopic Compositions of Trondhjemite from Zushidian Area, Hannan Region. *Geol. Rev.* **2014**, *60*, 1393–1408.
22. Wang, M.; Nebel, O.; Wang, C.Y. The flaw in the crustal ‘Zircon archive’: Mixed hf Isotope signatures record progressive contamination of late-stage liquid in mafic-ultramafic layered Intrusions. *J. Pet.* **2016**, *57*, 27–52. [CrossRef]
23. Su, L. *Studies of Neoproterozoic Mafic and Ultramafic Intrusions in Western-Central China and Their Constraints on Breakup of Rodinia Supercontinent*; Northwest University: Kirkland, WA, USA, 2004.
24. Putirka, K. Special collection: Rates and depths of magma ascent on earth: Amphibole thermometers and barometers for igneous systems and some implications for eruption mechanisms of felsic magmas at arc volcanoes. *Am. Mineral.* **2016**, *101*, 841–858. [CrossRef]
25. Zhang, R. *Mineral Thermometers and Mineral Manometers*; Geological Press: Beijing, China, 1983.
26. Obata, M.; Ozawa, K. Topotaxial relationships between spinel and pyroxene in kelyphite after garnet in mantle-derived peridotites and their implications to reaction mechanism and kinetics. *Mineral. Pet.* **2011**, *101*, 217–224. [CrossRef]
27. Engvik, A.K.; Putnis, A.; Fitz Gerald, J.D.; Austrheim, H. Albitization of granitic rocks: The mechanism of replacement of oligoclase by albite. *Can. Mineral.* **2008**, *46*, 1401–1415. [CrossRef]
28. Hövelmann, J.; Putnis, A.; Geisler, T.; Schmidt, B.C.; Golla-Schindler, U. The replacement of plagioclase feldspars by albite: Observations from hydrothermal experiments. *Contrib. Mineral. Pet.* **2010**, *159*, 43–59. [CrossRef]
29. Putnis, A.; Putnis, C.V. The mechanism of reequilibration of solids in the presence of a fluid phase. *J. Solid State Chem.* **2007**, *180*, 1783–1786. [CrossRef]
30. Spruzeniece, L.; Piazzolo, S.; Maynard-Casely, H.E. Deformation-resembling microstructure created by fluid-mediated dissolution-precipitation reactions. *Nat. Commun.* **2017**, *8*, 14032. [CrossRef]
31. Giuntoli, F.; Menegon, L.; Warren, C.J. Replacement reactions and deformation by dissolution and precipitation processes in amphibolites. *J. Metamorph. Geol.* **2018**, *36*, 1263–1286. [CrossRef]
32. Gratier, J.P.; Dysthe, D.K.; Renard, F. The role of pressure solution creep in the ductility of the Earth’s upper crust. *Adv. Geophys.* **2013**, *54*, 47–179.
33. Hyppolito, T.; García-Casco, A.; Juliani, C.; Meira, V.T.; Hall, C. Late Paleozoic onset of subduction and exhumation at the western margin of Gondwana (Chilenia Terrane): Counterclockwise P-T paths and timing of metamorphism of deep-seated garnet-mica schist and amphibolite of Punta Sirena, Coastal Accretionary Complex, central Chile (34 S). *Lithos* **2014**, *206*, 409–434.
34. Imon, R.; Okudaira, T.; Kanagawa, K. Development of shape- and lattice-preferred orientations of amphibole grains during initial cataclastic deformation and subsequent deformation by dissolution-precipitation creep in amphibolites from the Ryoke metamorphic belt, SW Japan. *J. Struct. Geol.* **2004**, *26*, 793–805. [CrossRef]
35. Pearce, M.A.; Wheeler, J.; Prior, D.J. Relative strength of mafic and felsic rocks during amphibolite facies metamorphism and deformation. *J. Struct. Geol.* **2011**, *33*, 662–675. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Petrogenesis of Middle Jurassic Syenite-Granite Suites and Early Cretaceous Granites with Associated Enclaves in Southwestern Zhejiang, SE China: Implications for Subduction-Related Tectonic Evolution Beneath Northeastern Cathaysia Block

Yu Wang ^{1,2}, Haoyuan Lan ^{1,2,3,*}, Chong Jin ⁴ and Yuhuang Zhang ⁵

¹ Key Lab of Submarine Geosciences and Prospecting Techniques, MOE and College of Marine Geosciences, Ocean University of China, Qingdao 266100, China; 21230411042@stu.ouc.edu.cn

² Laboratory for Marine Mineral Resources, Qingdao Marine Science and Technology Center, Qingdao 266237, China

³ Qingdao Institute of Marine Geology, Qingdao 266237, China

⁴ Zhejiang Institute of Geosciences, Hangzhou 310007, China; chong.jin78@gmail.com

⁵ Foshan Geological Survey Center, Guangdong Geological Bureau, Foshan 528000, China; 17852411351@163.com

* Correspondence: lanhaoyuan1993@163.com

Abstract: Late Mesozoic magmatism in Southeast China extensively reworked the Cathaysia Block's crust, linked to the Paleo-Pacific Plate subduction beneath East Asia. The northeastern Cathaysia Block, largely covered by Cretaceous volcanic-sedimentary basins, has limited Jurassic exposure to Early Cretaceous intrusions, which provides critical insights into deep crust-mantle processes. In this study, we present zircon U-Pb geochronology and Hf isotope, whole-rock geochemistry, and Sr-Nd isotopes of the Middle Jurassic syenite-granite suites and Early Cretaceous granites with enclaves in the Qingyuan area (SW Zhejiang Province) to constrain their petrogenesis and tectonic significance. Middle Jurassic syenites and alkali-feldspar granites (169–167 Ma) exhibit calc-alkaline to shoshonitic affinities and weakly peraluminous compositions. Early Cretaceous granites (134 Ma) and their enclaves (136 Ma) are high-K calc-alkaline and weakly peraluminous to metaluminous. All samples show LILE and LREE enrichment, HFSE depletion, and negative Eu and Sr anomalies, with only syenites displaying negative Ce anomalies. We suggest that the Middle Jurassic syenites originated from the partial melting of an enriched lithospheric mantle influenced by subduction-related metasomatism. Alkali-feldspar granites derived from partial melting of the basement of the Cathaysia Block. Early Cretaceous granites formed by partial melting of lower crustal mafic rocks, with enclaves representing earlier crystallization products, which were then mechanically mixed with granites. We propose the NE Cathaysia Block underwent significant reworking from the Middle Jurassic to the Early Cretaceous. Middle Jurassic syenites formed in a compressional setting linked to Paleo-Pacific Plate subduction, while Early Cretaceous magmatism reflects lithospheric extension and crust-mantle interaction triggered by slab rollback.

Keywords: Cathaysia block; intrusive rock; petrogenesis; magmatism; late Mesozoic

1. Introduction

The East Asian continental margin underwent a fundamental tectonic transition from passive to active regimes during the Mesozoic, with Southeast China (SE China) (Figure 1a)

serving as a critical region for deciphering this geodynamic transformation [1–5]. Late Mesozoic tectono-thermal events episodically reworked the continental crust through widespread magmatism, characterized by extensive intrusive and volcanic activity [6–9]. Jurassic–Cretaceous magmatism in SE China reflects a complex interplay between subduction dynamics, lithospheric thinning, and crust–mantle interactions [10–12]. While most scholars agree on the development of an active continental margin status during this period [13–15], significant debates persist regarding the timing and mechanisms of Paleo-Pacific Plate subduction [8,16]. Early Mesozoic magmatism in this region has been attributed to the Indosinian collisional orogeny or intraplate reactivation of the Wuyi–Yunkai orogenic belt, whereas Late Mesozoic magmatism is widely linked to Paleo-Pacific Plate subduction [1,17]. However, recent studies propose an Early Mesozoic initiation of subduction followed by slab break-off [18,19].

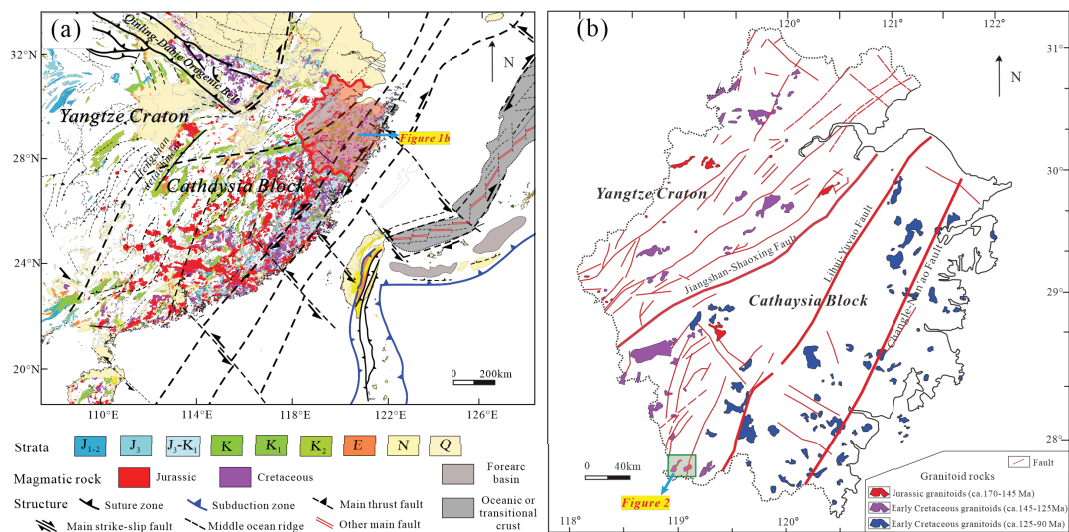


Figure 1. (a) Tectonic unit and distribution of Late Mesozoic magmatic rocks in Southeast China. (b) distribution of Late Mesozoic magmatic rocks in Zhejiang Province.

Late Mesozoic intrusive rocks in SE China exhibit a distinct inland-to-coastal younging trend [14,20]. Jurassic (180–145 Ma) magmatism, concentrated in the inland Nanling and Wuyi Mountain regions, is interpreted as the product of thickened lower crustal melting under compressional regimes [1,9,21,22]. However, the geodynamic drivers remain contentious, with proposal mechanisms including subduction [21], intraplate extension [23], or orogenic collapse [19]. Early Cretaceous (145–100 Ma) magmatism migrated coastward, featuring I- to A-type granites, syenites, and mafic intrusions [16,24,25]. Syenites from this period exhibit elevated K₂O and LREE enrichment, interpreted as melts from metasomatized lithospheric mantle interacting with crustal components [10]. Coexisting granites display higher SiO₂ and transitional I-A type signatures, reflecting anatexis of ancient crust with mantle-derived inputs [26,27]. Notably, Cretaceous magmatism was concentrated in present coastal areas, correlates with the transition from Paleo-Pacific (Izanagi) to Pacific Plate subduction [5,6,11,28]. This period also marked a shift from Andean-type to Western Pacific-type plate margins [24,29].

Late Mesozoic magmatism predominantly reworked the Cathaysia Block, yet critical uncertainties persist, particularly regarding magma sources, evolution, and geodynamic processes. In the northeastern Cathaysia Block, extensive Cretaceous volcanic-sedimentary basins obscure early Late Mesozoic magmatic-tectonic records. Studying intrusive rocks and their enclaves provides critical insights into deep crust–mantle interactions and tectonic evolution. However, Jurassic intrusions are sparsely exposed in coastal SE China, and

their magmatic activities and tectonic settings remain poorly constrained. In this study, we present zircon U-Pb-Hf isotopes, whole-rock geochemistry, and Sr-Nd isotopes of the representative Middle Jurassic syenites and alkali-feldspar granites, and Early Cretaceous granites hosting intermediate enclaves in the Qingyuan area, southwest Zhejiang Province, northeastern (NE) Cathaysia Block, aims to constrain their petrogenesis, magma source heterogeneity and constrain the evolution of Paleo-Pacific subduction dynamics.

2. Geological Background and Samples

The South China continent comprises the Cathaysia Block in the southeast and the Yangtze Craton in the northwest [30–32] (Figure 1a). SE China, situated within the Cathaysia Block, preserves a Precambrian metamorphic basement dominated by Paleoproterozoic to Neoproterozoic metamorphic rocks, including the Badu, Longquan, and Chencai Groups [33–36]. Late Mesozoic tectono-thermal events extensively reworked SE China, accompanied by large-scale Jurassic–Cretaceous magmatism, predominantly felsic with subordinate intermediate–basaltic compositions [8,37,38]. Jurassic magmatism, mainly granitoids, is concentrated in present inland regions, while Cretaceous magmatism, characterized by widespread volcanism, dominates present coastal areas [1,5,39,40]. Zhejiang Province is traversed by three major deep fault zones from northwest to southeast: the Jiangshan-Shaoxing Fault, the Yuyao-Lishui Fault, and the Changle-Nan’ao Fault [41,42].

The Qingyuan County, located in southwestern Zhejiang Province within the northeastern (NE) Cathaysia Block (Figure 1b), exhibits limited exposures of pre-Mesozoic strata and basement metamorphic rocks. The stratigraphic sequence comprises the Lower-Middle Jurassic Fengping Formation and the Lower Cretaceous Gaowu and Xishantou Formations of Yongkang Group. The Fengping Formation is characterized by quartz sandstone-siltstone and continental coal-bearing sediments interbedded with volcanic rocks. The Gaowu Formation consists predominantly of gray tuff, whereas the Xishantou Formation features purplish-gray to gray tuff interbedded with tuffaceous siltstone and mudstone.

This study focuses on two plutons in Qingyuan County: the Middle Jurassic Kengxi complex and the Early Cretaceous Xunkeng pluton (Figure 2). In the study area, the Lower Jurassic is represented by the Fengping Formation, while the Upper Jurassic is dominated by the Gaowu and Xishantou Formations.

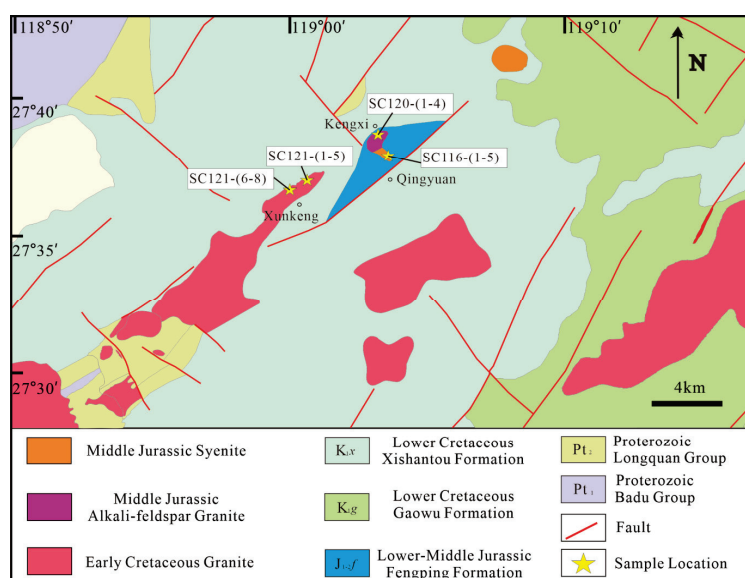


Figure 2. Geological map of the Qingyuan region in southwest Zhejiang Province with Late Mesozoic granitoid distributions.

Fresh Middle Jurassic syenite and alkali-feldspar granite samples were collected from the Kengxi pluton, located in Kengxi Village, north Qingyuan County (Figure 2). These intrusives intrude into the Early Jurassic Fengping Formation, with syenites exposed in the northern sector and alkali-feldspar granites in the southern sector. The syenites exhibit medium- to fine-grained granular textures (Figure 3a,b). The mineral composition includes alkali feldspar (45%–50%), plagioclase (20%–30%), amphibole (30%–35%) and quartz (<5%) (Figure 3b), with accessory zircon and apatite. The alkali-feldspar granites display medium- to fine-grained granular textures (Figure 3c,d), composing alkali feldspar (50%–60%), plagioclase (20%–30%), amphibole (15%–20%) and quartz (5%–10%) (Figure 3e), accompanied by accessory zircon and apatite.

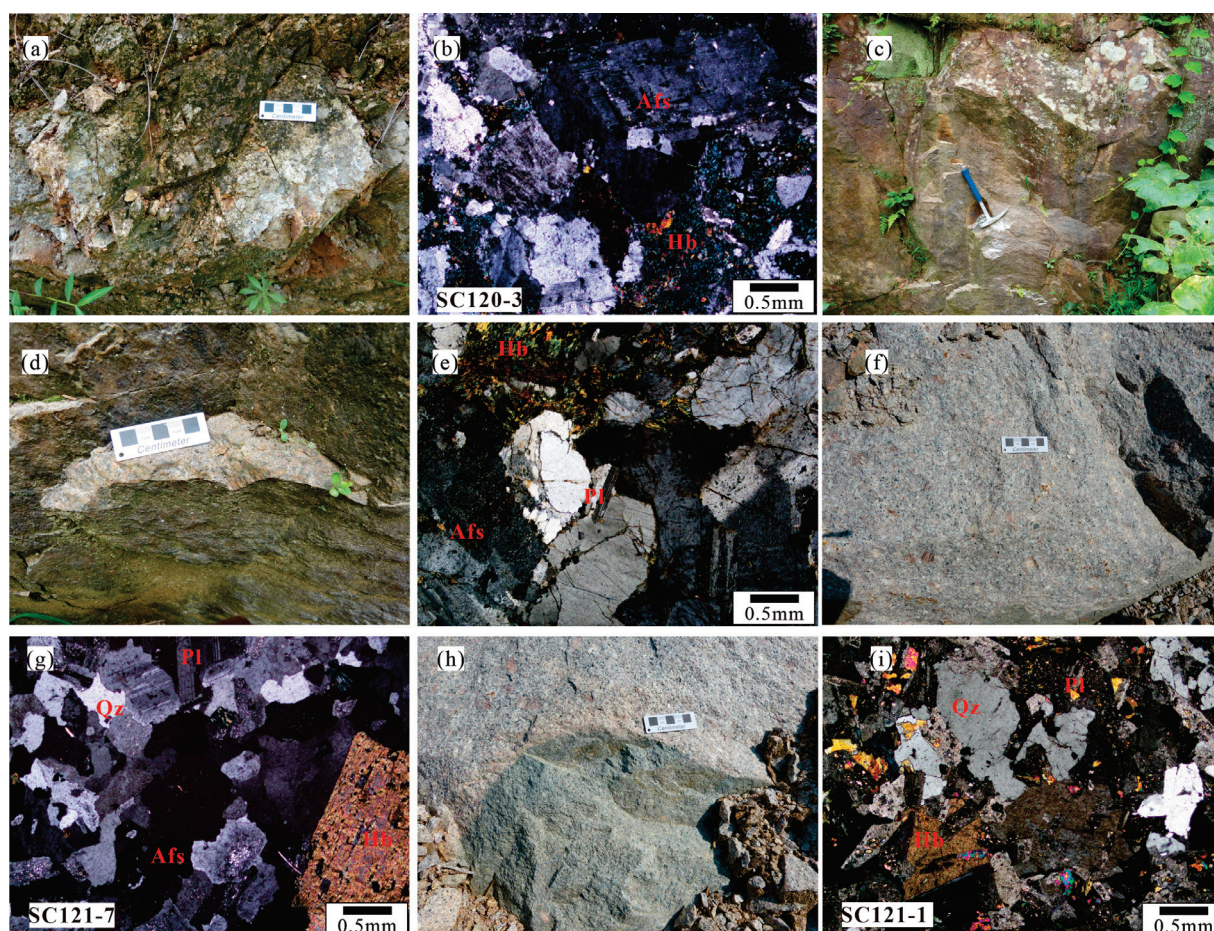


Figure 3. Photograph and photomicrographs of representative intrusive rocks in the Qingyuan region, southwest Zhejiang Province. (a) Middle Jurassic syenite; (b) Syenite sample SC120; (c,d) Middle Jurassic alkali-feldspar granite; (e) alkali-feldspar granite sample SC116; (f) Early Cretaceous granites; (g) granite sample SC121; (h) Early Cretaceous granite with intermediate enclave; (i) intermediate enclave sample SC121-1. Hb: Hornblende. Pl: plagioclase. Afs: alkali feldspar. Qz: Quartz.

Early Cretaceous granite and its enclaves were sampled from the Xunkeng pluton in Xunkeng Village, southwestern Qingyuan County (Figure 2). This pluton is mainly granite with its enclaves. The granite samples exhibit fine-grained granular textures (Figure 3f) featuring mineral grain sizes of 0.2 to 2 mm. The mineral composition of the granite includes alkali feldspar (25%–35%), plagioclase (20%–30%), quartz (25%–30%), amphibole (5%–10%) (Figure 3g), with accessory zircon and apatite. Enclaves within the granite, some exceeding 30 cm in size, display sharp angular to subrounded boundaries (Figure 3h). These gray enclaves exhibit medium- to fine-grained textures with grain sizes of 1 to 3 mm.

Their mineral composition consists of quartz (10%–15%), plagioclase (40%–50%), alkali feldspar (15%–20%), and amphibole (15%–20%) (Figure 3i).

3. Analytical Methods

3.1. Zircon U-Pb Dating

Zircon U–Pb dating was conducted by LA-ICP-MS at the Testing Center of Shandong Bureau, China Metallurgical Geology Bureau (TCSB, CMGB). Analyses utilized a Thermo Scientific iCAP™ Q ICP-MS (Thermo Fisher Scientific, Waltham, MA, USA) coupled to 193 nm ArF excimer Lasers (GeoLasPro, Coherent Inc., Santa Clara, CA, USA). Laser parameters were set to a spot size of 24 µm and repetition rate of 5 Hz in this study. Zircon 91500 served as the primary external standard for age calibration [43], while the Plešovice zircon standard (337 ± 0.37 Ma) [44] was analyzed as an unknown to monitor data quality. Detailed analytical procedures, including precision and accuracy assessments, follow those described by [45].

3.2. Whole-Rock Elemental Analysis

Major and trace element compositions of rock samples were performed at the TCSB, CMGB. Major elements were determined by X-ray fluorescence spectrometry (Thermo Scientific ARL 9900XP, Thermo Fisher Scientific, Waltham, MA, USA) on fused glass disks, with analytical accuracy better than 2%. For trace element analysis, the sample powders were digested in Teflon bombs using a mixture of hydrofluoric and nitric acids. The trace element was measured using a Thermo Scientific X Series 2 ICP-MS (Thermo Fisher Scientific, Hemel Hempstead, Hertfordshire, UK). Analytical uncertainties for most trace elements are better than 10%.

3.3. Sr-Nd Isotopic Analysis

Sr–Nd isotopic compositions of rock samples were performed at the Key Laboratory of Crust–Mantle Materials and Environments, Chinese Academy of Sciences, at the University of Science and Technology of China, Hefei., using a Finnigan MAT-262 thermal ionization mass spectrometer (TIMS, Thermo Fisher Scientific, Bremen, Germany). Measured $^{86}\text{Sr}/^{87}\text{Sr}$ and $^{146}\text{Nd}/^{144}\text{Nd}$ ratios were normalized to reference values of 0.1194 and 0.7219, respectively [46]. Detailed protocols for Sr and Nd separation and measurement are described in [47].

3.4. Zircon Lu-Hf Isotopic Analysis

In-situ zircon Hf isotopic analysis was conducted using a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Bremen, Germany) equipped with a Geolas HD excimer ArF laser ablation system (Coherent Inc., Santa Clara, CA, USA) at the Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. A 44 µm laser spot size and energy density of ~ 7.0 J/cm² were applied. Detailed analytical procedures and precision are outlined in [48]. Chondritic reference values ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$, $^{176}\text{Hf}/^{177}\text{Hf} = 0.0332$) [49] and the decay constant $\lambda^{176}\text{Lu} = 1.865 \times 10^{-11}$ /a [50] were used for $\epsilon_{\text{Hf}}(t)$ calculations.

4. Results

4.1. Zircon U-Pb Ages

Zircon U–Pb analytical data are presented in Table S1, with representative cathodoluminescence (CL) images and concordia plots shown in Figures 4 and 5. Zircons from syenite sample SC120-3 exhibit euhedral to subhedral morphologies and oscillatory zoning in CL images (Figure 4a). These grains display Th (157–1115 ppm) and U (316–985 ppm) concentrations with Th/U ratios of 0.46–1.19, indicative of magmatic origins. Twenty-six

analyses provide $^{206}\text{Pb}/^{238}\text{U}$ ages between 164 and 171 Ma. They have a weighted mean age of 167.5 ± 1.0 Ma (MSWD = 0.55, $n = 26$) (Figure 5a,b), interpreted as the crystallization age during the Middle Jurassic.

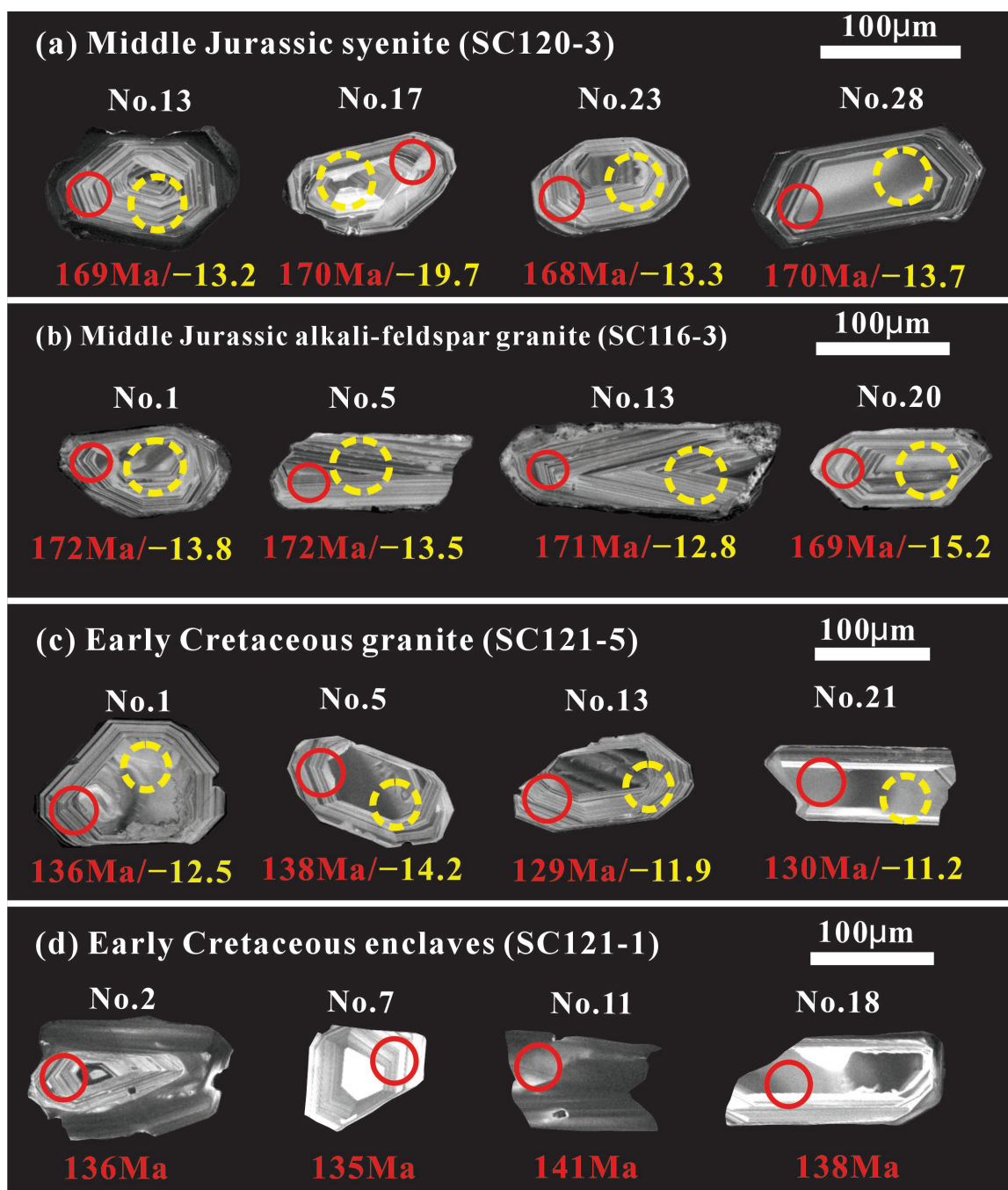


Figure 4. CL images of representative zircons from intrusive rocks in the Qingyuan region, southwest Zhejiang Province: SC120-3 (a), SC116-3 (b), SC121-5 (c), SC121-1 (d). Red solid circles indicate U–Pb dating spots and spot diameter, whereas yellow larger dashed circles indicate Hf isotopic analysis spots. Age and $\epsilon_{\text{Hf}}(t)$ values are also shown for each spot.

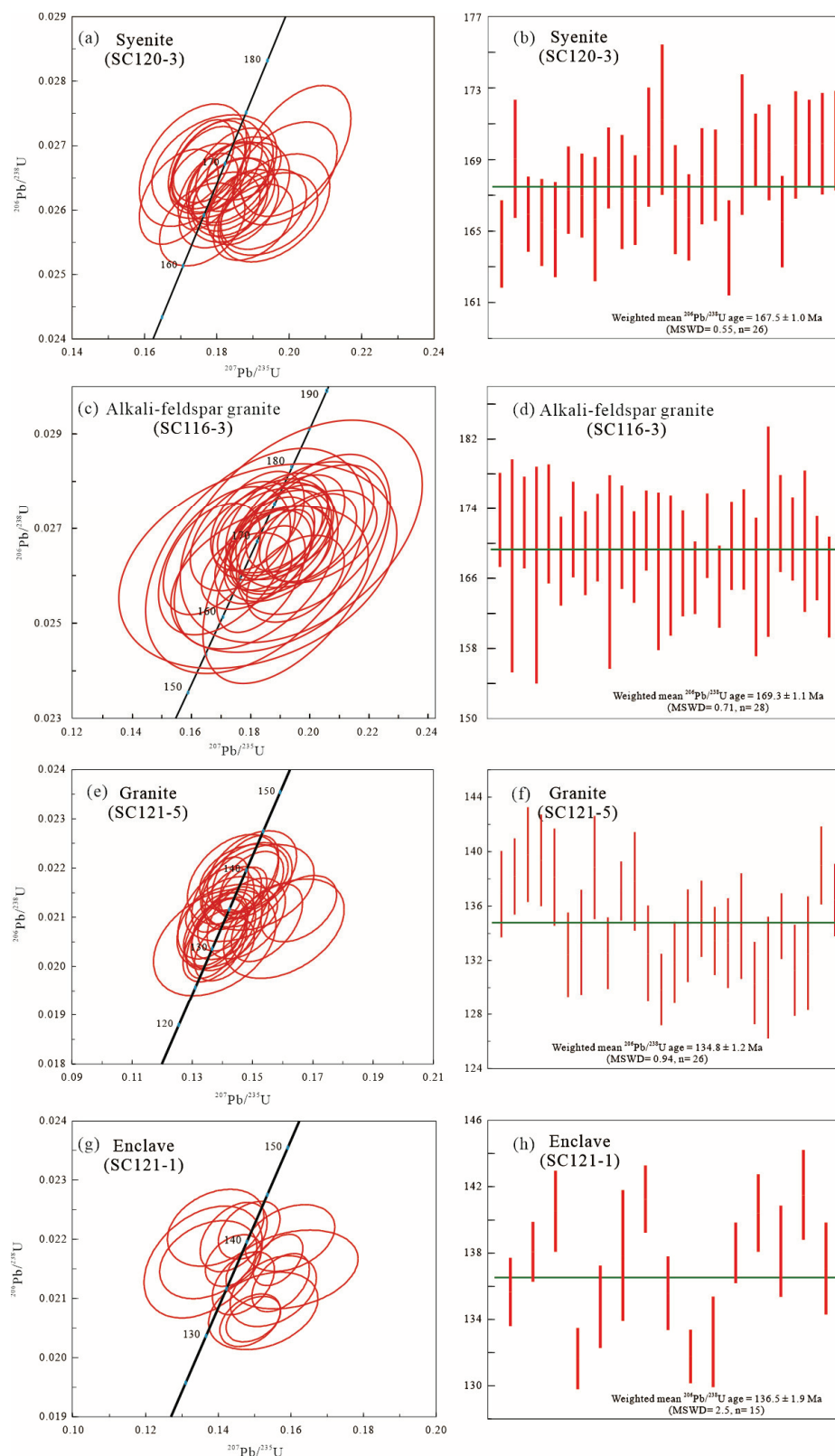


Figure 5. Zircon U–Pb concordia diagrams and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages for each sample in the Qingyuan region, southwest Zhejiang Province. SC120-3 (a,b), SC116-3 (c,d), SC121-5 (e,f), SC121-1 (g,h).

Alkali-feldspar granite sample SC116-3 contains zircons with similar oscillatory zoning (Figure 4b). These zircons contain 131–1043 ppm Th, 254–1084 ppm U, and Th/U ratios of 0.34–1.12, consistent with a magmatic origin. Twenty-eight analyses yield $^{206}\text{Pb}/^{238}\text{U}$

ages ranging from 165 to 172 Ma. They have a weighted mean age of 169.3 ± 1.1 Ma (MSWD = 0.71, $n = 28$) (Figure 5c,d), confirming Middle Jurassic magmatism.

Zircon grains from granite sample SC121-5 also contain oscillatory zoning (Figure 4c) with Th (156–4463 ppm), U (122–2250 ppm), and Th/U ratios (0.64–1.98). Twenty-six analyses yield $^{206}\text{Pb}/^{238}\text{U}$ ages of 130–140 Ma. These zircons show a weighted mean age of 135.4 ± 1.4 Ma (MSWD = 1.4, $n = 20$) (Figure 5e,f), representing the crystallization age of the granite.

Zircons from the enclave sample SC121-1 within the granite display oscillatory zoning (Figure 4d), lower Th (110–3388 ppm) and U (110–1628 ppm) concentrations but higher Th/U ratios (0.90–2.70), indicative of a magmatic origin. Fifteen analyses yield $^{206}\text{Pb}/^{238}\text{U}$ ages of 132 to 142 Ma and a weighted mean age of 136.5 ± 1.9 Ma (MSWD = 2.5, $n = 15$) (Figure 5g,h), interpreted as the crystallization age of the enclave. The elevated MSWD for enclaves suggests potential antecrystic or autocrystic contributions, warranting further population analysis [51–53].

4.2. Whole-Rock Major Elements

The major and trace elemental compositions of the samples are listed in Table S2. The Middle Jurassic syenite samples have lower SiO_2 contents (59.3–61.64 wt. %) than the alkali-feldspar granites (68.63–69.34 wt. %) (Figure 6a). They are characterized by elevated alkali contents ($\text{K}_2\text{O} = 2.47$ – 6.34 wt. %, $\text{Na}_2\text{O} = 4.03$ – 6.76 wt. %, and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios = 0.37–0.13). They also display weakly peraluminous features ($\text{A}/\text{CNK} = 1.0$ – 1.2 , $\text{A}/\text{NK} = 1.1$ – 1.5) (Figure 6b). The syenites samples exhibit higher Al_2O_3 (18.4–19.46 wt. %), MgO (1.10–1.49 wt. %) and $\text{Fe}_2\text{O}_3^{\text{T}}$ (3.91–4.40 wt. %) contents than the alkali-feldspar granites (14.86–16.27 wt. %, Al_2O_3 ; 0.55–1.04 wt. %, MgO ; 2.85–3.29 wt. %, $\text{Fe}_2\text{O}_3^{\text{T}}$), with similarly CaO (0.35–4.07 wt. %) (Figure 7). The limited variation in major element compositions suggests minimal magmatic differentiation.

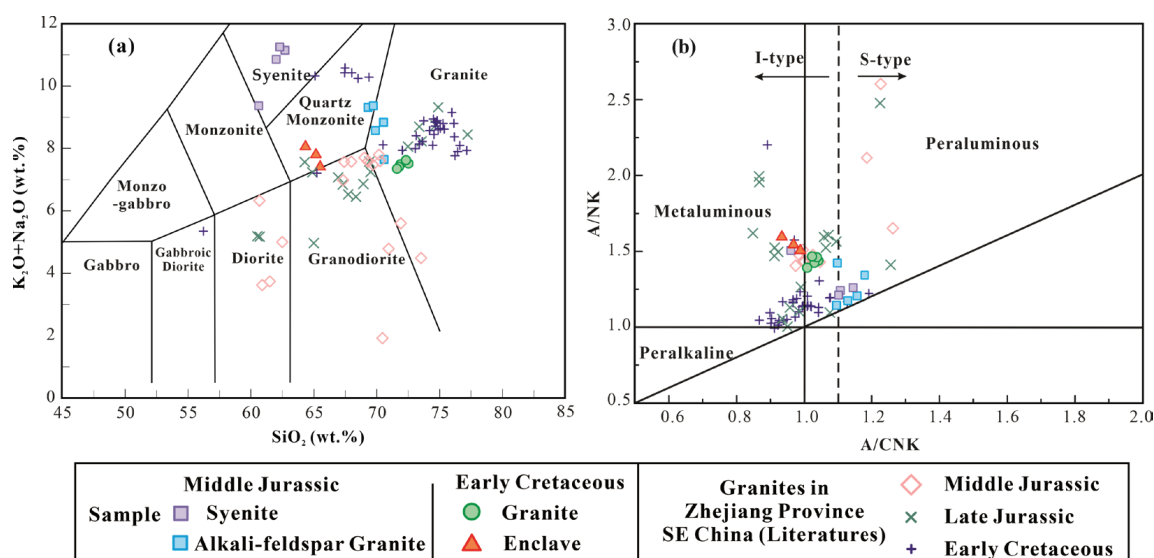


Figure 6. (a) $\text{K}_2\text{O}+\text{Na}_2\text{O}$ vs. SiO_2 diagram. All samples were normalized to 100% after accounting for loss of ignition. (b) A/NK vs. A/CNK (after [54]) diagrams. Data sources: Middle Jurassic [55–58]; Late Jurassic [40,59,60]; Early Cretaceous [37,61,62].

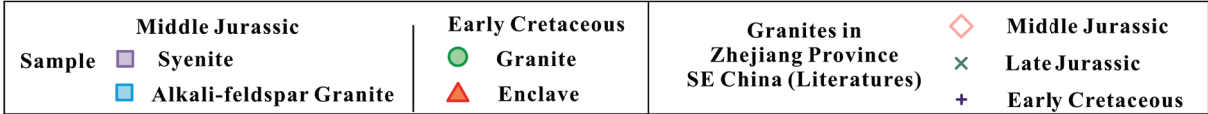


Figure 7. Variations of major elements with SiO₂. **(a)** Al₂O₃, **(b)** CaO, **(c)** Fe₂O₃^T, **(d)** MgO, **(e)** TiO₂ and **(f)** P₂O₅. Data sources are the same as in Figure 6.

In contrast, the Early Cretaceous granite samples have higher SiO₂ contents (70.56–71.85 wt. %) and are enriched in alkali elements (K₂O = 4.25–4.57 wt. %, Na₂O = 2.93–3.11 wt. %) with

higher K_2O/Na_2O ratios (1.38–1.54). They also show weak peraluminous characteristics with A/CNK of 1.01–1.04 and A/NK of 1.40–1.47 (Figure 6b). These granites have Al_2O_3 (13.78–14.12 wt. %), CaO (2.08–2.3 wt. %), MgO (0.7–0.84 wt. %) and $Fe_2O_3^T$ (2.49–2.93 wt. %) contents (Figure 7), with limited major element variation.

The intermediate enclaves within the granite exhibit moderate SiO_2 contents (61.89–64.45 wt. %) and plot within the quartz monzonite field. They have elevated alkali contents (K_2O of 3.51–3.92 wt. %, Na_2O of 3.55–4.24 wt. %, K_2O/Na_2O ratios of 0.83–1.05). These enclaves are also ranging from metaluminous to weakly peraluminous with A/CNK of 0.93–0.99 and A/NK of 1.51–1.60. They have higher contents of Al_2O_3 (15.84–16.29 wt. %), CaO (3.14–3.89 wt. %), MgO (1.40–1.52 wt. %) and $Fe_2O_3^T$ (4.47–4.54 wt. %) than those of the granites.

4.3. Whole-Rock Trace Elements

Middle Jurassic syenites ($\Sigma REE = 134.6$ – 309.5 ppm) and alkali-feldspar granites ($\Sigma REE = 101.1$ – 149.9 ppm) display right-inclined chondrite-normalized REE patterns (Figure 8a), with light rare earth element (LREE) enrichment. The syenite samples have REE ratios of $(La/Yb)_N = 9.5$ – 14.5 ; $(La/Sm)_N = 3.7$ – 4.3 ; $(Gd/Yb)_N = 1.7$ – 2.3 with negative Eu anomalies ($Eu/Eu^* = 0.53$ – 0.66). Additionally, some of them display notable negative Ce anomalies. The alkali-feldspar granites have higher $(La/Yb)_N$ (13.3–43.0), $(La/Sm)_N$ (4.0–7.0) and $(Gd/Yb)_N$ (2.3–4.1) with obvious negative Eu anomalies ($Eu/Eu^* = 0.43$ – 0.55). Primitive mantle-normalized spidergrams (Figure 8b) show large ion lithophile elements (LILEs; e.g., Rb, Th, U) enrichment and high field strength elements (HFSEs; e.g., Nb, Ta, Zr) depletion, with minor Ba and Sr depletion.

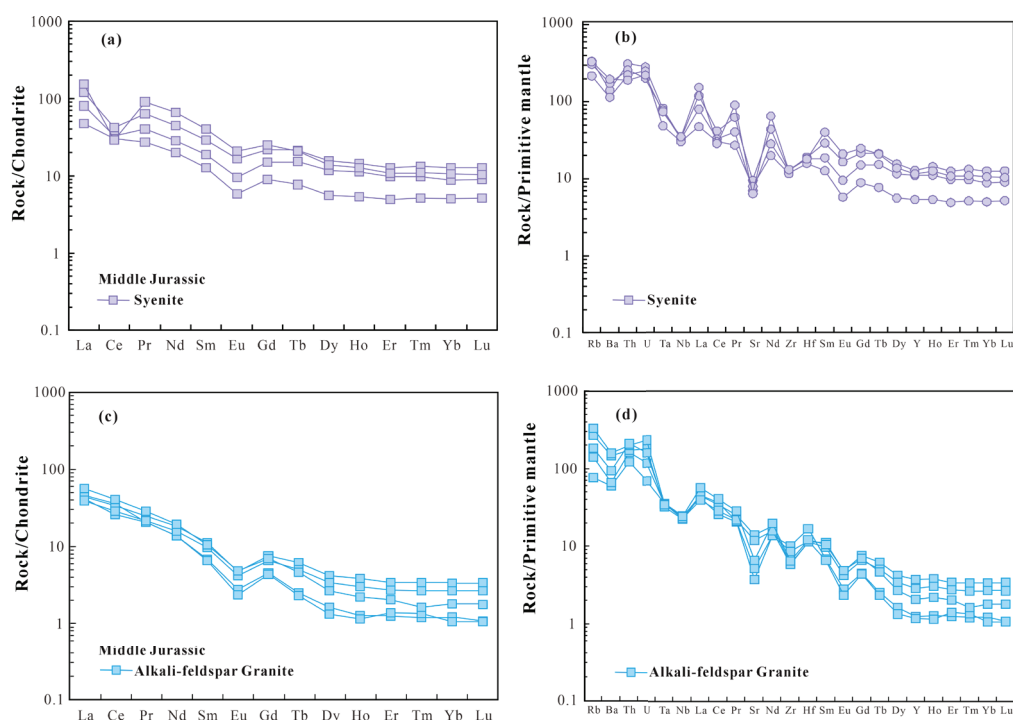


Figure 8. *Cont.*

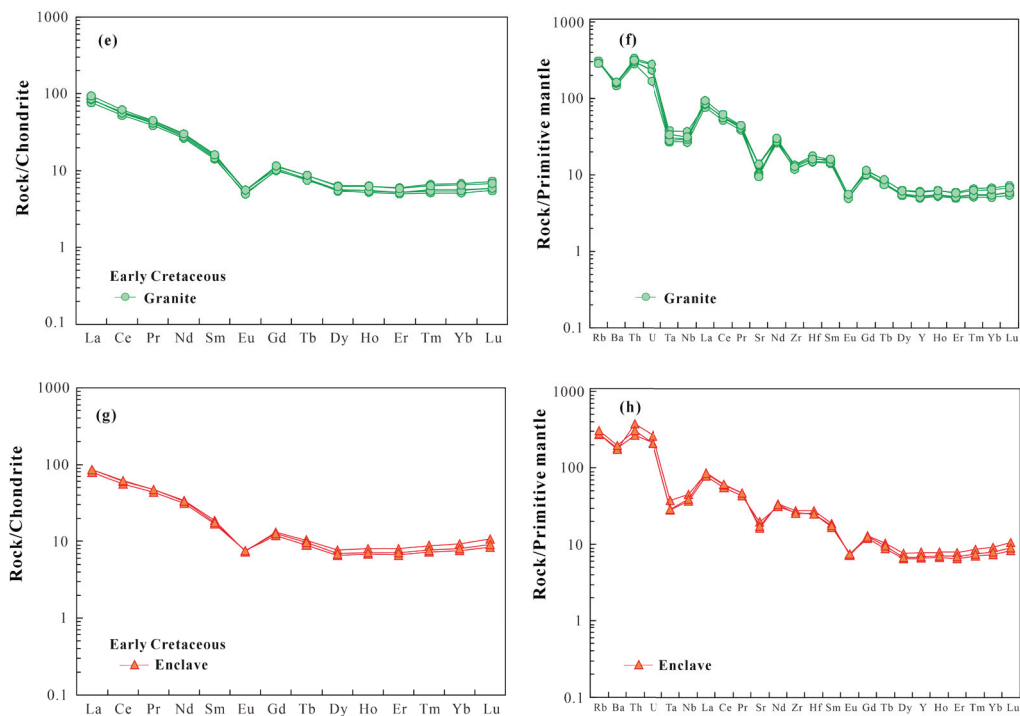


Figure 8. Chondrite-normalized REE patterns and primitive mantle-normalized spidergrams. Normalized values from [63]. (a,b) Middle Jurassic syenites; (c,d) Middle Jurassic alkali-feldspar granite; (e,f) Early Cretaceous granite; (g,h) intermediate enclaves.

Early Cretaceous granites ($\Sigma\text{REE} = 202.4\text{--}240.2$ ppm) exhibit right-inclined, indicating LREE enrichment ($(\text{La}/\text{Yb})_{\text{N}} = 12.4\text{--}15.7$; $(\text{La}/\text{Sm})_{\text{N}} = 5.3\text{--}5.9$; $(\text{Gd}/\text{Yb})_{\text{N}} = 1.7\text{--}2.0$) with obvious negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.40\text{--}0.43$), but no Ce anomaly. Compared to the Middle Jurassic samples, the granites display stronger LREE enrichment. They are similarly enriched in LILEs (e.g., Rb, Th, U) but depleted in Nb, Ta, Zr and Sr.

The enclaves within the granite have ΣREE concentrations of 223.1–244.1 ppm. Their chondrite-normalized REE patterns are right-inclined, with LREE enrichment ($(\text{La}/\text{Yb})_{\text{N}} = 9.1\text{--}10.7$; $(\text{La}/\text{Sm})_{\text{N}} = 4.5\text{--}4.9$; $(\text{Gd}/\text{Yb})_{\text{N}} = 1.4\text{--}1.6$) with similar negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.46\text{--}0.52$). Like the granites, the enclaves are enriched in LILEs (e.g., Rb, Th, U) but depleted in Nb, Ta and Sr. Zr and Hf anomalies are insignificant.

4.4. Whole-Rock Sr-Nd Isotopic Compositions

The Sr–Nd isotopic compositions of samples are listed in Table S3. The Middle Jurassic syenite and alkali-feldspar granite samples exhibit measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios ranging from 0.511904 to 0.511926 and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.717544 and 0.718494. Their calculated initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are calculated to be 0.711921–0.714026, with $\epsilon_{\text{Nd}}(t)$ values of -12.36 to -12.17 (Figure 9) and two-stage Nd model ages (T_{DM}^2) of 1.67–1.69 Ga.

The Early Cretaceous granite samples display initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.711949 to 0.713118, with $\epsilon_{\text{Nd}}(t)$ values of -12.70 to -12.61 and T_{DM}^2 ages of 1.68–1.69 Ga. Meanwhile, the enclaves within the granite yield similar initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.713148 to 0.713302, with $\epsilon_{\text{Nd}}(t)$ values of -12.84 to -12.64 and T_{DM}^2 ages of 1.68–1.70 Ga.

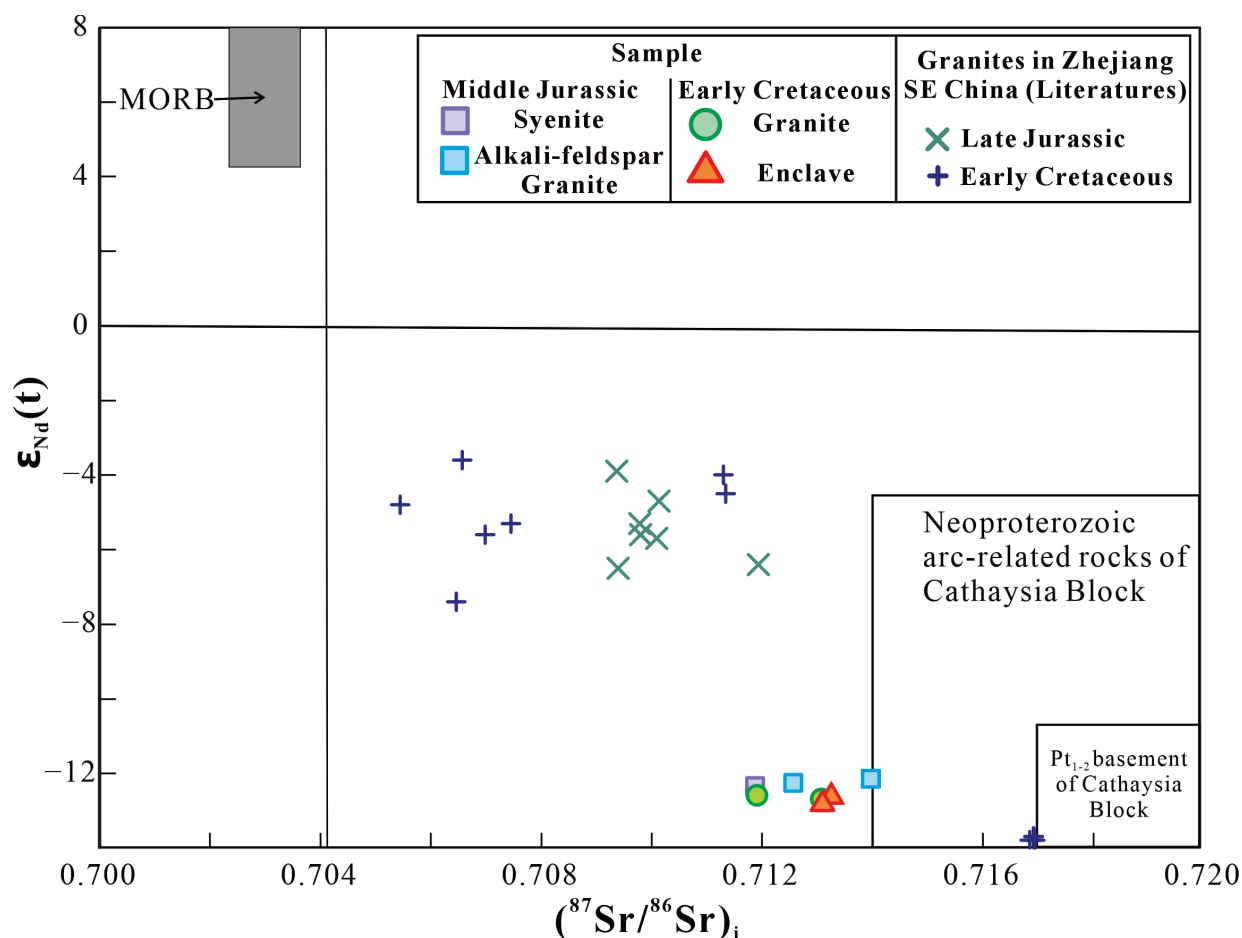


Figure 9. Whole-rock $(^{87}\text{Sr}/^{86}\text{Sr})_i$ vs. $\epsilon_{\text{Nd}}(t)$ value diagram. Data sources are the same as in Figure 6.

The Sr–Nd isotopic compositions of these samples are different from other Jurassic to Early Cretaceous granites in the Zhejiang Province (Figure 9).

4.5. Zircon Hf Isotopic Compositions

Zircon in situ Lu–Hf isotopic analyses were conducted on zircon crystals previously dated by U–Pb methods, with the results, are listed in Table S4. The zircon from the Middle Jurassic syenite samples exhibit measured $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of 0.282117–0.282294. Their $\epsilon_{\text{Hf}}(t)$ values vary from -13.19 to -19.66 (Figure 10), corresponding to two-stage Hf model ages of 2.05–2.45 Ga. The zircon grains from the alkali-feldspar granite also show comparable Lu–Hf isotopic compositions, with $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of 0.282210–0.282309. Their $\epsilon_{\text{Hf}}(t)$ values span a range from -12.80 to -16.26 , with two-stage Hf model ages of 2.03–2.24 Ga.

The zircon from the Early Cretaceous granite samples display measured $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of 0.282284–0.282375. Their $\epsilon_{\text{Hf}}(t)$ values range from -11.18 to -14.43 , with two-stage Hf model ages of 1.90–2.10 Ga.

The Hf isotopic compositions of zircon samples are different from the zircon grains of the Jurassic to Early Cretaceous granites in the Zhejiang Province (Figure 10).

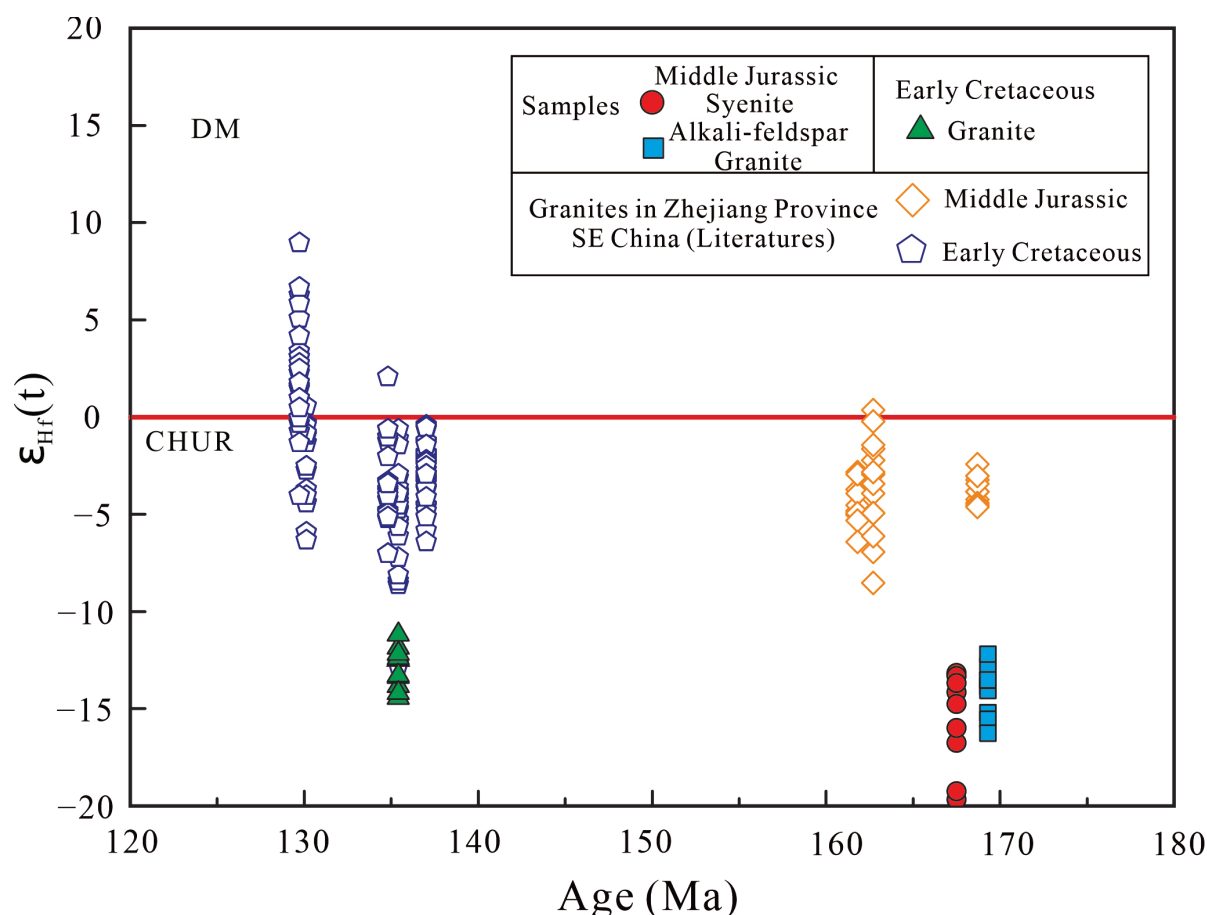


Figure 10. Zircon $^{206}\text{Pb}/^{238}\text{U}$ ages vs. $\epsilon_{\text{Hf}}(t)$ value diagram. Data sources are the same as in Figure 6.

5. Discussion

5.1. Petrogenesis and Sources of Middle Jurassic Syenite

In SE China, the Jurassic (178–165 Ma) syenites and syenite-granite suits are predominantly distributed in the inland Nanling Range region [9,64], contrasting with Cretaceous (particularly Late Cretaceous) syenites that dominate coastal regions [64]. This study focuses on Middle Jurassic syenite and alkali-feldspar granite samples from Zhejiang Province. The syenite samples exhibit typical syenitic compositions in the TAS diagram (Figure 6). Their geochemical signatures are distinct from most other Jurassic and Cretaceous granitoids in Zhejiang Province (Figure 8). Pronounced negative Eu and Sr anomalies, coupled with Ba depletion (Figures 8 and 11b), further support the fractional crystallization of feldspar.

The genesis of syenites is generally interpreted as the partial melting of sub-continental lithospheric mantle [9,10,17,22]. Cretaceous syenites in coastal SE China typically show positive whole-rock $\epsilon_{\text{Nd}}(t)$ and zircon $\epsilon_{\text{Hf}}(t)$ values, indicating derivation from a fertile lithospheric mantle metasomatized by subduction-related fluids/melts [9] or magma mixing between depleted asthenospheric melts and enriched mantle melts [10]. The studied syenite samples show negative whole-rock $\epsilon_{\text{Nd}}(t)$ and zircon $\epsilon_{\text{Hf}}(t)$ values (Figures 9 and 10). These isotopic characteristics of syenite are similar to the Late Mesozoic syenites in SE China, which are similar to EM2-type lithospheric mantle [9,64]. These features are usually explained by parental magma derived from an enriched lithospheric mantle source [10,65,66]. Their trace element patterns, including LILE enrichment and HFSE depletion, are characteristic of the subduction-modified mantle. Notably, the negative Ce anomalies in the syenites are commonly associated with the involvement of subducting

marine sediments prior to mantle melting [67,68]. Thus, the studied syenites are inferred to originate from the partial melting of an enriched lithospheric mantle metasomatized by subducted sedimentary materials.

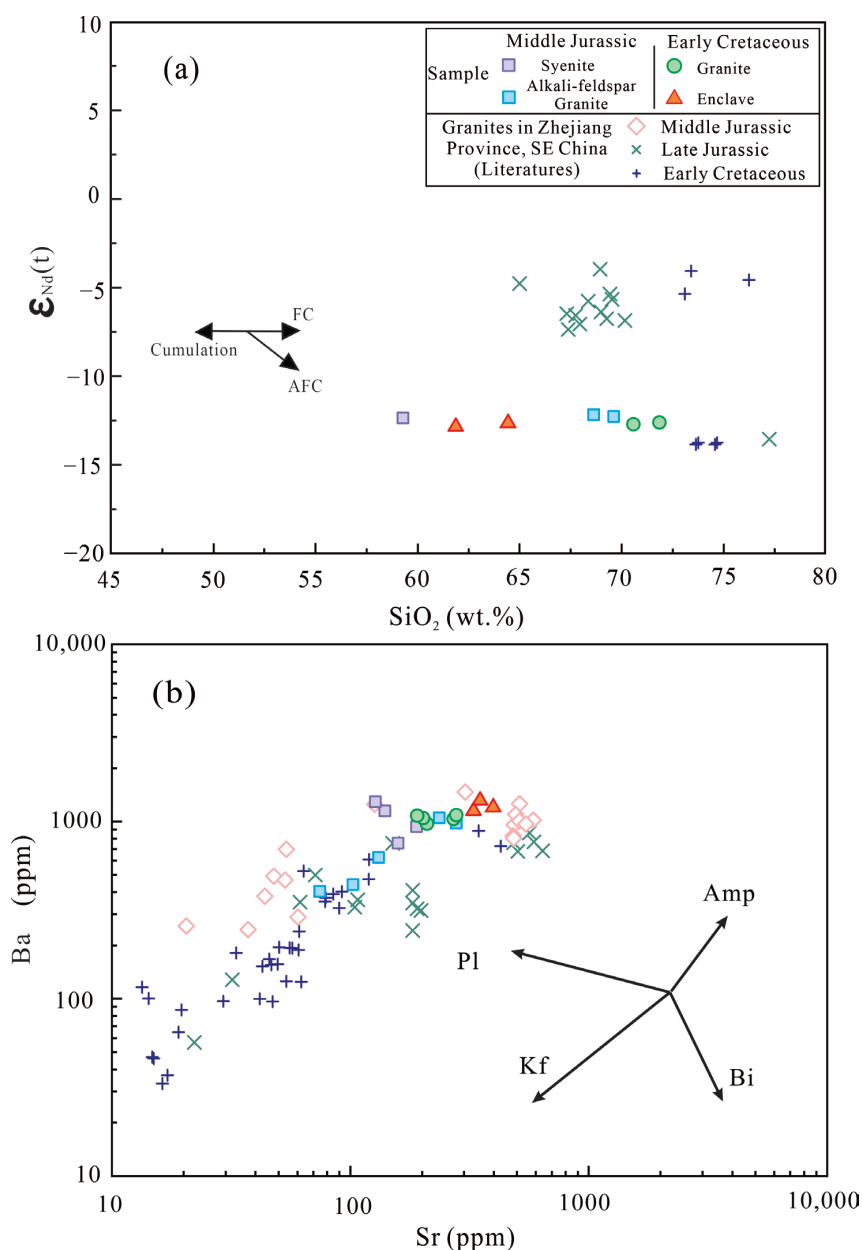


Figure 11. (a) $\epsilon_{Nd}(t)$ values vs. SiO_2 contents; (b) Ba (ppm) vs. Sr (ppm) diagrams. Data sources are the same as in Figure 6.

5.2. Petrogenesis and Sources of Middle Jurassic Alkali-Feldspar Granite

The geochemical signatures of the studied Middle Jurassic syenites and alkali-feldspar granites display scattered patterns in classification diagrams (Figure 6), indicating heterogeneous source compositions and evolutionary processes. The alkali-feldspar granites are characterized by higher silica and lower alkali contents compared to coeval syenites. Their geochemical compositions are different from those of Middle to Late Jurassic granitoids in Zhejiang Province (Figure 7). They also show limited variation in the Nd isotope with increasing SiO_2 (Figure 11a), indicating a fractional crystallization process. Most of them plot within the fields of fractionated granitoid rocks in rock classification diagrams

(Figure 12b,c). Pronounced negative Eu and Sr anomalies, coupled with systematic Ba and Sr depletions (Figure 11b), further support feldspar fractionation.

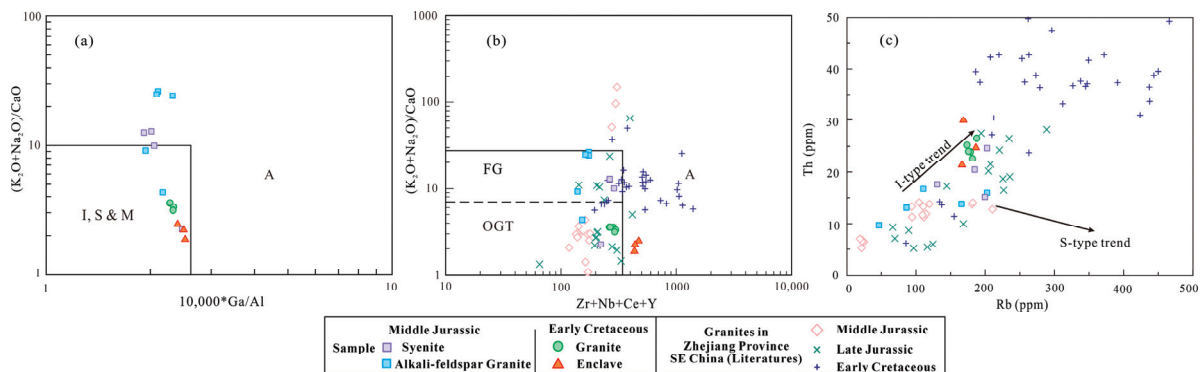


Figure 12. (a) Th vs. Rb; (b) $(K_2O + Na_2O)/CaO$ vs. $10,000 \cdot Ga/Al$; (c) $(K_2O + Na_2O)/CaO$ vs. $(Zr + Nb + Ce + Y)$ diagrams. Trends of I- and S- type granites [69]. Fields for I, S and M type granites (I, S and M), A-type granites (A), fractionated felsic granites (FG), unfractionated M-, I- and S-type granites (OGT) from [70]. Data sources are the same as in Figure 6.

The alkali-feldspar granites plot near the boundary between S- and I-type granites in the A/CNK-A/NK diagram. However, some other geochemical features of them are similar to the I-type granitoid rocks (Figures 6b and 12c). It implies that they have a transitional character. The sources of granitoids are often inferred from experimental melts of various lithologies [71]. The geochemical compositions of the alkali-feldspar granites exhibit pronounced scattering across the compositional fields defined by various source components (Figure 13a–c) and do not cluster within any specific end-member compositional field as illustrated in discrimination diagrams (Figure 8). Compared to syenites, the alkali-feldspar granites display higher zircon Hf isotopic compositions (Figure 10) and Nd isotopic signatures closer to those of the Cathaysia Block basement (Figure 9). However, the syenites and granites exhibit a distinct geochemical discontinuity, defining two compositionally discrete clusters in geochemical diagrams (Figures 6, 7 and 13). Meanwhile, the zircon U-Pb dating also shows the alkali-feldspar granite formation earlier than the syenites. These isotopic features, combined with magmatic evolution trends, suggest that the alkali-feldspar granites could derived from the partial melting of the basement of the Cathaysia Block.

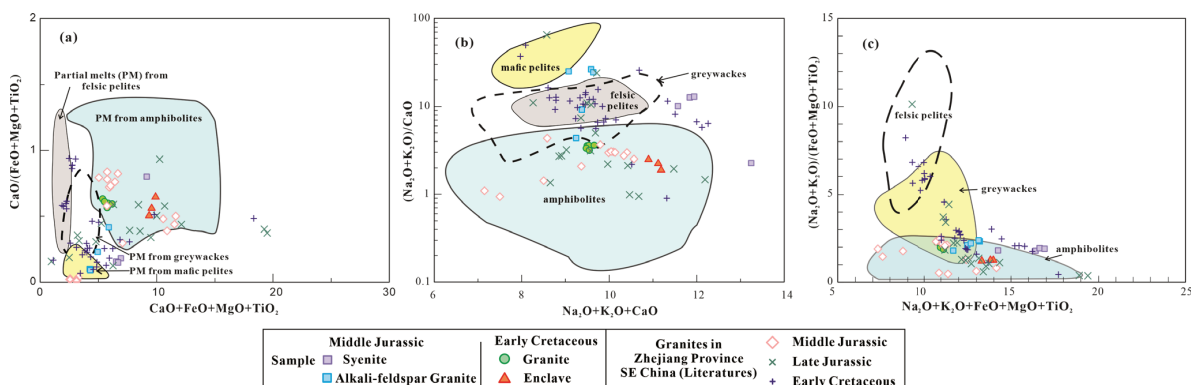


Figure 13. (a) $CaO/(FeO + MgO + TiO_2)$ vs. $CaO + FeO + MgO + TiO_2$; (b) $(Na_2O + K_2O)/CaO$ vs. $Na_2O + K_2O + CaO$; (c) $(Na_2O + K_2O)/(FeO + MgO + TiO_2)$ vs. $Na_2O + K_2O + FeO + MgO + TiO_2$. The compositions of melts produced by experimental melting of various lithologies and different granites are from [71]. Data sources are the same as in Figure 6.

5.3. Petrogenesis of Early Cretaceous Granite and Their Intermediate Enclave

5.3.1. Early Cretaceous Granite

The Early Cretaceous granite samples exhibit high-silica compositions (70.56–71.85 wt. %, SiO_2) and weakly peraluminous features. Their geochemical compositions resemble most Late Mesozoic granitoids in Zhejiang Province, though they differ slightly from some Cretaceous granitoids (Figure 7). These granites plot within the fields of unfractionated I-, S-, and M-type granitoids (Figure 12a,b). The elemental variation ranges observed in these granites suggest that they have undergone little fractional crystallization during their magmatic evolution. The geochemical classification of Early Cretaceous granite samples further supports their affinity to I-type granitoids (Figures 6b and 12c).

I-type granites are typically derived from igneous (meta-igneous) protoliths [72], distinct from intermediate crustal sources (e.g., tonalitic or granodioritic) that generate high-silica melts ($\text{SiO}_2 > 75$ wt. %) [71]. Their formation involves partial melting of mafic crustal sources (e.g., metabasalts, amphibolites) at lower- to mid-crustal depths (Figure 13) [73]. The genesis of Late Cretaceous I-type granitoids in coastal regions of SE China often reflects crust-mantle interactions with juvenile mantle-derived magmas (e.g., underplated basalts) [25,39]. These Late Cretaceous I-type granitoids show higher whole-rock $\epsilon_{\text{Nd}}(t)$ and zircon $\epsilon_{\text{Hf}}(t)$ values, which are near zero, implying the crustal- and mantle-derived magma mixing [39]. However, the Early Cretaceous granite samples show negative whole-rock $\epsilon_{\text{Nd}}(t)$ values (−12.70 to −12.61) and zircon $\epsilon_{\text{Hf}}(t)$ values (−19.57 to −13.16) (Figures 9 and 10). It suggests that they could be crustal-derived magmas formed by the melting of mafic crustal sources of basements.

5.3.2. Intermediate Enclave

The intermediate enclaves within the Early Cretaceous granites exhibit metaluminous characteristics, plotting near I-type granite fields in A/CNK-A/NK diagrams (Figures 6b and 12c). They plot within the fields of I-, S-, and M-type granites but out of fields of fractionated and unfractionated rocks on rock classification diagrams (Figure 12a,b), implying their features of I-type granites. The enclaves show limited variation in the Nd isotope with increasing SiO_2 (Figure 11a), indicating a fractional crystallization process. Variations in Ba and Sr contents further support fractional crystallization of amphibole (Figure 11b).

The origins of enclaves in granitoid rocks are usually explained by several models, such as magma mixing, crystallization products, and crustal xenoliths [74,75]. The enclaves formed by the mixing of mantle-derived mafic and crustal-felsic magmas are usually mafic microgranular enclaves (MMEs) and have different whole-rock $\epsilon_{\text{Nd}}(t)$ and zircon $\epsilon_{\text{Hf}}(t)$ values than the host rocks, implying the contribution of mantle-derived magma, which usually linked the crust-mantle interaction [26,74]. As to the crustal xenoliths, the enclaves are considered fragments of wall rocks captured during granite emplacement, which usually have obviously different geochemical features to the host rocks [76]. Enclaves result from the early-crystallized mafic minerals, and differentiation of magma is usually the concentration of minerals that are entrained within the granitic magma [75]. The characteristics of geochemistry indicated that the intermediate enclaves have the origin of fractional crystallization in the early stage of magma evolution. Their whole-rock $\epsilon_{\text{Nd}}(t)$ and the geochemical feature are similar to the host rocks and also indicate that their formation is closely linked to partial melting of mafic crustal sources, such as metabasaltic or amphibolites (Figure 13). Then, the intermediate enclaves formed as earlier crystallization products from genetically related granitic magmas subsequently entrained during magma ascent.

5.4. Implications for Crust-Mantle Interaction and Geodynamic Process

Jurassic-Cretaceous magmatism in SE China reflects a complex interplay between subduction dynamics, lithospheric evolution, and crust-mantle interactions [5,8,9,14,15,77]. Various tectonic models have been proposed to explain the Late Mesozoic geodynamic processes associated with the Paleo-Pacific Plate subduction beneath SE China, including changes in subduction angle [1], flat-slab subduction and foundering [18], oblique with ridge subduction [78] and repeated slab advance–retreat [16]. The Cretaceous lithospheric extension beneath SE China has been attributed to the slab rollback of the subducted Paleo-Pacific Plate [10].

The earliest Jurassic magmatism (200–180 Ma), represented by alkaline basalts and A-type granites in the Nanling Belt, likely reflects localized lithospheric delamination following the Indosinian orogeny [79,80]. Middle-Late Jurassic magmatism (170–150 Ma) along the Qin-Hang Belt records enhanced crust-mantle interaction, characterized by I-type granitoids and coeval mafic dikes [23,79]. These processes are linked to the westward subduction of the Paleo-Pacific Plate, which induced extension and triggered partial melting of both metasomatized lithospheric mantle and rejuvenated lower crust [10].

The SE China underwent a fundamental Mesozoic tectonic transition [5]. However, the initiation of Paleo-Pacific Plate subduction and the transition from compressional to extensional regimes during the Mesozoic era are still debated. For example, the Jincheng Early Jurassic granites in Fujian Province exhibit volcanic arc geochemical signatures, suggesting that oblique subduction of the Paleo-Pacific Plate commenced as early as the Early Jurassic [81]. Concurrently, Late Jurassic–Early Cretaceous (153–133 Ma) volcanic rocks in the Zhejiang-Fujian regions are usually weakly peraluminous I-type rhyolitic volcanic rocks display syn-collisional volcanic arc granite affinities, indicative of formation in a transitional tectonic setting [82]. Meanwhile, the Early-Middle Jurassic peraluminous high-K calc-alkaline volcanic rocks in southern Zhejiang Province exhibit volcanic arc characteristics, indicating that they had been influenced by the Paleo-Pacific Plate subduction [83]. During the Middle Jurassic, the Paleo-Pacific Plate subduction could induce mantle wedge-derived melts incorporating oceanic sediments and subducted slab components under the compressional regime (Figure 14a). In this study, the syenite samples are suggested to be derived from the partial melting of an enriched lithospheric mantle source, which is metasomatized by subducted sedimentary materials. The alkali-feldspar granites could be derived from the partial melting of the basement of the Cathaysia Block. These processes imply that the lithosphere of NE Cathaysia Block was influenced by the subduction of the Paleo-Pacific Plate during the Middle Jurassic.

From the Late Jurassic to the Early Cretaceous, the Paleo-Pacific Plate transitioned from low-angle advancing subduction to high-angle retreating subduction, accompanied by subducting slab rollback [8,16]. It implies a tectonic regime shift from compression to extension in SE China. By the Early Cretaceous (145–100 Ma), the magmatism migrated progressively coastward, characterized by a petrochemical transition from calc-alkaline to A-type affinities and the emergence of bimodal volcanic suites (basalt-rhyolite associations) [5,38,84,85]. The studied Early Cretaceous granites and intermediate enclaves were formed in 136–134 Ma. This is the early period of the Cretaceous tectonic transition, and the samples mainly show the melting of ancient basements of the NE Cathaysia Block. By the Early to Late Cretaceous, the slab rollback or retreating subduction continued and induced large-scale lithospheric thinning and asthenospheric upwelling with basaltic underplating beneath SE China, marked by widespread magmatic activity [25,86] (Figure 14b).

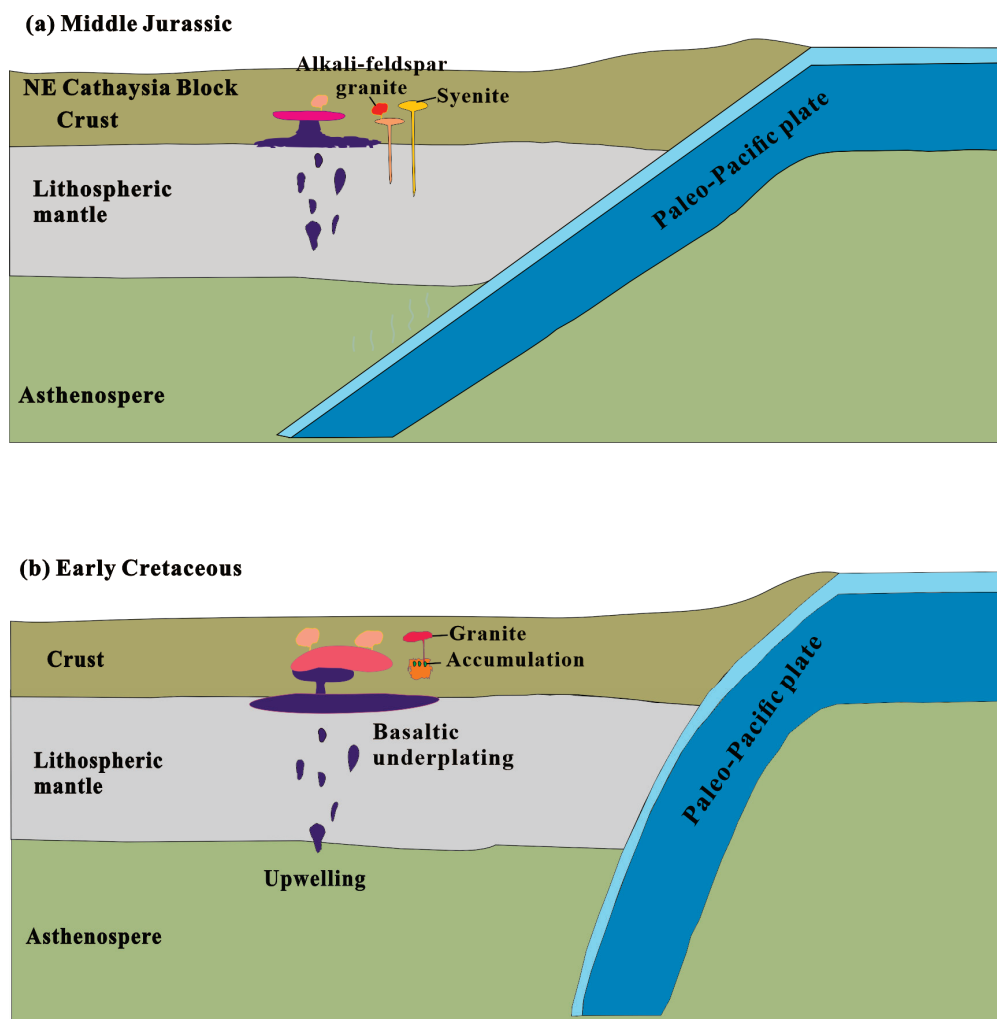


Figure 14. (a,b) Schematic cartoon for the genesis of the intrusive rocks beneath the southwest Zhejiang Province, NE Cathaysia Block.

6. Conclusions

- (1) The Middle Jurassic alkali-feldspar granites (169 Ma) and syenites (167 Ma) both exhibit subduction-related geochemical signatures. The syenites in the NE Cathaysia formed from metasomatized lithospheric mantle, while coeval alkali-feldspar granites derived from partial melting of the basement of the Cathaysia Block.
- (2) The Early Cretaceous granites (134 Ma) and their intermediate enclaves (136 Ma) are high-K calc-alkaline and weakly peraluminous to metaluminous. The granites and enclaves originated from lower crustal mafic melting, with enclaves representing earlier crystallization products, which were then mechanically mixed with granite.
- (3) The crustal reworking of NE Cathaysia Block transitioned from Middle Jurassic subduction-driven compression to Early Cretaceous extension due to slab rollback.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min15050474/s1>, Table S1: Zircon in-situ U-Pb isotopic compositions of the Middle Jurassic syenite-granite and Early Cretaceous granite with its enclave in SW Zhejiang, SE China; Table S2: Whole-rock major, trace elemental compositions of the Middle Jurassic syenite-granite and Early Cretaceous granite with its enclave in SW Zhejiang, SE China; Table S3: Whole-rock Sr-Nd isotopic compositions of the Middle Jurassic syenite-granite and Early Cretaceous granite with its enclave in SW Zhejiang, SE China; Table S4: Zircon in-situ Hf isotopic compositions

of the Middle Jurassic syenite-granite and Early Cretaceous granite with its enclave in SW Zhejiang, SE China.

Author Contributions: Conceptualization, Y.W. and H.L.; methodology, Y.W. and Y.Z.; software, Y.W. and H.L.; validation, Y.W. and C.J.; formal analysis, Y.W.; investigation, C.J.; resources, Y.Z.; data curation, Y.W.; writing—original draft preparation, Y.W. and H.L.; writing—review and editing, H.L.; visualization, Y.W. and H.L.; supervision, Y.Z. and C.J.; project administration, H.L. and C.J.; funding acquisition, H.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Science and Technology Innovation Project of Laoshan Laboratory, grant number LSKJ202204403, the Opening Foundation of Key Lab of Submarine Geosciences and Prospecting Techniques, MOE, Ocean University of China, grant number SGPT-2024OF-02.

Data Availability Statement: All data generated or analyses are included within this study and its Supplementary Materials.

Acknowledgments: We thank the reviewers and editors for their constructive comments and detailed suggestions, which greatly improved the manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Zhou, X.M.; Sun, T.; Shen, W.Z.; Shu, L.S.; Niu, Y.L. Petrogenesis of Mesozoic Granitoids and Volcanic Rocks in South China: A Response to Tectonic Evolution. *Episodes* **2006**, *29*, 26–33. [CrossRef] [PubMed]
2. Isozaki, Y.; Aoki, K.; Nakama, T.; Yanai, S. New Insight into a Subduction-Related Orogen: A Reappraisal of the Geotectonic Framework and Evolution of the Japanese Islands. *Gondwana Res.* **2010**, *18*, 82–105. [CrossRef]
3. Müller, R.D.; Seton, M.; Zahirovic, S.; Williams, S.E.; Matthews, K.J.; Wright, N.M.; Shephard, G.E.; Maloney, K.T.; Barnettmoore, N.; Hosseinpour, M. Ocean Basin Evolution and Global-Scale Plate Reorganization Events Since Pangea Breakup. *Annu. Rev. Earth Planet. Sci.* **2016**, *44*, 107–138. [CrossRef]
4. Li, J.; Dong, S.; Cawood, P.A.; Zhao, G.; Johnston, S.T.; Zhang, Y.; Xin, Y. An Andean-Type Retro-Arc Foreland System Beneath Northwest South China Revealed by SINOPROBE Profiling. *Earth Planet. Sci. Lett.* **2018**, *490*, 170–179. [CrossRef]
5. Li, S.Z.; Suo, Y.H.; Li, X.Y.; Zhou, J.; Santosh, M.; Wang, P.C.; Wang, G.Z.; Guo, L.L.; Yu, S.Y.; Lan, H.Y.; et al. Mesozoic Tectono-Magmatic Response in the East Asian Ocean-Continent Connection Zone to Subduction of the Paleo-Pacific Plate. *Earth-Sci. Rev.* **2019**, *192*, 91–137. [CrossRef]
6. Guo, F.; Wu, Y.; Zhang, B.; Zhang, X.; Zhao, L.; Liao, J. Magmatic Responses to Cretaceous Subduction and Tearing of the Paleo-Pacific Plate in SE China: An Overview. *Earth-Sci. Rev.* **2021**, *212*, 103448. [CrossRef]
7. Wang, X.L.; Liu, J.X.; Lü, Q.T.; Wang, S.; Wang, D.; Chen, X. Evolution of Deep Crustal Hot Zones Constrained by the Diversity of Late Mesozoic Magmatic Rocks in SE China. *Ore Geol. Rev.* **2021**, *134*, 104143. [CrossRef]
8. Xu, X.; Zhao, K.; He, Z.; Liu, L.; Hong, W. Cretaceous Volcanic-Plutonic Magmatism in SE China and a Genetic Model. *Lithos* **2021**, *402–403*, 105728. [CrossRef]
9. Yang, J.; Zhang, J.; Chen, J.; Sun, J. Mesozoic Continental Crustal Rejuvenation of South China: Insights from Zircon HfO Isotopes of Early Jurassic Gabbros, Syenites and a-Type Granites. *Lithos* **2021**, *402–403*, 105678. [CrossRef]
10. He, Z.Y.; Xu, X.S. Petrogenesis of the Late Yanshanian Mantle-Derived Intrusions in Southeastern China: Response to the Geodynamics of Paleo-Pacific Plate Subduction. *Chem. Geol.* **2012**, *328*, 208–221. [CrossRef]
11. Zhao, L.; Guo, F.; Zhang, X.; Wang, G. Cretaceous Crustal Melting Records of Tectonic Transition from Subduction to Slab Rollback of the Paleo-Pacific Plate in SE China. *Lithos* **2021**, *384–385*, 105985. [CrossRef]
12. Xu, X.S.; Xie, X. Late Mesozoic-Cenozoic Basaltic Rocks and Crust-Mantle Interaction, SE China. *Geol. J. China Univ.* **2005**, *11*, 318–334. [CrossRef]
13. Li, J.H.; Cawood, P.A.; Ratschbacher, L.; Zhang, Y.Q.; Dong, S.W.; Xin, Y.J.; Yang, H.; Zhang, P.X. Building Southeast China in the Late Mesozoic: Insights from Alternating Episodes of Shortening and Extension Along the Lianhuashan Fault Zone. *Earth-Sci. Rev.* **2020**, *201*, 103056. [CrossRef]
14. Suo, Y.; Li, S.; Cao, X.; Wang, X.; Somerville, I.; Wang, G.; Wang, P.; Liu, B. Mesozoic-Cenozoic Basin Inversion and Geodynamics in East China: A Review. *Earth-Sci. Rev.* **2020**, *210*, 103357. [CrossRef]
15. Xu, X.; Huang, Z.; Jiang, D.; Zeng, G.; Dai, L. Remnants and Fragments of the Subducted Paleo-Pacific Plate: Constraints From Geochemistry and Geophysics. *Sci. China Earth Sci.* **2024**, *67*, 3041–3061. [CrossRef]
16. Jiang, Y.H.; Wang, G.C.; Liu, Z.; Ni, C.Y.; Qing, L.; Zhang, Q. Repeated Slab Advance–Retreat of the Palaeo-Pacific Plate Underneath SE China. *Int. Geol. Rev.* **2015**, *57*, 472–491. [CrossRef]

17. Wang, Q.; Li, J.W.; Jian, P.; Zhao, Z.H.; Xiong, X.L.; Bao, Z.W.; Xu, J.F.; Li, C.F.; Ma, J.L. Alkaline Syenites in Eastern Cathaysia (South China): Link to Permian-Triassic Transtension. *Earth Planet. Sci. Lett.* **2005**, *230*, 339–354. [CrossRef]
18. Li, Z.X.; Li, X.H. Formation of the 1300-Km-Wide Intracontinental Orogen and Postorogenic Magmatic Province in Mesozoic South China: A Flat-Slab Subduction Model. *Geology* **2007**, *35*, 179–182. [CrossRef]
19. Meng, L.; Li, Z.; Chen, H.; Li, X.; Zhu, C. Detrital Zircon U–Pb Geochronology, Hf Isotopes and Geochemistry Constraints on Crustal Growth and Mesozoic Tectonics of Southeastern China. *J. Asian Earth Sci.* **2015**, *105*, 286–299. [CrossRef]
20. Sun, T. A New Map Showing the Distribution of Granites in South China and Its Explanatory Notes. *Geol. Bull. China* **2006**, *25*, 332–335.
21. Li, B.; Jiang, S.Y.; Lu, A.H.; Lai, J.Q.; Zhao, K.D.; Yang, T. Petrogenesis of Late Jurassic Granodiorites from Gutian, Fujian Province, South China: Implications for Multiple Magma Sources and Origin of Porphyry Cu–Mo Mineralization. *Lithos* **2016**, *264*, 540–554. [CrossRef]
22. Li, B.; Jiang, S.Y.; Zhang, Q.; Zhao, H.X.; Zhao, K.D. Geochemistry, Geochronology and Sr–Nd–Pb–Hf Isotopic Compositions of Middle to Late Jurassic Syenite–Granodiorites–Dacite in South China: Petrogenesis and Tectonic Implications. *Gondwana Res.* **2016**, *35*, 217–237. [CrossRef]
23. Jiang, S.; Zhao, K.; Jiang, Y.; Dao, B. Characteristics and Genesis of Mesozoic A-Type Granites and Associated Mineral Deposits in the Southern Hunan and Northern Guangxi Provinces along the Shi-Hang Belt, South China. *Geol. J. China Univ.* **2008**, *14*, 496–509. [CrossRef]
24. Li, Z.X.; Li, X.H.; Chung, S.L.; Lo, C.H.; Xu, X.S.; Li, W.X. Magmatic Switch-On and Switch-Off Along the South China Continental Margin Since the Permian: Transition from an Andean-Type to a Western Pacific-Type Plate Boundary. *Tectonophysics* **2012**, *532–535*, 271–290. [CrossRef]
25. Li, Z.; Qiu, J.S.; Yang, X.M. A Review of the Geochronology and Geochemistry of Late Yanshanian (Cretaceous) Plutons Along the Fujian Coastal Area of Southeastern China: Implications for Magma Evolution Related to Slab Break-Off and Rollback in the Cretaceous. *Earth-Sci. Rev.* **2014**, *128*, 232–248. [CrossRef]
26. Liu, L.; Qiu, J.; Li, Z. Origin of Mafic Microgranular Enclaves (MMEs) and their Host Quartz Monzonites from the Muchen Pluton in Zhejiang Province, Southeast China: Implications for Magma Mixing and Crust–Mantle Interaction. *Lithos* **2013**, *160*, 145–163. [CrossRef]
27. Li, Z.; Qiu, J.S.; Xu, X.S. Geochronological, Geochemical and Sr–Nd–Hf Isotopic Constraints on Petrogenesis of Late Mesozoic Gabbro–Granite Complexes on the Southeast Coast of Fujian, South China: Insights into a Depleted Mantle Source Region and Crust–Mantle Interactions. *Geol. Mag.* **2012**, *149*, 459–482. [CrossRef]
28. Li, X.Y.; Li, S.Z.; Suo, Y.H.; Huang, F.; Wang, P.C.; Luan, S.R.; Zhou, J. High-Silica Rhyolites in the Terminal Stage of Massive Cretaceous Volcanism, SE China: Modified Crustal Sources and Low-Pressure Magma Chamber. *Gondwana Res.* **2022**, *102*, 133–150. [CrossRef]
29. Zhu, K.Y.; Li, Z.X.; Xu, X.S.; Wilde, S.A. A Mesozoic Andean-Type Orogenic Cycle in Southeastern China as Recorded by Granitoid Evolution. *Am. J. Sci.* **2014**, *314*, 187–234. [CrossRef]
30. Li, X.H.; Li, Z.X.; Li, W.X. Detrital Zircon U–Pb Age and Hf Isotope Constrains on the Generation and Reworking of Precambrian Continental Crust in the Cathaysia Block, South China: A Synthesis. *Gondwana Res.* **2014**, *25*, 1202–1215. [CrossRef]
31. Yao, J.; Shu, L.; Santosh, M.; Li, J. Neoproterozoic Arc-Related Andesite and Orogeny-Related Unconformity in the Eastern Jiangnan Orogenic Belt: Constraints on the Assembly of the Yangtze and Cathaysia Blocks in South China. *Precamb. Res.* **2015**, *262*, 84–100. [CrossRef]
32. Shu, L.; Yao, J.; Wang, B.; Faure, M.; Charvet, J.; Chen, Y. Neoproterozoic Plate Tectonic Process and Phanerozoic Geodynamic Evolution of the South China Block. *Earth-Sci. Rev.* **2021**, *216*, 103596. [CrossRef]
33. Xu, X.S.; O'Reilly, S.Y.; Griffin, W.L.; Wang, X.; Pearson, N.J.; He, Z. The Crust of Cathaysia: Age, Assembly and Reworking of Two Terranes. *Precamb. Res.* **2007**, *158*, 51–78. [CrossRef]
34. Li, X.H.; Li, W.X.; Li, Z.X.; Lo, C.H.; Wang, J.; Ye, M.F.; Yang, Y.H. Amalgamation Between the Yangtze and Cathaysia Blocks in South China: Constraints from SHRIMP U–Pb Zircon Ages, Geochemistry and Nd–Hf Isotopes of the Shuangxiwu Volcanic Rocks. *Precamb. Res.* **2009**, *174*, 117–128. [CrossRef]
35. Yu, J.H.; O'Reilly, S.Y.; Zhou, M.F.; Griffin, W.L.; Wang, L.J. U–Pb Geochronology and Hf–Nd Isotopic Geochemistry of the Badu Complex, Southeastern China: Implications for the Precambrian Crustal Evolution and Paleogeography of the Cathaysia Block. *Precamb. Res.* **2012**, *222–223*, 424–449. [CrossRef]
36. Yao, J.L.; Shu, L.S.; Santosh, M. Neoproterozoic Arc-Trench System and Breakup of the South China Craton: Constraints From N-MORB Type and Arc-Related Mafic Rocks, and Anorogenic Granite in the Jiangnan Orogenic Belt. *Precamb. Res.* **2014**, *247*, 187–207. [CrossRef]
37. Wong, J.; Sun, M.; Xing, G.F.; Li, X.H.; Zhao, G.C.; Wong, K.; Wu, F.Y. Zircon U–Pb and Hf Isotopic Study of Mesozoic Felsic Rocks from Eastern Zhejiang, South China: Geochemical Contrast Between the Yangtze and Cathaysia Blocks. *Gondwana Res.* **2011**, *19*, 244–259. [CrossRef]

38. Guo, F.; Fan, W.; Li, C.; Zhao, L.; Li, H.; Yang, J. Multi-Stage Crust–Mantle Interaction in SE China: Temporal, Thermal and Compositional Constraints from the Mesozoic Felsic Volcanic Rocks in Eastern Guangdong–Fujian Provinces. *Lithos* **2012**, *150*, 62–84. [CrossRef]
39. Zhao, J.L.; Qiu, J.S.; Liu, L.; Wang, R.Q. The Late Cretaceous I- And a-Type Granite Association of Southeast China: Implications for the Origin and Evolution of Post-Collisional Extensional Magmatism. *Lithos* **2016**, *240–243*, 16–33. [CrossRef]
40. Li, Z.L.; Zhou, J.; Mao, J.R.; Santosh, M.; Yu, M.G.; Li, Y.Q.; Hu, Y.Z.; Langmuir, C.H.; Chen, Z.X.; Cai, X.X. Zircon U–Pb Geochronology and Geochemistry of Two Episodes of Granitoids from the Northwestern Zhejiang Province, SE China: Implication for Magmatic Evolution and Tectonic Transition. *Lithos* **2013**, *179*, 334–352. [CrossRef]
41. Zhou, J.; Jin, C.; Suo, Y.; Li, S.; Zhang, L.; Liu, Y.; Wang, G.; Wang, P.; Dai, L.; Santosh, M. The Yanshanian (Mesozoic) Metallogeneses in China Linked to Crust–Mantle Interaction in the Western Pacific Margin: An Overview From the Zhejiang Province. *Gondwana Res.* **2022**, *102*, 95–132. [CrossRef]
42. Shao, X.; Jin, C.; Jia, B.; Liu, Y.; Pan, F.; Zhu, Z. Genesis of the Panjia Wu–Cu–Mo Deposit: Evidence from the Geochemistry and Geochronology of the Datongkeng Pluton, Northeast South China Block. *Geol. J.* **2020**, *55*, 1064–1084. [CrossRef]
43. Wiedenbeck, M.; Allé, P.; Corfu, F.; Griffin, W.L.; Meier, M.; Oberli, F.; Quadt, A.V.; Roddick, J.C.; Spiegel, W. Three Natural Zircon Standards for U–Th–Pb, Lu–Hf, Trace Element and REE Analyses. *Geostand. Geoanal. Res.* **1995**, *19*, 1–23. [CrossRef]
44. Sláma, J.; Košler, J.; Condon, D.J.; Crowley, J.L.; Gerdes, A.; Hanchar, J.M.; Horstwood, M.S.A.; Morris, G.A.; Nasdala, L.; Norberg, N.; et al. Plešovice Zircon—A New Natural Reference Material for U–Pb and Hf Isotopic Microanalysis. *Chem. Geol.* **2008**, *249*, 1–35. [CrossRef]
45. Li, X.Y.; Li, S.Z.; Suo, Y.H.; Dai, L.M.; Guo, L.L.; Ge, F.J.; Lin, P.J. Late Cretaceous Basalts and Rhyolites from Shimaoshan Group in Eastern Fujian Province, SE China: Age, Petrogenesis, and Tectonic Implications. *Int. Geol. Rev.* **2018**, *60*, 1721–1743. [CrossRef]
46. Thirlwall, M.F. Long-Term Reproducibility of Multicollector Sr and Nd Isotope Ratio Analysis. *Chem. Geol. Isot. Geosci. Sect.* **1991**, *94*, 85–104. [CrossRef]
47. Chen, F.K.; Satir, M.; Ji, J.; Zhong, D. Nd–Sr–Pb Isotopes of Tengchong Cenozoic Volcanic Rocks from Western Yunnan, China: Evidence for an Enriched-Mantle Source. *J. Asian Earth Sci.* **2002**, *21*, 39–45. [CrossRef]
48. Hu, Z.C.; Liu, Y.S.; Gao, S.; Liu, W.; Zhang, W.; Tong, X.R.; Lin, L.; Zong, K.Q.; Li, M.; Chen, H.; et al. Improved in Situ Hf Isotope Ratio Analysis of Zircon Using Newly Designed X Skimmer Cone and Jet Sample Cone in Combination with the Addition of Nitrogen by Laser Ablation Multiple Collector ICP–MS. *J. Anal. At. Spectrom.* **2012**, *27*, 1391–1399. [CrossRef]
49. Blichert-Toft, J.; Albarède, F. The Lu–Hf Isotope Geochemistry of Chondrites and the Evolution of the Mantle–Crust System. *Earth Planet. Sci. Lett.* **1997**, *148*, 243–258. [CrossRef]
50. Scherer, E.; Münker, C.; Mezger, K. Calibration of the Lutetium–Hafnium Clock. *Science* **2001**, *293*, 683–687. [CrossRef]
51. Siégl, C.; Bryan, S.E.; Allen, C.M.; Gust, D.A. Use and abuse of zircon-based thermometers: A critical review and a recommended approach to identify antecrystic zircons–ScienceDirect. *Earth–Sci. Rev.* **2018**, *176*, 87–116. [CrossRef]
52. Lim, H.; Nebel, O.; Weinberg, R.F.; Nebel-Jacobsen, Y.; Barrote, V.R.; Park, J.; Myeong, B.; Cawood, P.A. Lower crustal hot zones as zircon incubators: Inherited zircon antecryts in diorites from a mafic mush reservoir. *Geol. Soc. Lond. Spec. Publ.* **2023**, *537*, 411–433. [CrossRef]
53. Dahlquist, J.A.; Morales Cámara, M.M.; Moreno, J.A.; Basei, M.A.S.; da Cruz, G.S.; Oliveira, E.P. A conceptual model for the evolution of a magmatic system based on U–Pb zircon studies on the Devonian granites of Sierra de San Luis, Argentina. *Int. Geol. Rev.* **2024**, *66*, 1794–1814. [CrossRef]
54. Maniar, P.D.; Piccoli, P.M. Tectonic Discrimination of Granitoids. *Geol. Soc. Am. Bull.* **1989**, *101*, 635–643. [CrossRef]
55. Wang, Y.; Zeng, Q.; Zhang, S.; Chen, P.; Gao, S. Spatial–Temporal Relationships of Late Mesozoic Granitoids in Zhejiang Province, Southeast China: Constraints on Tectonic Evolution. *Int. Geol. Rev.* **2018**, *60*, 1529–1559. [CrossRef]
56. Tang, Y.; Li, X.; Xie, Y.; Liu, L.; Lan, T.; Meffre, S.; Huang, C. Geochronology and Geochemistry of Late Jurassic Adakitic Intrusions and Associated Porphyry Mo–Cu Deposit in the Tongcun Area, East China: Implications for Metallogeneses and Tectonic Setting. *Ore Geol. Rev.* **2017**, *80*, 289–308. [CrossRef]
57. Jia, S.H.; Zhao, Y.Y.; Wang, Z.Q.; Wu, Y.D.; Wang, T.; Chen, L. Zircon U–Pb Dating and Geochemical Characteristics of Granodiorite–Porphyry in the Linghou Copper Deposit, Western Zhejiang, and Their Geological Significance. *Acta Geol. Sin.* **2014**, *88*, 2071–2085.
58. Chen, S.Q. Discussion on the Yanshan Epoch Rock Characteristics and Ore-Forming Background in Zhejiang Kaihua Region. Master’s Thesis, China University of Geosciences, Beijing, China, 2011.
59. Tang, Y.; Li, X.; Xie, Y.; Huang, C.; Wei, H.; Cai, J.; Qin, C.; Liu, R. Geology, Geochemistry, and Genesis of the Tongcun Porphyry Mo (Cu) Deposit, NW Zhejiang Province, China. *Acta Geol. Sin. (Engl. Ed.)* **2014**, *88*, 614–615. [CrossRef]
60. Zhang, J.F.; Jie, H.S.; Xu, X.M.; Gong, R. Geological and Geochemical Characteristics and Tectonic and Prospecting Significance of the Shanxi–Guangshan Intrusions in Lizhu Area, Zhejiang Province. *Geol. China* **2013**, *40*, 403–413.
61. Yang, S.; Jiang, S.; Zhao, K.; Jiang, Y.; Ling, H.; Luo, L. Geochronology, Geochemistry and Tectonic Significance of Two Early Cretaceous a-Type Granites in the Gan–Hang Belt, Southeast China. *Lithos* **2012**, *150*, 155–170. [CrossRef]

62. Li, Y.; Wei, J.; Chen, H.; Tan, J.; Fu, L.; Wu, G. Origin of the Maoduan Pb–Zn–Mo Deposit, Eastern Cathaysia Block, China: Geological, Geochronological, Geochemical, and Sr–Nd–Pb–S Isotopic Constraints. *Miner. Depos.* **2012**, *47*, 763–780. [CrossRef]
63. McDonough, W.F.; Sun, S.S. The Composition of the Earth. *Chem. Geol.* **1995**, *120*, 223–253. [CrossRef]
64. He, Z.Y.; Xu, X.S.; Niu, Y.L. Petrogenesis and Tectonic Significance of a Mesozoic Granite–Syenite–Gabbro Association from Inland South China. *Lithos* **2010**, *119*, 621–641. [CrossRef]
65. Ying, J.F.; Zhang, H.F.; Tang, Y.J. Crust–Mantle Interaction in the Central North China Craton During the Mesozoic: Evidence from Zircon U–Pb Chronology, Hf Isotope and Geochemistry of Syenitic–Monzonitic Intrusions from Shanxi Province. *Lithos* **2011**, *125*, 449–462. [CrossRef]
66. Sun, Y.; Xiao, L.; Zhan, Q.Y.; Wu, J.X.; Zhu, D.; Huang, W.; Bai, M.; Zhang, Y.H. Petrogenesis of the Kuangshancun and Hongshan Intrusive Complexes from the Handan–Xingtai District: Implications for Iron Mineralization Associated with Mesozoic Magmatism in the North China Craton. *J. Asian Earth Sci.* **2015**, *113*, 1162–1178. [CrossRef]
67. Class, C.; le Roex, A.P. Ce Anomalies in Gough Island Lavas—Trace Element Characteristics of a Recycled Sediment Component. *Earth Planet. Sci. Lett.* **2008**, *265*, 475–486. [CrossRef]
68. Plank, T.; Langmuir, C.H. Tracing Trace Elements from Sediment Input to Volcanic Output at Subduction Zones. *Nature* **1993**, *362*, 739–743. [CrossRef]
69. Yang, H.; Zhang, H.; Xiao, W.; Tao, L.; Gao, Z.; Luo, B.; Zhang, L. Multiple Early Paleozoic Granitoids from the Southeastern Qilian Orogen, NW China: Magma Responses to Slab Roll-Back and Break-Off. *Lithos* **2021**, *380–381*, 105910. [CrossRef]
70. Whalen, J.B.; Currie, K.L.; Chappell, B.W. A-Type Granites: Geochemical Characteristics, Discrimination and Petrogenesis. *Contrib. Mineral. Petrol.* **1987**, *95*, 407–419. [CrossRef]
71. Patiño Douce, A.E. What do Experiments Tell Us about the Relative Contributions of Crust and Mantle to the Origin of Granitic Magmas? *Geol. Soc. Lond. Spec. Publ.* **1999**, *168*, 55–75. [CrossRef]
72. Chappell, B.W.; White, A.J.R. Two Contrasting Granite Types: 25 Years Later. *Aust. J. Earth Sci.* **2001**, *48*, 489–499. [CrossRef]
73. Gao, P.; Zheng, Y.F.; Zhao, Z.F. Experimental melts from crustal rocks: A lithochemical constraint on granite petrogenesis. *Lithos* **2016**, *266–267*, 133–157. [CrossRef]
74. Chen, J.Y.; Yang, J.H.; Zhang, J.H.; Sun, J.F.; Wilde, S.A. Petrogenesis of the Cretaceous Zhangzhou Batholith in Southeastern China: Zircon U–Pb Age and Sr–Nd–Hf–O Isotopic Evidence. *Lithos* **2013**, *162–163*, 140–156. [CrossRef]
75. Jiang, Y.H.; Ling, H.F.; Jiang, S.Y.; Fan, H.H.; Shen, W.Z.; Ni, P. Petrogenesis of a Late Jurassic Peraluminous Volcanic Complex and its High-Mg, Potassic, Quenched Enclaves at Xiangshan, Southeast China. *J. Petrol.* **2005**, *46*, 1121–1154. [CrossRef]
76. McLeod, C.L.; Davidson, J.P.; Nowell, G.M.; de Silva, S.L.; Schmitt, A.K. Characterizing the Continental Basement of the Central Andes: Constraints from Bolivian Crustal Xenoliths. *Geol. Soc. Am. Bull.* **2013**, *125*, 985–997. [CrossRef]
77. Chen, J.; Yang, J.; Zhang, J.; Sun, J. Diachronous Slab-Driven Early Cretaceous Crustal Extension and Pulsed Magmatic Response in Southeastern China: Insight From a-Type Granite and Related Rocks. *Gondwana Res.* **2024**, *126*, 22–39. [CrossRef]
78. Sun, W.D.; Ding, X.; Hu, Y.H.; Li, X.H. The Golden Transformation of the Cretaceous Plate Subduction in the West Pacific. *Earth Planet. Sci. Lett.* **2007**, *262*, 533–542. [CrossRef]
79. Ye, H.M.; Mao, J.R.; Zhao, X.L.; Liu, K.; Chen, D.D. Revisiting Early–Middle Jurassic Igneous Activity in the Nanling Mountains, South China: Geochemistry and Implications for Regional Geodynamics. *J. Asian Earth Sci.* **2013**, *72*, 108–117. [CrossRef]
80. Liang, X.Q.; Fan, W.M.; Wang, Y.J.; Li, X.H. Early Mesozoic, Post-collisional Shoshonitic Lamprophyres along the Western Margin of the South China Orogen: Geochemical Characteristics and Tectonic Implications. *Int. Geol. Rev.* **2006**, *48*, 311–328. [CrossRef]
81. Liu, Q.; Yu, J.; Su, B.; Wang, Q.; Tang, H.F.; Xu, H.; Cui, X. Discovery of the 187Ma Granite in Jincheng Area, Fujian Province: Constraint on Early Jurassic Tectonic Evolution of Southeastern China. *Acta Petrol. Sin.* **2011**, *27*, 3575–3589.
82. Xing, X.L. Chronology and Petrogenesis of Jurassic–Cretaceous Volcanism in the Area of Zhejiang–Fujian Boundary. Master’s Thesis, Chengdu University of Technology, Chengdu, China, 2016.
83. Xing, X.L.; Xing, G.F.; Chen, S.Z.; Zhao, X.L.; Duan, Z. LA-ICP-MS Zircons U–Pb Ages and Geological Characteristics of Early–Middle Jurassic Volcanic Rocks in the Qingyuan Area, Zhejiang Province. *Geol. Bull. China* **2017**, *36*, 1583–1590.
84. Li, C.L.; Wang, Z.X.; Wang, D.X.; Cao, W.T.; Yu, X.Q.; Zhou, G.Z.; Gao, W.L. Crust–Mantle Interaction Triggered by Oblique Subduction of the Pacific Plate: Geochronological, Geochemical, and Hf Isotopic Evidence from the Early Cretaceous Volcanic Rocks of Zhejiang Province, Southeast China. *Int. Geol. Rev.* **2014**, *56*, 1732–1753. [CrossRef]

85. Chen, Q.; Cheng, H.; Liu, P.; Sun, M. Late Cretaceous Basalts in the Eastern South China Block: The Result of Slab Tearing During Retreating Subduction of the Paleo-Pacific Plate. *J. Asian Earth Sci.* **2024**, *261*, 105979. [CrossRef]
86. Liu, L.; Qiu, J.S.; Zhao, J.L.; Yang, Z.L. Geochronological, Geochemical, and Sr–Nd–Hf Isotopic Characteristics of Cretaceous Monzonitic Plutons in Western Zhejiang Province, Southeast China: New Insights into the Petrogenesis of Intermediate Rocks. *Lithos* **2014**, *196*, 242–260. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Petrography, Geochemistry, and Magmatic Processes of Oligocene-Miocene Tuzla Volcanics, Biga Peninsula, NW Türkiye

Didem Kiray ^{1,*} and Oya Cengiz ²¹ Lider Yönetim OSGB, 17020 Çanakkale, Türkiye² Department of Geological Engineering, Süleyman Demirel University, 32260 Isparta, Türkiye; oyacengiz@sdu.edu.tr

* Correspondence: dkiray17@gmail.com; Tel.: +90-2862122118

Abstract

The Tuzla area, located in the Ayvacık district of Çanakkale (Biga Peninsula, northwestern Türkiye), hosts a Oligocene-Miocene volcanic system comprising andesitic, dacitic, rhyolitic lavas, trachyandesite, pyroclastics, and ignimbrites, and the Kestanbol Pluton. Petrographic and X-ray diffraction (XRD) analyses indicate that the altered volcanic units are dominated by porphyritic dacitic/rhyodacitic and trachyandesitic rocks, with silicification, iron oxide formation, and opacification. XRD results reveal smectite, smectite–illite/mica, illite–mica, kaolinite, cristobalite–opal, K-feldspar, plagioclase, dolomite, hematite, and quartz as the principal mineral phases. Geochemical data, including rare earth elements (REEs), suggest that fractional crystallization of primary mineral phases played a major role in controlling magmatic evolution. Chondrite-normalized REE patterns display enrichment in light REEs relative to heavy REEs, indicating derivation from a common magma source. K_2O-Na_2O and $(Na_2O + K_2O)-FeO^t-MgO$ (AFM) diagrams show high-K calc-alkaline, calc-alkaline, and tholeiitic affinities, with most rhyodacite/dacite and all trachyandesite samples plotting in the tholeiitic field. Tectonic discrimination diagrams indicate formation in both volcanic arc and intraplate tectonic settings. Moderate enrichments in Ba and Sr reflect magmatic evolution and source characteristics, whereas the highest concentrations are attributed to post-magmatic fluid–rock interaction. Overall, the Tuzla volcanic rocks originated from a collision-related enriched lithospheric mantle source and subsequently evolved through fractional crystallization and assimilation processes, accompanied by crustal contamination and variable hydrothermal overprint.

Keywords: Biga Peninsula; Tuzla; Oligocene-Miocene volcanic rocks; rare earth elements (REE); fractional crystallization; lithospheric mantle

1. Introduction

The Biga Peninsula in northwestern Anatolia is a geologically and economically significant region due to its complex tectonic evolution, widespread magmatism, and abundant mineral and geothermal resources. The peninsula exposes a mosaic of metamorphic, ophiolitic, and Neogene sedimentary and magmatic rocks, recording multiple tectonic events from the Palaeozoic to the Quaternary. The widespread Cenozoic volcano-plutonic units are particularly important for understanding the region's tectono-magmatic evolution, hydrothermal systems, and potential for metallic and industrial mineral deposits [1,2].

Turkey, located within the Alpine–Himalayan orogenic belt, represents one of the key geodynamic regions where volcanic and plutonic rocks are widely exposed. Northwestern Anatolia, in particular, is characterized by collisional magmatism, well-defined crust–mantle interaction signatures, and the coexistence of magmatic and tectonic processes within a structurally complex framework [3–5]. In terms of the regional structural framework, the east–west–trending orogenic system of Türkiye is subdivided into four main tectonic units from north to south: the Pontides, Anatolides, Taurus, and marginal fold belt, as illustrated in Figure 1 [6]. Northwestern Türkiye is bounded by the Intra-Pontide Suture Zone to the north and the İzmir–Ankara–Erzincan Suture Zone to the south and corresponds to the Pontides (or the Sakarya Zone) [7,8]. Within this tectonic setting, the Biga Peninsula represents a key exposure of the Sakarya Zone basement, comprising the Kazdağ, Karadağ, Çamlıca, and Karabiga massifs [7,9].

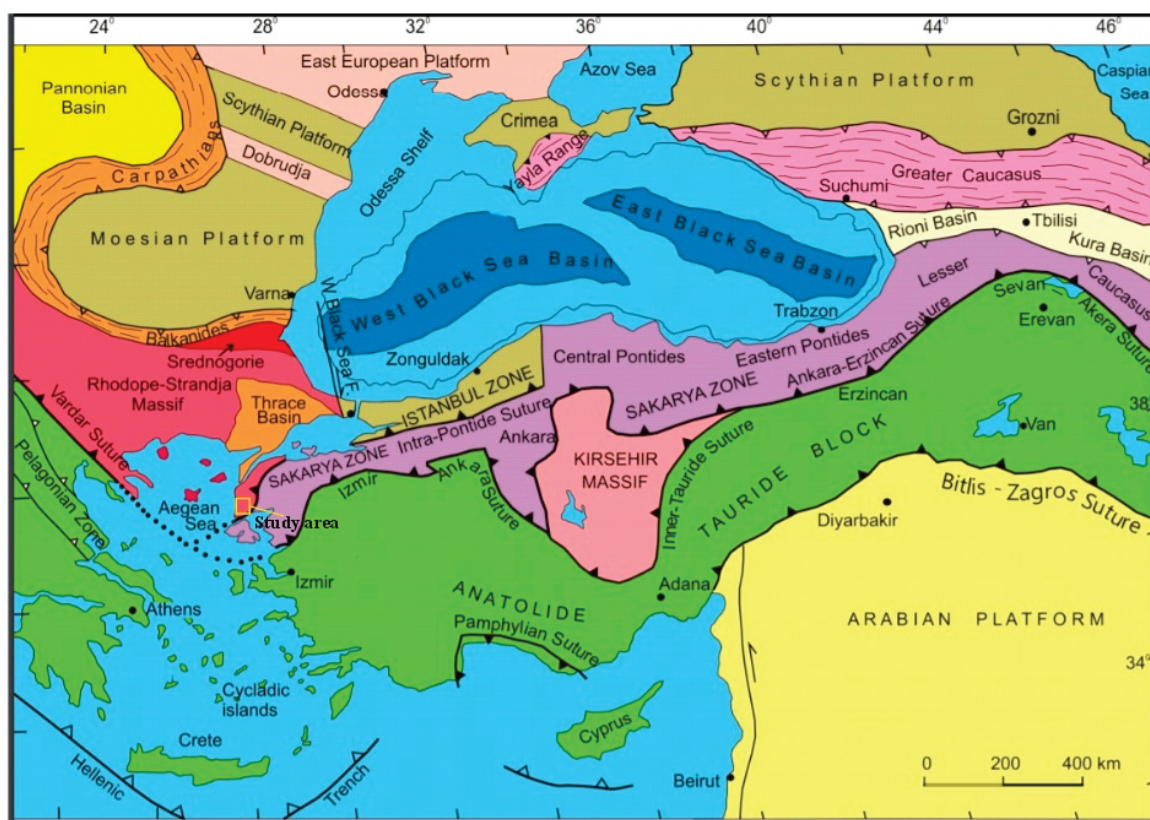


Figure 1. Tectonic map of northwestern Anatolia showing the location of the study area (modified after [10]).

The Biga Peninsula records Paleogene–Neogene magmatism in three main stages—Eocene, Oligocene, and Miocene—and is widely interpreted as being of post-collisional origin [8,11–16]. Subduction of the Neo-Tethyan oceanic lithosphere beneath the Sakarya Zone commenced in the Early Cretaceous (~105 Ma) and was followed by collision between the Sakarya and Tauride–Anatolide continental blocks during the Eocene [7,10,11,17]. The earliest magmatic products associated with this collision include Middle Eocene granitic plutons and andesitic volcanic rocks [11,18–20]. Early–Middle Miocene magmatism in the Biga Peninsula is characterized by widespread andesitic, dacitic, rhyolitic, and pyroclastic units, indicating intense and sustained volcanic activity [3,21]. Preceding magmatic phases during the Oligocene to Early Miocene produced granitic intrusions and compositionally related volcanic units [22–25]. Geochemical trends indicate a systematic evolution from medium-K calc-alkaline compositions in the Eocene, to high-K

calc-alkaline affinities in the Oligocene, and ultimately to high-K alkaline and shoshonitic compositions during the Miocene. Na-rich alkaline volcanic products represent the final magmatic stage following the Early Miocene [3,4,15,16,26,27].

The present study investigates the petrographic, geochemical, and petrogenetic characteristics of the Oligocene-Miocene Tuzla volcanic rocks in the Ayvacık region. By providing new constraints on magma evolution and associated hydrothermal processes, this study aims to address existing gaps in the understanding of post-collisional volcanism within in this geodynamically complex area.

2. Geological Setting

The study area is located within the Tuzla volcanic–geothermal system near Ayvacık in the Biga Peninsula (Çanakkale, northwestern Türkiye), where Oligocene-Miocene volcanic and plutonic units are widely exposed. This region forms part of the Sakarya Zone, bounded by the Intra-Pontid Suture to the north and the İzmir–Ankara–Erzincan Suture to the south (Figure 1). The geological evolution of the area reflects prolonged tectonic processes, including continental collisions, oceanic basin closure, magmatic arc development, and post-collisional extension since the Paleozoic [28–30]. The basement of the peninsula is represented by the amphibolite-facies Kazdağ Kazdağ Group, which comprises, from bottom to top, the Findıklı, Tozlu, Sarıkız, and Sutüven formations [29]. These metamorphic units are unconformably overlain by Paleozoic recrystallized limestones, which are, in turn, covered by Miocene rhyolitic tuffs and agglomerates. Tectonically overlying the basement are the Permo–Triassic Karakaya Complex—composed of partially metamorphosed and strongly deformed clastic and volcanic rocks belonging to the Nilüfer, Hodul, Orhanlar, and Çal units—and the Cretaceous Çetmi ophiolitic mélange [9]. To the north of the Sakarya Zone, the Ezine Zone is exposed and comprises the Ezine Group, the Çamlıca metamorphics, and the tectonically emplaced Denizgören Ophiolite. This zone is separated from the Sakarya Zone by the Çetmi Mélange. The Çamlıca metamorphics contain high-pressure/low-temperature eclogitic relics, indicating Maastrichtian metamorphism (65–69 Ma) [31]. The Ezine Group consists mainly of Permo–Triassic carbonates and epicontinental sedimentary rocks metamorphosed under greenschist-facies conditions [32]. The Çetmi Mélange, composed of spilite, greywacke, shale, serpentinite, and radiolarite, represents an ophiolitic unit emplaced during the Late Cretaceous and transported southward during the Paleocene collision [33,34]. The Denizgören ophiolite, consisting predominantly of partially serpentinized harzburgites, tectonically overlies both the Çamlıca metamorphics and Ezine Group [9].

Eocene magmatism in the region is represented by granitic plutons and their volcanic equivalents [14,35]. During the Early Miocene, post-collisional magmatic activity produced high-K calc-alkaline to shoshonitic, I-type plutonic rocks (e.g., the Kestanbol Pluton: 21.5 ± 1.6 Ma [36]; 22.3 ± 0.2 Ma and 22.8 ± 0.2 Ma [35]) as well as coeval calc-alkaline to shoshonitic volcanic units [3,36–38]. This magmatic episode is widely interpreted as a consequence of post-collisional continental extension [3,38–40]. Miocene magmatic units in the study area include the Tuzla Volcanics and the quartz monzonite–monzogranite Kestanbol Pluton [23]. Volcanic activity commenced with the eruption of rhyolitic tuffs and agglomerates, followed by trachytic–trachyandesitic lava flows, and culminated in extensive rhyolitic tuff and ignimbrite deposition [2]. ^{40}Ar – ^{39}Ar ages obtained of biotite (21.22 ± 0.09 Ma) and leucite (22.21 ± 0.07 Ma) crystals indicate that tephriphonolite dyke emplacement was coeval with the intrusion of the Kestanbol Pluton during the Early Miocene (21.5 ± 1.6 , 22.8 ± 0.2 Ma) [41].

The Tuzla Volcanics, representing the most widespread volcanic unit of the Oligocene-Miocene, consist predominantly of hydrothermally altered porphyritic andesites,

basaltic–andesitic lavas, and associated pyroclastic deposits. These units are exposed around Babadere, Naldöken, Taşboğaz, Çamköy and Kestanelik (Figure 2) and are intruded at depth by the Kestanbol Pluton. The volcanic succession is subdivided into three principal units: (i) Oligocene–Early Miocene felsic lava flows (rhyolite–dacite), characterized by massive, hard, and brittle flows locally associated with flow breccias. These rocks display colors ranging from grey to greenish and reddish-brown, and well-developed joint and fracture systems are common. (ii) Lava–pyroclastic alternations composed of well-bedded pumice and crystal tuffs, volcanic blocks, and bombs. These units are commonly affected by hydrothermal alteration, resulting in yellow, light brown, or cream-colored hues (Figure 3a–c). (iii) Later-stage andesitic–trachyandesitic lava flows, locally intercalated with flow breccias, lahar deposits, and lacustrine sandstones [38].

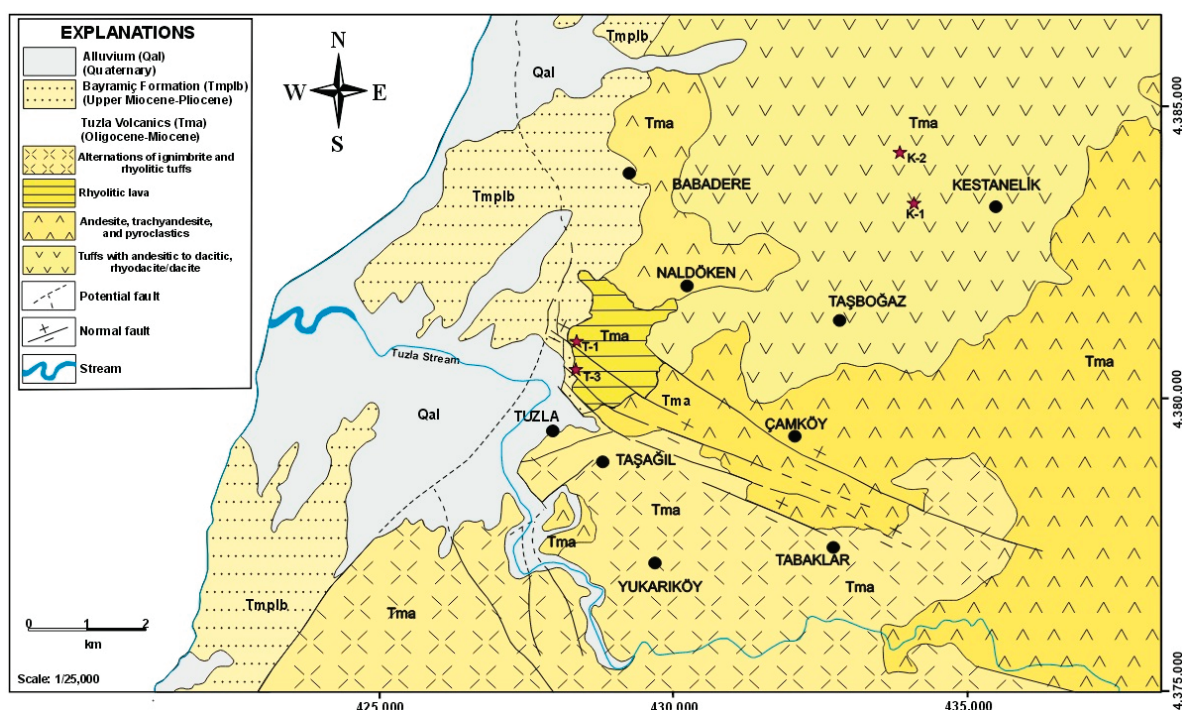


Figure 2. Geological map of the study area showing sample locations and sample codes (modified after [37,38,42]).

K–Ar dating of rhyolitic tuffs yields an age 26.5 ± 1.1 Ma (Late Oligocene) [30], whereas andesitic and trachyandesitic units were dated at 21.2 ± 0.9 Ma using the K–Ar method and 22.72 ± 0.19 Ma and 22.97 ± 0.23 Ma based on SHRIMP U–Pb zircon analysis [15]. Volcanic activity was largely controlled by NE–SW to NW–SE trending fault zones, which also governed in localized subsidence and episodic lacustrine sedimentation.

The Late Miocene volcanic succession exposed south of the Kestanbol Pluton constitutes the most extensive ignimbrite sequence in the region. These ignimbrites are exposed north of the Tuzla and Kestanelik and are predominantly pyroclastic in origin. According to [38], the ignimbrite succession displays a tripartite architecture comprising a basal surge unit, a welded ignimbrite, and an overlying unwelded pumice-rich tuff. Columnar jointing is common in the upper levels, whereas progressive welding in the lower to middle parts produces distinct petrographic zonation. The lower part of the succession begins with latite and andesite lava flows, which are intruded by basaltic and andesitic dykes. The most widespread ignimbrite unit attains a thickness of approximately 40–45 m and contains intermediate volcanic lithic fragments as well as granitic clasts. The upper part of the succession consists of alternating ignimbrite and andesite layers, forming the most extensive

pyroclastic sequence in the area. Locally, late-stage rhyolite domes (Tuzla and Ortatepe) developed with compositions similar to those of the Ayvacık volcanics. U–Pb zircon ages obtained from the ignimbrites cluster around the Early Miocene age of $\sim 22.3 \pm 1.2$ Ma [38].

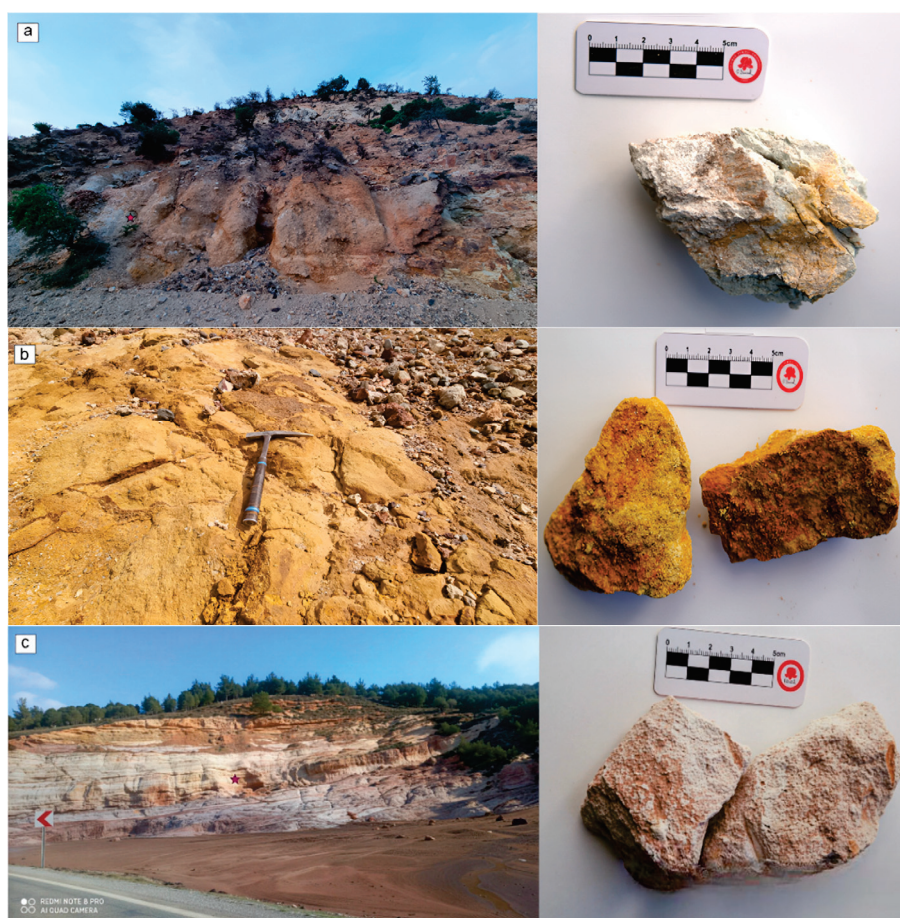


Figure 3. Field views of the volcanics. (a) Rhyodacitic–dacitic outcrop at Kestanelik, showing alteration zones and local yellow–brown surface oxidation, with a representative hand specimen. (b) Tuzla outcrop, displaying intense alteration, fractures, and widespread yellow discoloration, with a hand specimen showing strong surface oxidation. (c) Tuzla outcrop, with well-developed layering and widespread yellow–brown oxidation, together with a hand specimen illustrating pronounced surface alteration.

The ignimbrite succession represents the late stage of regional volcanism and comprises Middle–Late Miocene ignimbrites, pumice-rich ignimbrites, tuffs, and agglomerates exposed around Taşağıl, Tabaklar, and Yukarıköy (Figure 2). The youngest volcanic products in the area are Late Miocene alkaline basalts. All volcanic and plutonic units are unconformably overlain by the Upper Miocene–Pliocene Bayramiç Formation, which consists composed of continental conglomerates, mudstones, marls, and lacustrine limestones [29,43].

3. Materials and Methods

This study is based on volcanic samples collected from the field, including six samples (K-1, K-2 code) from the Kestanelik area and eight samples (T-1, T-3 code) from the Tuzla area. An integrated approach was applied to comprehensively characterize the studied rocks. Mineralogical and petrographic characteristics were investigated using standard thin section petrography and X-ray diffraction (XRD; $n = 9$). Major and trace element geochemical compositions were determined for all 14 samples. The combined results of these

analyses were used to constrain magma source characteristics, fractional crystallization and assimilation processes, and the tectonic setting of the volcanic rocks.

3.1. Mineralogical–Petrographic Analysis

Fourteen representative thin sections were prepared from volcanic rock samples. The samples, cut to dimensions of $5 \times 5 \times 5$ cm, were processed at the Mineralogy–Petrography Laboratory of the Department of Mineral Analyses and Technology, General Directorate of Mineral Research and Exploration (MTA). Petrographic examinations were conducted using a Leica BX–51 polarizing microscope (Leica Microsystems, Wetzlar, Germany) at magnifications of 4×10 and 10×10 in the “Water–Rock and Mineral Analysis Laboratory” of the Department of Geological Engineering, Süleyman Demirel University (SDU). Petrographic observations focused on rock classification, textural characteristics, and mineral assemblages. Photomicrographs were acquired using a 5.1-megapixel digital camera (Lumenera Corporation, Ottawa, ON, Canada) mounted on the microscope.

Nine powder samples were analyzed by X-ray diffraction (XRD) at the Mineralogy–Petrography Unit of the Department of Mineral Analysis and Technology, General Directorate of Mineral Research and Exploration (MTA). The analyses were performed using a Shimadzu XRD-6000 diffractometer (Shimadzu Corporation, Kyoto, Japan) with $\text{CuK}\alpha$ radiation and a Ni filter. Clay mineral assemblages were examined in detail using XRD patterns obtained under scanning conditions ($2\text{--}70^\circ 2\theta$), as well as oriented mounts analyzed under air-dried ($2\text{--}30^\circ 2\theta$), ethylene glycol-treated ($2\text{--}30^\circ 2\theta$), and heat-treated conditions.

3.2. Geochemical Analysis

Nine representative rock samples were pulverized to <200 mesh at Activation Laboratories Ltd. (Actlabs, Canada) for whole-rock chemical analysis. Major oxides and trace elements concentrations were determined using inductively coupled plasma–emission spectrometry (ICP-ES). For rare earth element (REE) analyses, the samples were digested in dilute nitric acid and subsequently fused with a lithium metaborate/tetraborate flux to ensure complete dissolution. The resulting solutions were analyzed by inductively coupled plasma–mass spectrometry (ICP-MS).

4. Results

4.1. Petrographic Characteristics

4.1.1. Optical Microscopy

A total of 14 thin sections were prepared from the volcanic rocks collected in the study area. Petrographic analyses were performed under plane-polarized and cross-polarized light using a polarizing microscope, and representative photomicrographs were obtained. The principal phenocryst phases in the rhyodacite/dacite and andesite/trachyandesite samples are plagioclase, quartz, and biotite, accompanied by subordinate amphibole and opaque minerals (Figure 4). In the rhyodacite/dacite thin sections (Figure 4a,b,d,e), plagioclase crystals commonly exhibit polysynthetic twinning and zoning, whereas biotite shows pronounced opacification (Figure 4a). Figure 4b displays subhedral plagioclase with well-developed twinning, euhedral to subhedral quartz, and opaque minerals, together with hexagonal microcrystalline quartz and minor relict feldspar grains. The groundmass is predominantly glassy and exhibits intense staining related to Fe–Ti oxide-bearing phases associated with plagioclase, quartz, and biotite. Silicification and opacification are also widely observed (Figure 4c). Microcrystalline quartz and quartz veins of variable thickness and orientation occur as products of silica-rich fluids. The introduction of calcium together with silica locally resulted in calcite formation. Iron-rich zones display strong iron oxide enrichment and pervasive opacification, with euhedral opaque minerals occurring

both within these zones and along quartz veins (Figure 4c). Microcrystalline quartz and quartz veins of variable thicknesses and orientations occur within silica-rich solutions. The introduction of calcium alongside silica led to the formation of calcite. Iron-rich areas exhibit intense iron oxide enrichment and widespread opacification, with euhedral opaque minerals present both in iron-rich zones and within the quartz veins (Figure 4c). In Figure 4d, anhedral quartz, amphibole, and biotite crystals are observed, whereas Figure 4e shows biotite flakes with a spherulitic texture. These spherulitic domains may represent early-formed components that were subsequently remobilized and reintroduced into the magma. Figure 4f illustrates sanidine crystals within trachyandesite/andesite displaying a vesicular texture, where some crystals are well preserved while others show varying degrees of alteration.

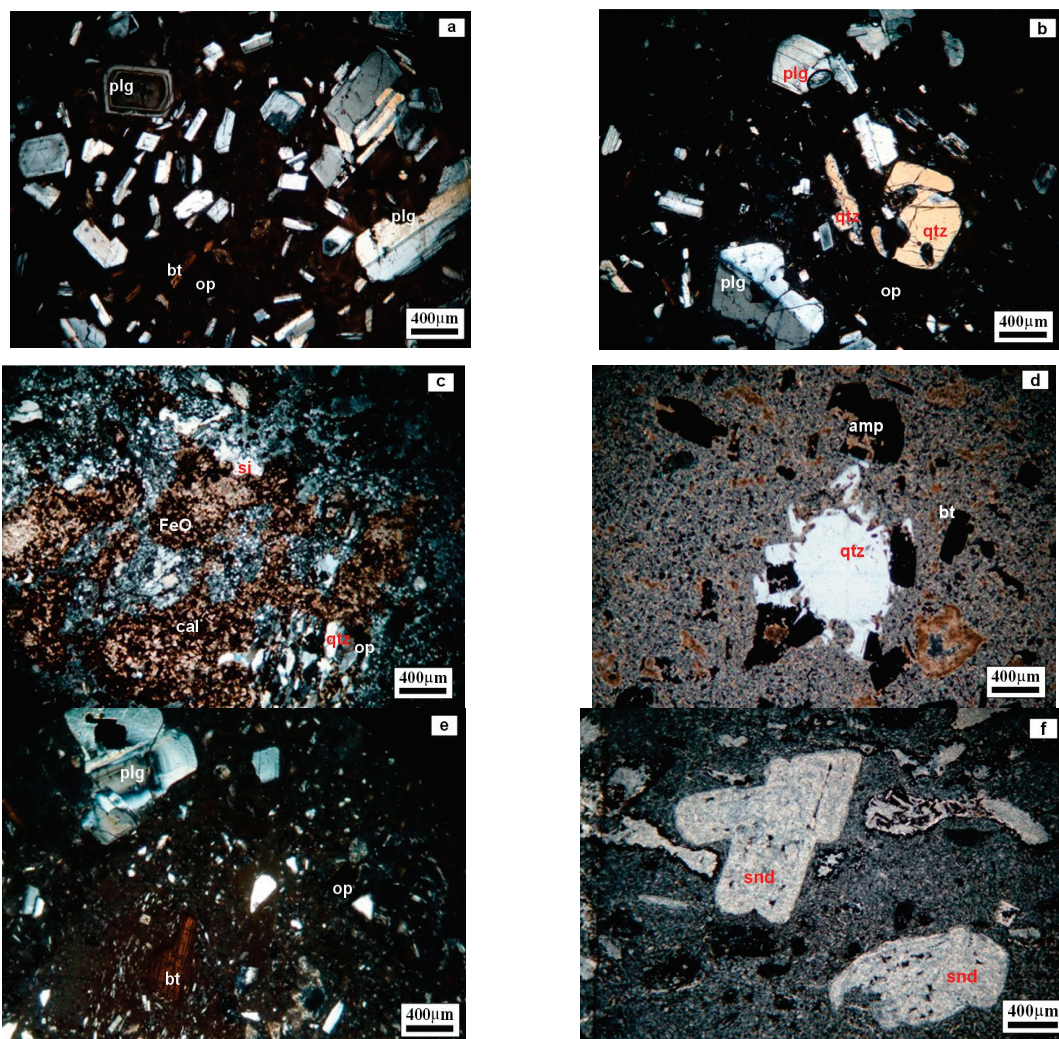


Figure 4. Polarizing microscope images of Tuzla volcanics. (a) Porphyritic rhyodacitic/dacitic rock with euhedral–subhedral plagioclase (plg) phenocrysts in a fine-grained groundmass, with biotite (bt) and opaque minerals (op). (b) Porphyritic rhyodacitic/dacitic rock with plagioclase (plg) and quartz (qtz) phenocrysts; quartz (qtz) locally fractured, with opaque minerals (op). (c) Trachyandesitic rock showing silicification (si) and calcite (cal) with local FeO enrichment, with quartz (qtz) and opaque minerals (op). (d) Rhyodacitic/dacitic rock with amphibole (amp) and biotite (bt) associated with a quartz (qtz) phenocryst, locally embayed margins. (e) Porphyritic rhyodacitic/dacitic rock with plagioclase (plg) phenocrysts and biotite (bt) with brown pleochroism, with scattered opaque minerals (op). (f) Trachyandesitic rock with sanidine (snd) phenocrysts, semi-euhedral to anhedral, in a dark, fine-grained to microlitic matrix. Abbreviations: plagioclase (plg), quartz (qtz), biotite (bt), sanidine (snd), amphibole (amp), opaque (op), calcite (cal), silicification (si), iron oxidation (FeO).

4.1.2. X-Ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) analyses of volcanic rock samples collected from surface units in the Tuzla field reveal well-defined clay mineral assemblages. Representative diffraction patterns and corresponding analytical results are shown in Figure 5. The samples are dominated by smectite, smectite–illite/mica interstratifications, illite/mica, and kaolinite. Analysis of the clay fraction indicates that illite exhibits basal reflections with $d(001)$ spacings ranging from 9.95 to 10.33 Å, $d(002)$ spacings from 4.36 to 5.70 Å, and $d(003)$ spacings from 2.45 to 2.58 Å. Smectite displays a wider range of basal spacings, with $d(001)$ values between 11.16 and 14.94 Å, $d(002)$ values from 3.47 to 3.57 Å, and $d(003)$ values from 1.49 to 1.54 Å. Air-dried (AD), ethylene glycol–treated (EG), and heat-treated preparations at 350 and 550 °C show that the 001 and 002 reflections of smectite remain largely stable, whereas the 003 reflection disappears following these treatments. In long-scan analyses of samples in which smectite is not readily apparent, the characteristic smectite $d(001)$ peak becomes evident after AD and EG treatments, confirming the presence of minor or poorly crystallized smectite layers. In some samples, EG treatment results in smectite expansion up to 21.77 Å, indicating well-developed swelling behavior. Heating at 350 and 550 °C leads to a progressive decrease in the $d(001)$ spacing, consistent with the structural collapse of smectite layers.

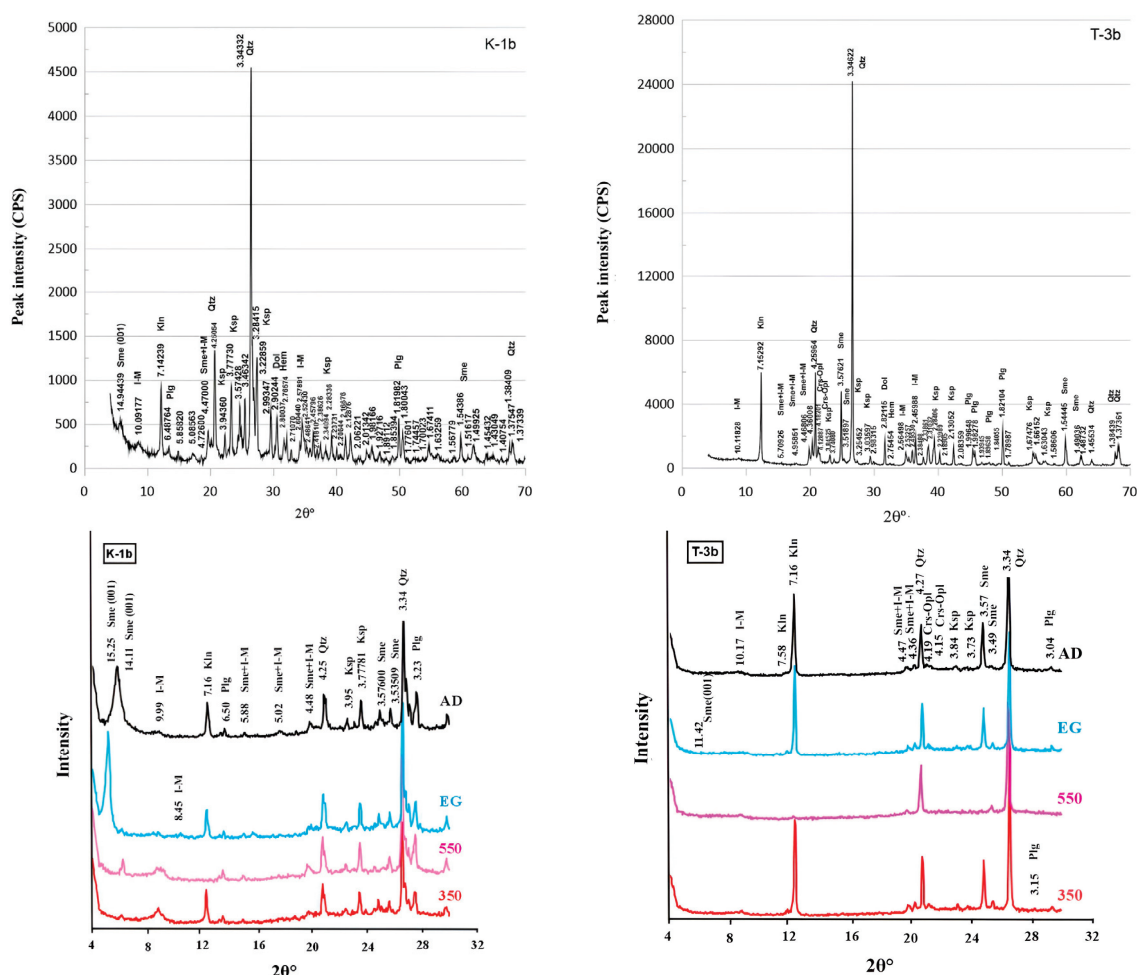


Figure 5. Mineralogical composition and relative abundances of minerals in the volcanic rock samples collected from the Tuzla field, determined by X-ray diffraction (XRD) analysis. The figure presents bulk-rock and clay-fraction diffractograms for each sample (AD: air-dried; EG: ethylene–glycol–solvated; 350 °C and 550 °C: heated preparations). Abbreviations: Smectite (Sme), illite-mica (I-M) smectite+illite-mica (Sme+I-M), kaolinite (Kln), cristobalite (Ksp), plagioclase (Plg), dolomite (Dol), hematite (Hem), and quartz (Qtz).

4.2. Geochemistry

Fourteen volcanic rock samples collected from surface exposures in the Tuzla field were analyzed for major oxides, trace elements, and rare earth elements (REEs). The analytical results are summarized in Table 1. The rhyodacite/dacite samples show SiO₂ contents ranging from 51.80 to 73.36 wt.%, Al₂O₃ from 10.32 to 17.68 wt.%, Fe₂O₃ from 0.76 to 9.47 wt.%, MgO from 0.02 to 2.26 wt.%, CaO from 0.07 to 11.15 wt.%, K₂O from 0.81 to 7.05 wt.%, and Na₂O from 0.06 to 2.05 wt.%. These major-element compositions indicate pronounced differentiation and a wide range of compositional variability. The systematic decrease in MgO and CaO with increasing SiO₂ reflects progressive magmatic evolution, primarily controlled by fractional crystallization of mafic minerals and plagioclase. Locally elevated Fe₂O₃ contents, reaching up to 9.47 wt.% in some samples, suggest variable redox conditions and secondary enrichment related to hydrothermal alteration. The trachyandesite samples are characterized by SiO₂ contents between 58.23 and 76.53 wt.%, Al₂O₃ ranging from 12.63 to 17.89 wt.%, and Fe₂O₃ contents from 1.23 to 6.53 wt.%. Alkali contents vary between 0.13 and 4.35 wt.% for K₂O and between 0.10 and 1.58 wt.% for Na₂O, whereas the remaining major oxides generally occur at concentrations below 1 wt.%. Sample K-2c, collected from a locality marked by pronounced iron-oxide enrichment, exhibits a relatively high Fe₂O₃ content, reflecting localized oxidation processes. The upper range of SiO₂ values in the trachyandesite samples overlaps with that of the rhyodacite/dacite group, indicating transitional compositions and/or advanced stages of magmatic differentiation. Overall, the volcanic rocks of the Tuzla field display a broad range of silica contents, varying from 51.80 to 76.53 wt.% SiO₂, with an average value of 67.80 wt.%. Their relatively high SiO₂ and Al₂O₃ contents, together with generally low concentrations of other major oxides (typically < 1 wt.%), indicate that these rocks represent silica-rich and highly evolved volcanic products. Variations in K₂O and Na₂O contents reflect differential behavior of alkali elements during magma evolution and post-magmatic processes. In particular, low Na₂O values in some samples are likely attributable to plagioclase fractionation and/or sodium loss during hydrothermal alteration, whereas locally elevated K₂O contents suggest potassic enrichment related to crustal input or fluid–rock interaction. The geochemical characteristics of sample K-2c further highlight the influence of localized oxidation and hydrothermal processes within the Tuzla field.

Trace-element data indicate that Sr concentrations range from 20 to 5320 ppm in the rhyodacite/dacite samples and from 306 to 1042 ppm in the trachyandesites, whereas Ba contents vary from 233 to 1287 ppm in the rhyodacite/dacite samples and from 264 to 20,050 ppm in the trachyandesites (Table 1). Moderate Sr concentrations may reflect limited plagioclase fractionation and/or local plagioclase accumulation during magma evolution, whereas lower Sr values are consistent with Sr depletion resulting from plagioclase removal during advanced stages of magmatic differentiation. In contrast, the extremely high Ba contents—particularly values reaching up to 20,050 ppm in some trachyandesite samples—cannot be satisfactorily explained by primary magmatic processes alone (Table 1). Such anomalously high Ba concentrations strongly suggest the involvement of secondary processes, most likely related to hydrothermal alteration and the precipitation of Ba-bearing minerals, such as barite, within fractures, veins, or pore spaces. Similar secondary Ba enrichment has been widely documented in geothermal and hydrothermal systems, where circulating fluids mobilize and redeposit large-ion lithophile elements (LILEs).

Table 1. Major oxide (wt.%), trace and rare earth elements (ppm) concentrations of Tuzla volcanic rocks samples (Key notes: DL, detection limit; LOI, lost on ignition).

Major Oxides (wt.%)	Rhyodacite/Dacite								Trachyandesite						
	DL	T-1a-2	T-1e	T-3b	K-1a	K-1b	K-2d	K-2e	T-1b	T-1c	T-1g	T-3a	T-3c	K-2a	K-2b
SiO ₂	0.01	65.39	51.80	69.89	73.36	67.47	64.36	69.38	70.27	76.53	58.23	66.20	71.18	72.37	72.79
Al ₂ O ₃	0.01	11.62	13.21	16.29	10.32	14.66	14.67	17.68	14.07	12.50	17.89	13.21	12.63	12.63	15.84
Fe ₂ O ₃	0.04	1.25	4.28	0.76	3.66	2.99	9.47	3.21	3.46	2.52	4.28	6.53	1.23	4.73	1.68
MgO	0.01	0.02	1.53	0.15	2.26	1.21	0.64	0.79	0.18	0.04	0.26	0.22	0.15	0.20	0.43
CaO	0.01	0.26	11.15	0.72	1.23	0.99	0.07	0.19	0.72	0.37	0.99	0.81	0.99	0.33	0.13
Na ₂ O	0.01	0.67	2.05	1.43	0.10	0.23	0.07	0.06	1.56	0.35	1.39	1.58	1.01	0.10	0.12
K ₂ O	0.01	1.93	1.16	0.81	3.62	7.05	3.15	3.34	0.94	0.13	1.33	0.91	0.74	3.26	4.35
TiO ₂	0.01	0.555	0.481	0.740	0.993	0.433	0.453	0.447	0.585	0.446	0.800	0.795	0.581	0.939	0.865
P ₂ O ₅	0.01	0.79	0.15	0.27	0.66	0.16	0.30	0.17	0.13	0.07	0.27	0.17	0.14	0.16	0.13
MnO	0.01	0.010	0.031	0.030	0.066	0.052	0.014	0.016	0.019	0.012	0.022	0.014	0.021	0.008	0.007
LOI	−5.1	14.72	12.87	9.58	3.85	5.49	7.18	5.60	9.01	6.65	12.67	8.92	9.03	5.78	4.26
Total	0.01	97.23	98.69	100.7	100.1	100.7	100.4	100.9	101.00	99.62	98.12	99.37	97.69	100.5	100.6
Trace element (ppm)															
Ba	2	1287	701	233	357	987	763	535	1192	13,060	264	1292	20,050	5089	1003
Cs	0.1	0.9	46.2	7.7	2.6	5.3	8.6	11.4	25.1	3.5	23.3	26.8	11.7	4.5	8.2
Ni	20	<20	50	<20	130	20	<20	50	30	30	50	<20	40	<20	<20
Co	1	3	11	3	22	8	7	13	10	2	6	3	14	9	1
V	5	87	92	137	143	70	58	55	60	40	90	151	66	133	148
Cu	10	20	20	60	60	20	50	60	60	10	40	20	20	30	30
Zn	30	<30	60	<30	50	50	110	90	100	30	70	<30	40	<30	<30
Pb	5	203	34	905	74	36	29	41	92	26	52	85	59	37	40
Rb	1	11	59	42	174	311	146	170	68	10	92	79	49	121	190
Sr	2	5320	797	967	202	211	54	20	581	722	572	939	1042	539	306
Y	0.5	27.8	17.6	23.8	28.1	13.0	16.5	16.1	16.3	21.8	13.1	20.4	15.2	21.0	19.0
Zr	1	198	141	310	351	167	173	164	302	292	216	294	385	313	289
Nb	0.2	10.9	8.7	15.1	16.2	7.9	8.5	7.4	12.9	15.6	17.7	14.9	10.3	18.1	15.3
Th	0.05	50.9	11.4	57.4	53.1	15.8	22.6	16.8	34.2	35.2	35.4	41.5	33.8	40.9	32.2
W	0.5	6.2	1.8	1.8	8.7	4.8	13.8	3.8	9.1	3.9	5.8	1.3	7.7	9.4	11.2
Hf	0.1	3.8	4.7	8.0	10.9	4.9	6.0	4.8	8.9	7.9	6.7	7.9	11.1	9.3	11.3
U	0.01	10.60	3.19	59.00	14.60	5.12	4.33	4.91	6.96	1.24	4.93	5.70	9.76	12.10	14.40
Ta	0.01	1.23	0.60	1.67	1.87	0.70	0.74	0.68	1.38	1.17	1.42	1.58	1.36	2.14	1.65
Sb	0.2	5.8	7.9	9.6	1.9	1.8	3.8	0.8	13.2	3.1	11.3	13.0	22.0	0.8	2.7
Rare Earth Element (ppm)															
La	0.05	96.9	34.5	91.8	85.6	40.6	39.2	37.9	52.2	63.8	75.2	68.7	49.1	80.1	78.8
Ce	0.05	184.0	67.9	17.0	167.0	76.5	72.9	72.8	94.3	114.0	142.0	128.0	91.0	147.0	143.0
Pr	0.01	20.0	7.9	18.6	21.0	8.7	8.3	8.5	10.8	12.5	15.8	13.8	10.3	17.0	17.5
Nd	0.05	72.7	28.3	64.2	77.0	30.9	28.4	29.4	36.4	42.8	46.0	47.7	36.9	61.3	62.7
Sm	0.01	14.40	5.44	11.50	13.70	5.20	5.02	5.71	6.06	7.22	5.10	9.02	6.20	8.80	9.45
Eu	0.005	3.77	1.16	2.20	2.53	1.03	0.85	1.06	1.39	1.22	0.82	1.93	1.21	1.28	1.57
Gd	0.01	11.10	4.05	6.59	9.18	3.69	4.11	4.90	4.14	4.99	2.93	5.84	4.28	4.00	4.88
Tb	0.01	1.29	0.57	0.85	1.27	0.45	0.56	0.68	0.51	0.72	0.42	0.74	0.55	0.64	0.71
Dy	0.01	5.70	3.16	4.60	5.63	2.42	2.97	3.22	2.92	3.78	2.33	3.98	2.72	3.87	3.68
Ho	0.01	0.89	0.61	0.83	0.99	0.44	0.52	0.55	0.56	0.77	0.44	0.73	0.52	0.76	0.63
Er	0.01	2.24	1.71	2.33	2.49	1.29	1.52	1.54	1.59	2.10	1.38	2.16	1.47	2.01	1.78
Tm	0.005	0.312	0.229	0.344	0.342	0.185	0.206	0.223	0.223	0.292	0.202	0.328	0.228	0.274	0.246
Yb	0.01	2.00	1.42	2.20	2.17	1.20	1.42	1.40	1.59	1.87	1.53	2.07	1.64	1.59	1.54
Lu	0.002	0.303	0.240	0.343	0.363	0.186	0.244	0.239	0.274	0.330	0.261	0.316	0.260	0.250	0.253

In the Zr/TiO₂-Nb/Y discrimination diagram of [44], which employs major and selected trace-element concentrations for volcanic rock classification, the studied samples plot predominantly within the rhyodacite/dacite and trachyandesite fields (Figure 6a). According to the K₂O-SiO₂ diagram of [45], the rhyodacite/dacite samples are mainly distributed within the calc-alkaline field, whereas most of the trachyandesite samples fall within the tholeiitic field (Figure 6b). In the AFM ternary diagram of [46], the majority of the rhyodacite/dacite samples plot within the tholeiitic field, with only two samples extending into the calc-alkaline field, while all trachyandesite samples are restricted to the tholeiitic domain (Figure 6c). Overall, these geochemical classifications indicate that the magmatic evolution of the Tuzla volcanic rocks reflects a complex differentiation history involving both tholeiitic and calc-alkaline evolutionary trends.

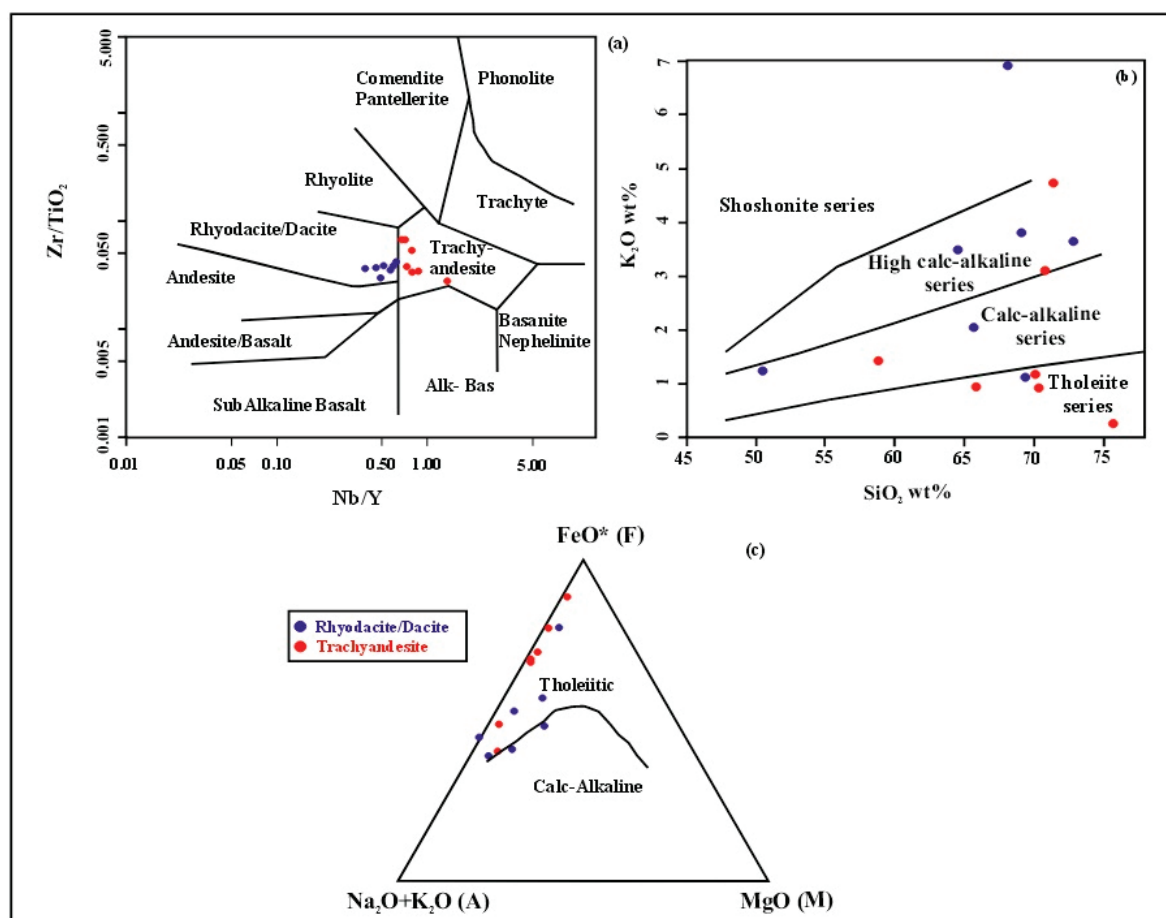


Figure 6. (a) Rock classification graph of volcanics [44]. (b) K₂O-Si₂O [45] diagrams, (c) AFM (FeO*-Na₂O + K₂O-MgO) diagram showing the boundary between tholeiitic and calcaline series [46].

Chondrite-normalized rare earth element (REE) spider diagrams of the studied volcanic rocks [47] are shown in Figure 7. The rhyodacite/dacite and trachyandesite samples exhibit pronounced enrichment in light rare earth elements (LREEs) relative to heavy rare earth elements (HREEs), with La_N/Sm_N ratios ranging from 3.93 to 9.28 and La_N/Yb_N ratios between 16.38 and 34.50. These values indicate broadly similar REE distribution patterns among the investigated rock types (Figure 7a). Such LREE enrichment relative to HREEs is a typical geochemical characteristic of calc-alkaline volcanic suites [48,49].

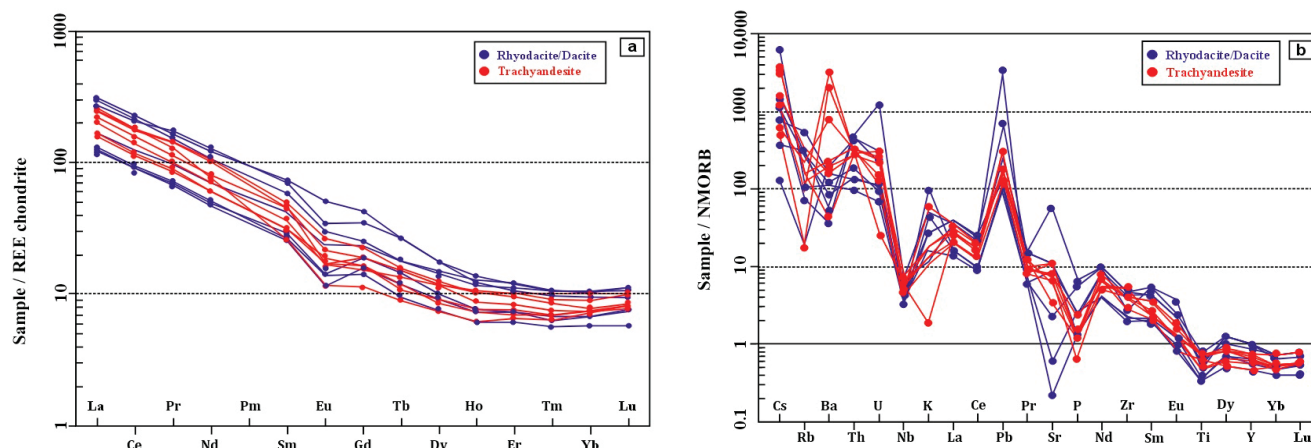


Figure 7. (a) Chondrite-normalized rare earth element (REE) patterns [47]. (b) N-MORB-normalized trace element distribution patterns of the volcanic rocks from the study area [47].

The observed REE patterns indicate that the studied volcanic rocks evolved through differentiation of parental magma(s) derived from a common source. The volcanic rocks display slight negative Eu anomalies superimposed on LREE-enriched patterns (Figure 7a). The average Eu/Eu^* values range from 0.57 to 0.91 for the rhyodacite/dacite samples and from 0.62 to 0.85 for the trachyandesites. These negative Eu anomalies are interpreted to result from plagioclase fractionation and may also reflect assimilation of Eu-depleted continental crustal material.

The studied volcanic rocks show enrichment in light rare earth elements (LREEs) relative to heavy rare earth elements (HREEs) in N-MORB-normalized trace element patterns (Figure 7b). They are characterized by enrichment in large ion lithophile elements (LILEs), such as K, Pb, and Th, together with depletion in Rb and Sr. High field strength elements (HFSEs), including Nb, Zr, Ti, P, and Yb, are also depleted. In addition, Ba displays both positive and negative anomalies (Figure 7b).

5. Discussion

5.1. Tectonic Setting

To constrain the tectonic setting of the Tuzla volcanics, several widely used geochemical discrimination diagrams were applied [50,51]. In the Th/Ta versus Yb diagram, most samples plot within the oceanic arc field, while a limited number extend toward the active continental margin domain (Figure 8a). Likewise, the Th/Yb versus La/Th diagram places all samples within the oceanic arc field (Figure 8b). For comparison, Oligocene–Miocene calc-alkaline volcanic rocks from the Büyükbostancı–Çiçekpınar villages (Balıkesir, NW Turkey) plot within the active continental margin field in the Th/Ta versus Yb diagram, reflecting a different tectonomagmatic setting [52]. Ref. [53] showed that the Gökçeada volcanic rocks fall within the oceanic arc field on the same diagram and display a vertically elongated distribution indicative of subduction-related enrichment, a pattern closely comparable to that observed in the Tuzla volcanics. Overall, these geochemical signatures indicate that the Tuzla volcanic rocks were predominantly generated in an oceanic arc-related tectonic setting, with a subordinate contribution from active continental margin processes. This interpretation is consistent with other Oligocene–Miocene magmatic suites in NW Türkiye and with comparable subduction-related volcanic sequences documented in comparable tectonic settings worldwide.

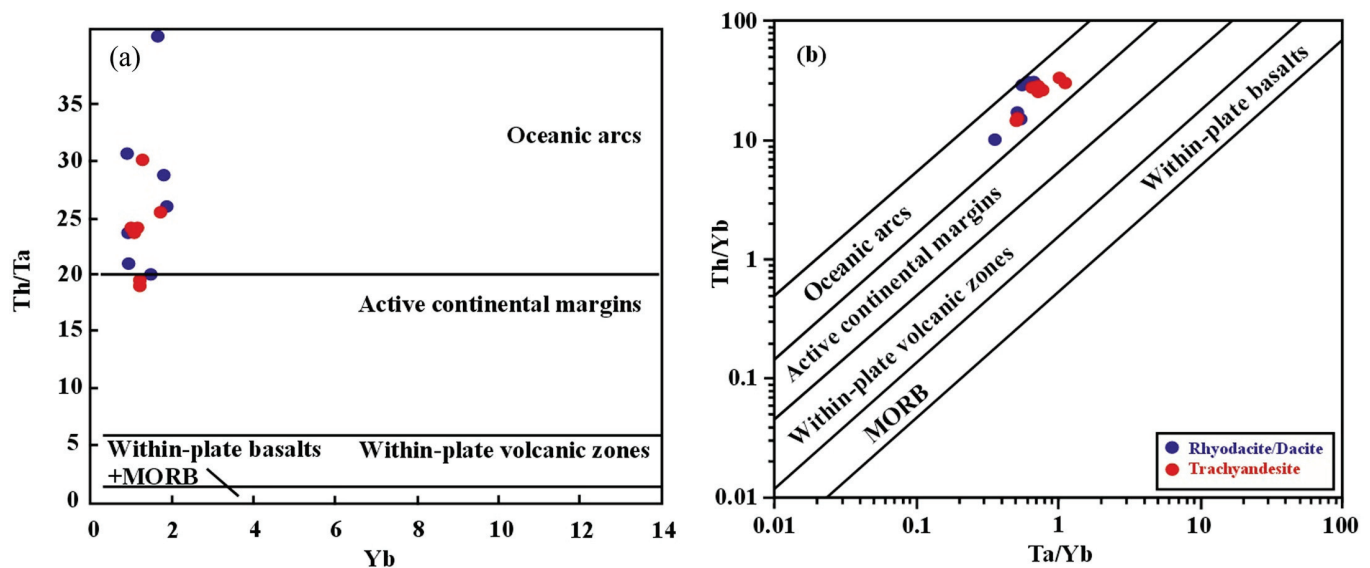


Figure 8. Geochemical discrimination diagrams for the Tuzla volcanic rocks: (a) Th/Ta versus Yb diagram [50]; (b) Ta/Yb versus Th/Yb diagram (after [51]).

The Tuzla volcanic rocks display mixed geochemical affinities, as they are distributed across both the volcanic arc and intraplate fields in the Rb/10–Hf–Ta*3 and Rb/30–Hf–Ta*3 triangular diagrams (Figure 9a,b) [54]. The rhyodacite/dacite samples predominantly plot within the volcanic arc field, whereas the trachyandesites mainly fall within the intraplate field, indicating contributions from both arc-related and intraplate magmatic processes. For comparison, the Yürekli volcanic rocks, which are spatially adjacent to the Tuzla volcanics, are mainly composed of andesite–trachyandesite–dacite, with minor basaltic andesite. In the Rb/10–Hf–Ta*3 diagram, these samples plot largely within the volcanic arc field, whereas in the Rb/30–Hf–Ta*3 diagram they are distributed between the pre-collisional and post-collisional fields, with only a few samples plotting in the volcanic arc field [55]. This comparison highlights the differences in magmatic evolution and source contributions between the Tuzla and Yürekli volcanic suites.

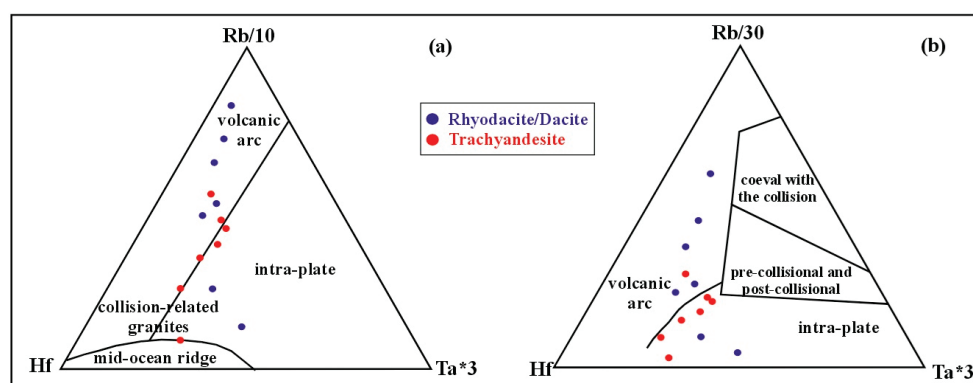


Figure 9. Distribution of rhyodacite/dacite and trachyandesite samples from the Tuzla volcanic rocks in (a) the Rb/10–Hf–Ta*3 diagram and (b) the Rb/30–Hf–Ta*3 diagram [54].

In particular, because Rb is a large-ion lithophile element that is highly mobile and sensitive to hydrothermal fluids, the distributions observed in these discrimination diagrams may reflect not only primary magmatic signatures but also the effects of hydrothermal alteration and fluid–rock interactions. The dispersion of samples across both the volcanic arc and intraplate fields in the Rb/10–Hf–Ta*3 diagram suggests a multi-source magmatic system; however, it also implies that the positions of some samples may have been second-

darly modified by Rb enrichment or depletion. In this context, the overlap between the arc and intraplate fields observed in the Rb/10–Hf–Ta*3 diagram can be partly attributed to the influence of alteration on Rb distribution. By contrast, the clearer separation observed between rock types in the Rb/30–Hf–Ta*3 diagram indicates that this diagram more effectively preserves the primary magmatic signal, as it is less sensitive to Rb mobility. The predominance of rhyodacite/dacite samples within the volcanic arc field suggests that their characteristic geochemical signatures—reflecting contributions from subduction-related metasomatized mantle sources and crustal components—have been largely retained despite hydrothermal overprinting. Conversely, the concentration of trachyandesite samples within the intraplate field implies derivation from enriched lithospheric mantle sources and indicates a post-arc/intraplate magmatic affinity.

5.2. Magma Source

The studied volcanic rocks are characterized by pronounced enrichment in large ion lithophile elements (LILEs; Rb, Ba, and K) and light rare earth elements (LREEs) relative to high field strength elements (HFSEs; Nb, Ti, Zr, Hf, and Y) and heavy rare earth elements (HREEs) (Figure 8b). This geochemical signature indicates a metasomatized mantle source enriched in LILEs by a subduction-related component. [55]. The presence of negative Nb, P, Zr, and Ti anomalies, together with LREE enrichment relative to HREEs, further supports a subduction-related continental arc affinity for the parental magmas [51,56–59]. Elevated Th/Yb ratios, coupled with enrichment in Ce, Th, and other LILE elements (Sr, K, Ba, Rb), suggest that the parental magmas were derived predominantly from the lithospheric mantle [60–64]. Moreover, the marked depletion of Nb relative to LILEs implies that the mantle source region was metasomatized by fluids and/or melts released from the subducting slab or associated sediments, reinforcing a subduction-modified mantle origin for the magmas [51,61,65]. Comparable trace element characteristics have also been reported for volcanic rocks from the Ezine–Gülpınar–Ayvacık region in western Anatolia, Türkiye [3], indicating similar magmatic processes and tectonomagmatic settings.

High-field strength elements (HFSEs), such as Nb, are commonly depleted relative to light rare earth elements (LREEs; e.g., La) in the lithospheric mantle. Consequently, high Nb/La ratios (>1) are generally interpreted to indicate an asthenospheric mantle source, whereas low Nb/La ratios (<0.5) are characteristic of a lithospheric mantle origin [66,67]. In the investigated rhyodacite/dacite samples, Nb/La ratios range from 0.11 to 0.25, while La/Yb ratios vary between 24.30 and 48.45. The trachyandesite samples yield Nb/La ratios of 0.19–0.25 and La/Yb ratios of 32.83–51.17. The combination of low Nb/La and high La/Yb ratios indicates that the parental magmas were predominantly derived from a lithospheric mantle source (Figure 10). For comparison, Lower Miocene Şapçı volcanic rocks, which exhibit geochemical characteristics similar to those of the Tuzla volcanics [68], plot within the same field on the Nb/La versus La/Yb diagram. In contrast, Mesozoic volcanic rocks from central Lebanon (Middle East) fall within the HIMU–OIB field on the same diagram [69], reflecting a significant contribution from an asthenospheric mantle source.

The Nb/Y and Th/Y ratios are widely used geochemical parameters for distinguishing between crustal contamination and homogenization of magma sources. The Nb/Y versus Th/Y discrimination diagram [51] (Figure 11) is commonly applied to differentiate between subduction-enriched and melt-enriched magmatic systems. In the present study, the volcanic rock samples display relatively elevated Th/Y ratios. This geochemical trend points to the influence of assimilation and fractional crystallization processes and further suggests that the mantle source was metasomatized by fluids released from the subducting slab.

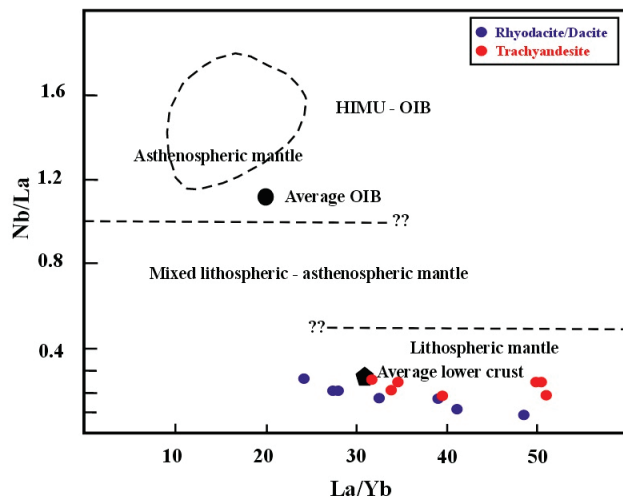


Figure 10. Nb/La versus La/Yb diagram. Mean OIB values are from [66], and mean lower crust values are from [67]. Dashed lines separating asthenospheric, lithospheric, and mixed mantle domains are based on [67]. The HIMU–OIB field is defined using data from the oceanic islands of St. Helena, Bouvet, and Ascension as reported by [70], assuming $Yb = Tb \div 0.5$. (OIB: Ocean Island Basalt; HIMU–OIB: asthenospheric mantle source characterized by high μ (U/Pb) ratios).

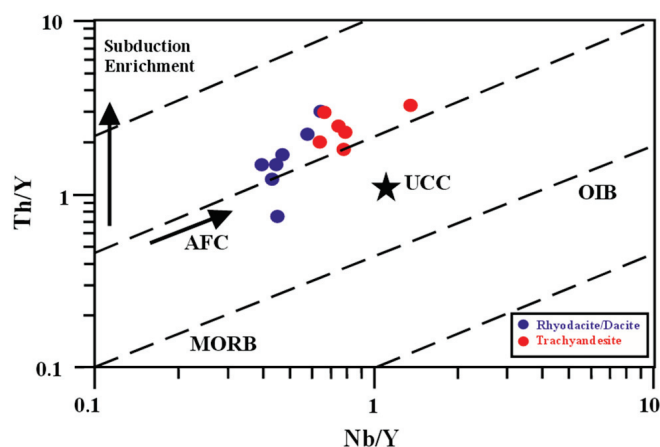


Figure 11. Nb/Y–Th/Y diagram of the studied volcanic rocks [51]. (AFC: Assimilation–Fractional Crystallization, UCC: Upper Continental Crust, OIB: Ocean Island Basalt, MORB: Mid-Ocean Ridge Basalt).

In the Ta/Yb–Th/Yb discrimination diagram (Figure 12), the studied volcanic rocks are characterized by elevated Th/Yb ratios and define a trend parallel to the mantle array. This distribution indicates the combined influence of subduction-related enrichment and a decrease in the degree of partial melting. Such a pattern suggests that the parental magmas were derived from a mantle source enriched by fluids released during subduction-related metasomatism and subsequently generated under relatively low degrees of partial melting. In other words, the melts originated from a mantle source that had been previously modified by subduction-derived fluids and later underwent partial melting at reduced extents [71,72]. The Ta/Yb and Th/Yb ratios are widely used to evaluate mantle source characteristics and the extent of crustal contamination, as Th is more sensitive to crustal processes than Yb and Ta [73]. The position of the samples on the diagram further implies that assimilation–fractional crystallization (AFC) processes played a significant role in the magmatic evolution of the studied volcanic rocks. A comparable influence of fractional crystallization has also been documented for Miocene–Pliocene volcanic rocks from central Armenia [74].

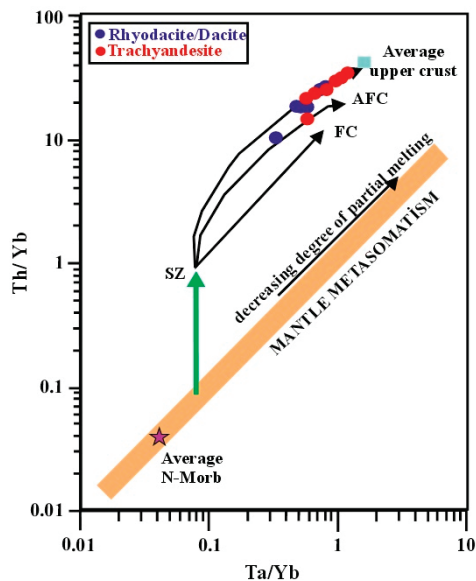


Figure 12. Th/Yb versus Ta/Yb diagram of rhyodacite/dacite and trachyandesite samples from the Tuzla volcanic rocks [73]. Vectors indicating subduction enrichment and mantle metasomatism are after [73]. N-type OIB and average upper continental crust compositions were taken from [47] and [75], respectively. FC, fractional crystallization vector; AFC, assimilation coupled with fractional crystallization curve. (AFC: Assimilation–Fractional Crystallization, FC: Fractional Crystallization, SZ: Subduction Zone).

In the La/Nb versus Ba/Nb discrimination diagram (Figure 13), the studied volcanic rocks cluster within a field proximal to arc-related volcanic compositions. During subduction, light rare earth elements (LREEs) and large ion lithophile elements (LILEs; Ba, Sr, K, and Rb) are transported upward by fluids released from the subducting slab [61,62]. The elevated La/Nb and Ba/Nb ratios observed in these volcanic rocks therefore indicate that their mantle source was significantly influenced by subduction-related enrichment. For comparison, the Taşlyayla volcanic rocks (Çaykara, Trabzon, NE Turkey) also plot within the arc volcanic field on the La/Nb–Ba/Nb diagram [76], exhibiting geochemical characteristics closely comparable to those of the Tuzla volcanics.

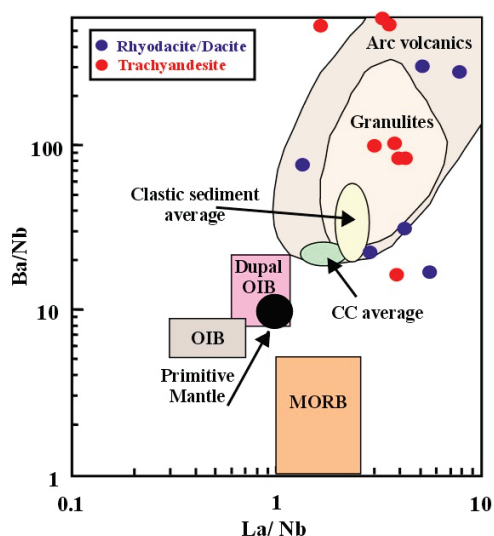


Figure 13. La/Nb–Ba/Nb diagram of the investigated volcanic rocks (Primitive mantle from [47]; Continental crust from [75,77]; Dupal-OIB from [78]; Arc volcanics and Archean granulites from [79]. (OIB: Ocean Island Basalt, MORB: Mid-Ocean Ridge Basalt, CC: Continental Crust).

Although no isotope analyses were performed in the present study, the magma source characteristics of Miocene volcanic rocks in western Anatolia have been well constrained by previous isotopic investigations. Sr–Nd–Pb isotope data indicate that Miocene calc-alkaline to shoshonitic volcanic rocks were derived from a heterogeneous and enriched lithospheric mantle source that was variably modified by subduction-related components and subjected to limited crustal assimilation [3,80,81]. Elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and negative ϵNd values are generally interpreted to reflect enriched mantle domains rather than extensive upper-crustal contamination, whereas Pb isotope systematics point to mixing between depleted asthenospheric mantle and enriched mantle components. Furthermore, zircon Lu–Hf and $\delta^{18}\text{O}$ isotope data from felsic volcanic and plutonic rocks indicate predominantly mantle-derived magmas with subordinate crustal input during magma evolution [35,82]. Taken together, these regional isotopic constraints support a multi-component mantle source for Oligocene–Miocene magmatism in Western Anatolia related to post-collisional lithospheric thinning and asthenospheric upwelling.

5.3. Fractional Crystallization and Assimilation– Fractional Crystallization

The studied volcanic rocks are characterized by enrichment in light rare earth elements (LREEs) together with elevated La/Yb ratios, suggesting that fractional crystallization of hornblende played a significant role in controlling the relative depletion or enrichment of heavy rare earth elements (HREEs) [83]. Likewise, the presence or absence of Eu anomalies appears to be largely governed by the extent of plagioclase equilibration and/or fractionation within the magma [84]. These geochemical features indicate that the investigated volcanic rocks likely evolved from parental magmas derived from a common source. Comparative evaluation with the Yürekli volcanic rocks of northwest Türkiye [55] and the Early Miocene Şapçı volcanic rocks [61] further supports derivation from a similar magmatic source and a broadly comparable evolutionary history.

The interaction of mantle-derived magmas with crustal material during ascent, and the resulting contamination, provides important constraints on the source characteristics of volcanic rocks [73]. Previous studies have shown that fractional crystallization and assimilation–fractional crystallization (FC–AFC) processes play a fundamental role in the petrogenesis of intermediate calc-alkaline volcanic rocks formed in subduction-zone settings [85–87]. Trace element and rare earth element (REE) abundances, as well as their ratios, represent key geochemical indicators of the mineral phases removed from parental magmas during partial melting and subsequent evolutionary processes, including fractional crystallization, assimilation, and crustal contamination [87]. Accordingly, assimilation of crustal material is regarded as a major geodynamic process that significantly modifies and redistributes the trace element compositions of mantle-derived magmas [63,64].

Chondrite-normalized REE patterns and N-MORB–normalized multi-element diagrams of the studied volcanic rocks are presented in Figure 8. The samples are characterized by enrichment in large ion lithophile elements (LILEs; U, Th, Rb, and K), light rare earth elements (LREEs), and particularly Pb, whereas high field strength elements (HFSEs; Nb and Ti) are depleted. The weakly developed Eu anomalies observed in the samples (Figure 8a) indicate crystallization and/or fractionation of plagioclase and K-feldspar, while pronounced P depletions in the multi-element patterns (Figure 8b) point to apatite fractionation. The presence of marked negative Nb anomalies coupled with positive Pb anomalies (Figure 8b) is a typical geochemical feature reflecting continental crustal influence.

Within the calc-alkaline series, Ref. [88] used the CaO–Y diagram to distinguish between J- and L-type trends, corresponding to relative Y depletion and enrichment, respectively, compared to the standard calc-alkaline trend. In the CaO–Y diagram (Figure 14), nearly all of the studied samples plot on the Y-depleted side of the calc-alkaline reference

line, defining a J-type trend. This distribution emphasizes the significant role of hornblende and plagioclase fractionation in the petrogenesis of the volcanic rocks. Similar mineralogical controls have been reported for Upper Oligocene–Lower Miocene volcanic rocks from the Karakavak and Çukurhüseyin villages (Balıkesir Province, northwestern Türkiye) [89], as well as for Early Eocene volcanic rocks from the Artvin region in, northeastern Türkiye [90].

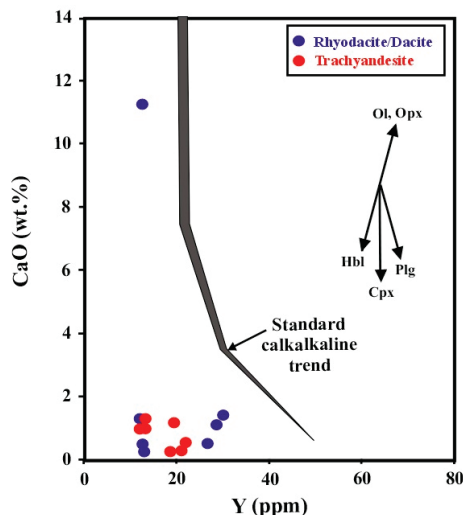


Figure 14. Y (ppm)-CaO (wt.%) diagram of volcanic rocks in the study area [91].

The relationship between fractional crystallization, source metasomatism, and/or crustal assimilation associated with subduction-derived fluids can be effectively evaluated using the Rb/Y versus Nb/Y diagram [73]. In this diagram, the studied volcanic rocks define a predominantly vertical trend and plot within the field characteristic of subduction-zone enrichment and/or crustal contamination (Figure 15). In contrast, intraplate magmatic enrichment is typically expressed by a positive correlation between Rb and Nb, corresponding to Nb/Y values of approximately 1 [91]. In the Tuzla volcanic suite, Nb/Y ratios range from 0.39 to 0.63 in the rhyodacite/dacite samples and from 0.68 to 1.35 in the trachyandesites, reflecting relative HFSE depletion that is characteristic of subduction-related magmatism. Comparable geochemical trends indicative of subduction-related enrichment or crustal contamination have also been documented in Late Cretaceous high-K volcanic rocks from the Central Pontides orogenic belt [92] and in Eocene–Oligocene volcanic units from the Momen Abad, eastern Iran [93].

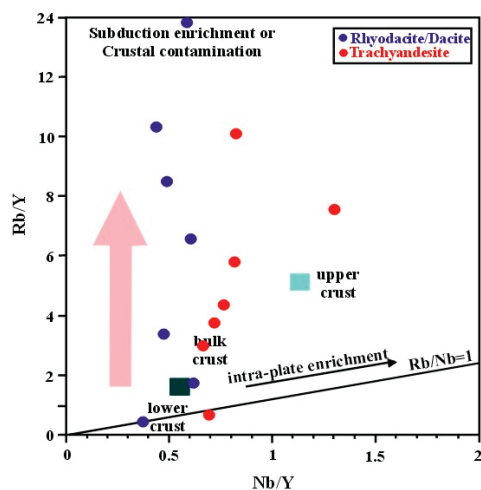


Figure 15. Nb/Y and Rb/Y graphs of Tuzla field volcanics [79]. (compositions of upper and lower crusts according to [75]).

6. Conclusions

Mineralogical, petrographic, and geochemical investigations of the Oligocene-Miocene volcanic rocks exposed in the Tuzla field, many of which record varying degrees of hydrothermal alteration, provide important constraints on the tectonic setting, magma source characteristics, and the roles of fractional crystallization and assimilation processes. The main conclusions can be summarized as follows:

- The Tuzla area hosts a complex Miocene volcanic system composed of andesitic, dacitic, and rhyolitic lavas, trachyandesites, pyroclastic deposits, ignimbrites, and the Kestanbol Pluton.
- Petrographic observations and X-ray diffraction (XRD) analyses indicate that the volcanic units are dominated by porphyritic dacitic–rhyodacitic and trachyandesitic rocks, which have been variably affected by pervasive silicification, iron oxide formation, and mineral opacification related to hydrothermal alteration.
- Geochemical data, particularly rare earth element (REE) systematics, demonstrate that fractional crystallization of primary mineral phases played a major role in the magmatic evolution of the Tuzla volcanics. Chondrite-normalized REE patterns show enrichment in light REEs relative to heavy REEs and broadly similar distribution trends, suggesting derivation from a common parental magma source.
- K_2O – Na_2O and AFM diagrams indicate high-K calc-alkaline, calc-alkaline, and tholeiitic affinities. Most rhyodacite/dacite samples and all trachyandesites plot within the tholeiitic field, reflecting compositional diversity within the volcanic suite.
- Tectonic discrimination diagrams collectively suggest that the Tuzla volcanic rocks were generated in both volcanic arc-related and intraplate magmatic settings, reflecting a complex tectonomagmatic evolution.
- Although moderate enrichments in Ba and Sr may partly reflect magma source characteristics and differentiation processes, the highest Ba and Sr concentrations are interpreted to result from post-magmatic hydrothermal fluid–rock interaction rather than primary magmatic compositions.
- The Tuzla volcanic suite includes rocks that preserve primary magmatic geochemical signatures as well as samples that have experienced varying degrees of hydrothermal overprinting. Overall, the volcanics were derived from a collision-related, enriched lithospheric mantle source and subsequently evolved through fractional crystallization and assimilation processes, accompanied by crustal contamination.

Author Contributions: Conceptualization, D.K. and O.C.; Methodology, D.K. and O.C.; Formal analysis, D.K. and O.C.; Investigation, D.K.; Resources, D.K. and O.C.; Writing—original draft, D.K. and O.C.; Writing—review & editing, D.K. and O.C.; Visualization, D.K. and O.C.; Project administration, D.K. and O.C.; Funding acquisition, D.K. and O.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the TÜBİTAK 1002 Program (Scientific and Technological Research Council of Turkey), Project No. 123Y088.

Data Availability Statement: Data are contained within the article.

Acknowledgments: This study is part of a broader research project that includes field investigations. The authors thank Erhan Şener (Süleyman Demirel University, Isparta, Turkey) for his support during the fieldwork. The authors also thank the anonymous reviewers for their constructive comments and suggestions, which helped to improve the quality of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Erenoğlu, R.C.; Arslan, N.; Erenoğlu, O.; Arslan, E. Application of spectral analysis to Determine geothermal anomalies in the Tuzla Region, NW Turkey. *Arab. J. Geosci.* **2019**, *12*, 439. [CrossRef]
2. Genç, Ş.C.; Dönmez, M.; Akçay, A.E.; Altunkaynak, Ş.; Eyüpoğlu, M.; Ilgar, Y. *Biga Yarımadası Tersiyer Volkanizmasının Stratigrafik, Petrografik ve Kimyasal Özellikleri Biga Yarımadası'nın Genel ve Ekonomik Jeolojisi*, MTA Rapor No: 11101. Ankara, Türkiye. 2009; Unpublished.
3. Aldanmaz, E.; Pearce, J.A.; Thirlwall, M.F.; Mitchell, J.G. Petrogenetic evolution of Late Cenozoic, post collision volcanism in Western Anatolia, Turkey. *J. Volcanol. Geotherm. Res.* **2000**, *102*, 67–95. [CrossRef]
4. Altunkaynak, Ş.; Genç, Ş.C. Petrogenesis and time-progressive evolution of the Cenozoic continental volcanism in the Biga Peninsula, NW Anatolia. *Lithos* **2008**, *102*, 316–340. [CrossRef]
5. Topuz, G.; Okay, A.I. Late Eocene–early Oligocene two-mica granites in NW Turkey (the Uludağ Massif): Water-fluxed melting products of a mafic metagreywacke. *Lithos* **2017**, *268*, 334–350. [CrossRef]
6. Ketin, İ. Anadolu'nun Tektonik Birlikleri. *Bull. Miner. Res. Explor.* **1966**, *66*, 20–34.
7. Şengör, A.M.C.; Yılmaz, Y. Tethyan evolution of Turkey: A plate tectonic approach. *Tectonophysics* **1981**, *75*, 181–241. [CrossRef]
8. Yılmaz, Y. Comparison of Young Volcanic Associations of Western and Eastern Anatolia under Compressional Regime; A Review. *J. Volcanol. Geotherm. Res.* **1990**, *44*, 69–87. [CrossRef]
9. Okay, A.İ.; Siyako, M.; Bürkan, K.A. Biga Yarımadası'nın Jeolojisi ve Tektonik Evrimi. *TPJD Bülteni* **1990**, *2*, 83–121.
10. Okay, A.İ.; Tüysüz, O. Tethyan sutures of northern Turkey. In *Mediterranean Basins: Tertiary Extension Within the Alpine Orogen*; Durand, B., Jolivet, L., Horvath, F., Seranne, M., Eds.; Geological Society Special Publications: London, UK, 1999; Volume 156, pp. 475–515.
11. Harris, N.B.; Kelley, S.; Okay, A.I. Post-collision magmatism and tectonics in northwest Anatolia. *Contrib. Mineral. Petrol.* **1994**, *117*, 241–252. [CrossRef]
12. Okay, A.; Satır, M.; Maluski, H.; Siyako, M.; Monie, P.; Metzger, R.; Akyüz, S. Paleo- and Neo-Tethyan events in northwest Turkey: Geological and geochronological constraints. In *Tectonics of Asia*; Yin, A., Harrison, M., Eds.; Cambridge University Press: Cambridge, UK, 1996; pp. 420–441.
13. Okay, A.I.; Tansel, İ.; Tüysüz, O. Obduction, subduction and collision as reflected in the Upper Cretaceous-Lower Eocene sedimentary record of western Turkey. *Geol. Mag.* **2001**, *138*, 117–142. [CrossRef]
14. Altunkaynak, S.; Dilek, Y. *Timing and Nature of Postcollisional Volcanism in Western Anatolia and Geodynamic Implications. Postcollisional Tectonics and Magmatism in the Mediterranean Region and Asia*; Dilek, Y., Pavlides, S., Eds.; Geological Society of America Special Paper: Boulder, CO, USA, 2006; Volume 409, pp. 321–351.
15. Aslan, Z.; Erdem, D.; Temizel, İ.; Arslan, M. SHRIMP U–Pb zircon ages and whole-rock geochemistry for the Şapçı volcanic rocks, Biga Peninsula, Northwest Turkey: Implications for pre-eruption crystallization conditions and source characteristics. *Int. Geol. Rev.* **2017**, *59*, 1764–1785. [CrossRef]
16. Aslan, Z.; Demir, H.; Altın, İ. U–Pb zircon geochronology and petrology of the early Miocene Göloba and Şaroluk plutons in the Biga Peninsula, NW Turkey: Implications for post-collisional magmatism and geodynamic evolution. *J. Afr. Earth Sci.* **2020**, *172*, 103998. [CrossRef]
17. Okay, A.I. Geology of Turkey: A synopsis. *Anschnitt* **2008**, *21*, 19–42.
18. Genç, S.C.; Yılmaz, Y. *Post Collisional Magmatism in Armutlu Peninsula, NW Anatolia*; Abstracts; IAVCEI International Volcanology Congress: Ankara, Türkiye, 1994.
19. Delaloye, M.; Bingöl, E. Granitoids from Western and Northwestern Anatolia: Geochemistry and Modeling of Geodynamic Evolution. *Int. Geol. Rev.* **2000**, *42*, 241–268. [CrossRef]
20. Altunkaynak, Ş. Collision-Driven Slab Break off Magmatism in North Western Anatolia. Turkey. *J. Geol.* **2007**, *115*, 63–82. [CrossRef]
21. Ercan, T.; Satır, M.; Steinitz, G.; Dora, A.; Sarıfakıoğlu, E.; Adis, C.; Walter, H.J.; Yıldırım, T. Biga Yarımadası ile Gökçeada, Bozcaada ve Tavşan Adalarındaki KB Anadolu Tersiyer Volkanizmasının Özellikleri. *MTA Derg.* **1995**, *117*, 55–86.
22. Yılmaz, Y. An approach to the origin of young volcanic rocks of western Turkey. In *Tectonic Evolution of the Tethyan Region*; Springer: Dordrecht, The Netherlands, 1989; pp. 159–189.
23. Genç, S.C. Evolution of the Bayramiç Magmatic Complex, Northwestern Anatolia. *J. Volcanol. Geotherm. Res.* **1998**, *85*, 233–249. [CrossRef]
24. Özgenc, I.; İlbeli, N. Petrogenesis of the Late Cenozoic Egrigöz pluton in western Anatolia, Turkey: Implications for magma genesis and crustal processes. *Int. Geol. Rev.* **2008**, *50*, 375–391. [CrossRef]
25. Akay, E. Geology and petrology of the Simav Magmatic Complex (NW Anatolia) and its comparison with the Oligo-Miocene granitoids in NW Anatolia: Implications on Tertiary tectonic evolution of the region. *Int. J. Earth Sci.* **2009**, *98*, 1655–1675. [CrossRef]

26. Prelević, D.; Akal, C.; Foley, S.F.; Romer, R.L.; Stracke, A.; Van Den Bogaard, P. Ultrapotassic mafic rocks as geochemical proxies for post-collisional dynamics of orogenic lithospheric mantle: The case of southwestern Anatolia, Turkey. *J. Petrol.* **2012**, *53*, 1019–1055. [CrossRef]
27. Aysal, N.; Öngen, A.S.; Şahin, S.Y.; Kasapci, C.; Hanilçi, N.; Peytcheva, I. Peritectic assemblage entrainment and mafic-felsic magma interaction in the Late Oligocene–Early Miocene Karadağ Pluton in the Biga Peninsula, northwest Turkey: Petrogenesis and geodynamic implications. *Turk. J. Earth Sci.* **2021**, *30*, 279–312. [CrossRef]
28. Krushensky, R.D. Volcanic rocks of Turkey. *Bull. Geol. Surv. Jpn.* **1976**, *26*, 393–412.
29. Duru, M.; Pehlivan, Ş.; Şentürk, Y.; Yavaş, F.; Kar, H. New Results on the Lithostratigraphy of the Kazdağ Massif in Northwest Turkey. *Turk. J. Earth Sci.* **2004**, *13*, 177–186.
30. Dönmez, M.; Akçay, A.E.; Genç, Ş.C.; Acar, Ş. Middle-late Eocene volcanism and marine ignimbrites in Biga peninsula (NW Anatolia-Turkey). *Bull. Miner. Res. Explor.* **2005**, *131*, 21.
31. Okay, A.İ.; Satır, M. Coeval plutonism and metamorphism in a Latest Oligocene metamorphic core complex in northwest Turkey. *Geol. Mag.* **2000**, *137*, 495–516. [CrossRef]
32. Beccalotto, L.; Jenny, C. Geology and correlations of the Ezine Zone: A Rhodope fragment in NW Turkey. *Turk. J. Earth Sci.* **2004**, *13*, 145–176.
33. Okay, A.I. The oxygen fugacity stability of deerite: An alternative view. *J. Metamorph. Geol.* **1987**, *5*, 553–555. [CrossRef]
34. Şentürk, K.; Okay, A.I. Blueschists discovered east of Saros Bay in Thrace. *MTA Derg.* **1984**, *97*, 68–72.
35. Altunkaynak, Ş.; Dilek, Y.; Genç, C.Ş.; Sunal, G.; Gertisser, R.; Furnes, H.; Foland, K.A.; Yang, J. Spatial, temporal and geochemical evolution of Oligo–Miocene granitoid magmatism in Western Anatolia, Turkey. *Gondwana Res.* **2012**, *21*, 961–986. [CrossRef]
36. Birkle, P.; Satır, M.; Erler, A.; Ercan, T.; Bingöl, E.; Orcen, S. Dating, geochemistry and geodynamic significance of the Tertiary magmatism of the Biga Peninsula, NW Turkey. *Geol. Black Sea Reg.* **1995**, *117*, 171–180.
37. Karacık, Z. Ezine-Ayvacık (Çanakkale) Dolayında Genç Volkanizma–Plütonizma İlişkileri [Relationship Between Young Volcanism and Plutonism in Ezine-Ayvacık (Çanakkale) Region]. Ph.D. Thesis, İstanbul Technical University, İstanbul, Turkey, 1995.
38. Karacık, Z.; Yılmaz, Y. Geology of ignimbrites and the associated volcano-plutonic complex of the Ezine area, northwestern Anatolia. *J. Volcanol. Geotherm. Res.* **1998**, *85*, 251–264. [CrossRef]
39. Yılmaz, Y. Geology of Western Anatolia: Active tectonics of northwestern Anatolia. In *The Marmara Poly Project*; VDF; Hochschulverlag Ag An Der ETH: Zürich, Switzerland, 1997; pp. 1–20.
40. Yılmaz, Y.; Genç, Ş.C.; Karacık, Z.; Altunkaynak, S. Two contrasting magmatic associations of NW Anatolia and their tectonic significance. *J. Geodyn.* **2001**, *31*, 243–271. [CrossRef]
41. Akal, C. Coeval shoshonitic-ultrapotassic dyke emplacements within the Kestanbol pluton, Ezine–Biga peninsula (NW Anatolia). *Turk. J. Earth Sci.* **2013**, *22*, 220–238. [CrossRef]
42. Şener, M.; Gevrek, A.I. Distribution and significance of hydrothermal alteration minerals in the Tuzla hydrothermal system, Çanakkale, Turkey. *J. Volcanol. Geotherm. Res.* **2000**, *96*, 215–228. [CrossRef]
43. Gevrek, A.İ.; Şener, M.; Ercan, T. Çanakkale-Tuzla Jeotermal alanının hidrotermal alterasyon etüdü ve volkanik kayaların petrolojisi. *Bull. Miner. Res. Explor.* **1985**, *103*, 82–103.
44. Winchester, J.A.; Floyd, P.A. Geochemical discrimination of different magma series and their differentiation products using immobile elements. *Chem. Geol.* **1977**, *20*, 325–343. [CrossRef]
45. Peccerillo, A.; Taylor, S.R. Geochemistry of Eocene calc-alkaline volcanic rocks from the Kastamonu Area, northern Turkey. *Contrib. Mineral. Petrol.* **1976**, *58*, 63–81. [CrossRef]
46. Irvine, T.N.; Baragar, W.A.R. A guide to chemical classification of common volcanic rocks. *Can. J. Earth Sci.* **1971**, *8*, 523–547. [CrossRef]
47. Sun, S.S.; McDonough, W.F. Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes. In *Magmatism in Oceanic Basins*; Saunders, A.D., Norry, M.J., Eds.; Geological Society Special Publications: London, UK, 1989; Volume 42, pp. 313–345.
48. Wood, D.A.; Joron, J.L.; Treuil, M.; Norry, M.; Tarney, J. Elemental and Sr isotope variations in basic lavas from Iceland and the surrounding ocean floor: The nature of mantle source inhomogeneities. *Contrib. Mineral. Petrol.* **1979**, *70*, 319–339. [CrossRef]
49. Wilson, F.H. Geologic Setting, Petrology, and Age of Pliocene to Holocene Volcanoes of the Stepovak Bay Area. In *US Geological Survey Bulletin*; Government Printing Office: Washington, DC, USA, 1983; pp. 84–95.
50. Gorton, M.P.; Schandl, E.S. From continents to island arcs: A geochemical index of tectonic setting for arc-related and within-plate felsic to intermediate volcanic rocks. *Can. Mineral.* **2000**, *38*, 1065–1073. [CrossRef]
51. Pearce, J.A. Role of the sub-continental lithosphere in magma genesis at active continental margins. In *Continental Basalts and Mantle Xenoliths* (s. 230–249); Hawkesworth, C.J., Norry, M.J., Eds.; Shiva Publications: Nantwich, UK, 1983.
52. Bozan, F.; Aslan, Z. Büyükbostancı–Çiçekpınar (Balıkesir, KB Türkiye) yöresindeki Oligosen–Miyosen yaşlı kalk-alkalen volkanik kayaların mineral kimyası, jeokimyası ve petrolojisi. *Türkiye Jeol. Bülteni* **2022**, *65*, 117–148.

53. Şen, P.; Sarı, R.; Şen, E.; Dönmez, C.; Özkümüş, S.; Küçükefe, Ş. Geochemical features and petrogenesis of Gökçeada volcanism, Çanakkale, NW Turkey. *Bull. Miner. Res. Explor.* **2020**, *161*, 81–99. [CrossRef]
54. Harris, N.B.; Pearce, J.A.; Tindle, A.G. Geochemical characteristics of collision-zone magmatism. *Geol. Soc. Lond. Spec. Publ.* **1986**, *19*, 67–81. [CrossRef]
55. Saatçi, E.S.; Aslan, Z. Yürekli (Balıkesir) volkanitinin petrografisi ve petrolojisi: Biga yarımadasında (KB Türkiye) çatışma sonrasında felsik volkanizmaya bir örnek. *MTA Derg.* **2018**, *157*, 105–122.
56. Pearce, J.A.; Parkinson, I.J. Trace element models for mantle melting: Application to volcanic arc petrogenesis. In *Magmatic Processes and Plate Tectonics*; Prichard, H.M., Ed.; Geological Society Special Publications: London, UK, 1993; pp. 373–403.
57. Stolz, A.J.; Varne, R.; Davies, G.R.; Wheller, G.E.; Foden, J.D. Magma source components in an arc-continent collision zone: The Flores-Lembata sector, Sunda arc, Indonesia. *Contrib. Mineral. Petrol.* **1990**, *105*, 585–601. [CrossRef]
58. Kelemen, P.B.; Johnson, K.T.M.; Kinzler, R.J.; Irving, A.J. High-field-strength element depletions in arc basalts due to mantle–magma interaction. *Nature* **1990**, *345*, 521–524. [CrossRef]
59. Ringwood, A.E. Slab-mantle interactions: 3. Petrogenesis of intraplate magmas and structure of the upper mantle. *Chem. Geol.* **1990**, *82*, 187–207. [CrossRef]
60. Pearce, J.A.; Peate, D.W. Tectonic implications of the composition of volcanic arc magmas. *Annu. Rev. Earth Planet. Sci. Lett.* **1995**, *23*, 251–285. [CrossRef]
61. Elburg, M.A.; Bergen, M.V.; Hoogewerff, J.; Foden, J.; Vroon, P.; Zulkarmain, I.; Nasution, A. Geochemical trends across an arc-continent collision zone: Magma sources and slab-wedge transfer processes below the Pantar Strait volcanoes. *Indones. Geochim. Cosmochim. Acta* **2002**, *66*, 2771–2789. [CrossRef]
62. Churikova, T.; Dorendorf, F.; Wörner, G. Sources and fluids in the mantle wedge below Kamchatka, evidence from across-arc geochemical variation. *J. Petrol.* **2001**, *42*, 1567–1593. [CrossRef]
63. Zellmer, G.F.; Annen, C.; Charlier, B.L.A.; George, R.M.M.; Turner, S.P.; Hawkesworth, C.J. Magma evolution and ascent at volcanic arcs: Constraining petrogenetic processes through rates and chronologies. *J. Volcanol. Geotherm. Res.* **2005**, *140*, 171–191. [CrossRef]
64. McDermott, F.; Delfin, F.G.; Defant, M.J.; Turner, S.; Maury, R. The petrogenesis of magmas from Mt. Bulusan and Mayon in the Bicol arc, the Philippines. *Contrib. Mineral. Petrol.* **2005**, *150*, 652–670. [CrossRef]
65. Hawkesworth, C.J.; Turner, S.P.; McDermott, F.; Peate, D.W.; Van Calsteren, P. U-Th isotopes in arc magmas: Implications for element transfer from the subducted crust. *Science* **1997**, *276*, 551–555. [CrossRef] [PubMed]
66. Bradshaw, T.K.; Smith, E.I. Polygenetic Quaternary volcanism at Crater Flat, Nevada. *J. Volcanol. Geotherm. Res.* **1994**, *63*, 165–182. [CrossRef]
67. Smith, E.I.; Sánchez, A.; Walker, J.D.; Wang, K. Geochemistry of mafic magmas in the Hurricane Volcanic Field, Utah: Implications for small- and large scale chemical variability of the lithospheric mantle. *J. Geol.* **1999**, *107*, 433–448. [CrossRef]
68. Erdem, D.; Aslan, Z. Kalk-alkalen Şapçı (Balıkesir) Volkanitlerin Petrografisi ve Petrolojisi: Biga Yarımadası’nda (Kuzeybatı Türkiye) Çarpışma ile İlişkili Volkanizma. *Türkiye Jeol. Bülteni* **2015**, *58*, 1–22. [CrossRef]
69. Abdel-Rahman, A.F.M. Mesozoic volcanism in the Middle East: Geochemical, isotopic and petrogenetic evolution of extension-related alkali basalts from central Lebanon. *Geol. Mag.* **2002**, *139*, 621–640. [CrossRef]
70. Weaver, B.L.; Wood, D.A.; Tarney, J.; Joron, J.L. Geochemistry of ocean island basalts from the south Atlantic: Ascension, Bouvet, St. Helena, Gough and Tristan da Cunha. *Geol. Soc. Lond. Spec. Publ.* **1987**, *30*, 253–267. [CrossRef]
71. Arslan, M.; Temizel, I.; Abdioglu, E.; Kolaylı, H.; Yücel, C.; Boztuğ, D.; Şen, C. 40Ar–39Ar dating, whole-rock and Sr–Nd–Pb isotope geochemistry of post-collisional Eocene volcanic rocks in the southern part of the Eastern Pontides (NE Turkey): Implications for magma evolution in extension-induced origin. *Contrib. Mineral. Petrol.* **2013**, *166*, 113–142. [CrossRef]
72. Aydınçakır, E.; Şen, C. Petrogenesis of the post-collisional volcanic rocks from the Borçka (Artvin) area: Implications for the evolution of the Eocene magmatism in the Eastern Pontides (NE Turkey). *Lithos* **2013**, *172*, 98–117. [CrossRef]
73. Pearce, J.A.; Bender, J.F.; De Long, S.E.; Kidd, W.S.F.; Low, P.J.; Güner, Y.; Şaroğlu, F.; Yılmaz, Y.; Moor bath, S.; Mitchell, J.J. Genesis of collision volcanism in eastern Anatolia Turkey. *J. Volcanol. Geotherm. Res.* **1990**, *44*, 189–229. [CrossRef]
74. Lebedev, V.A.; Chernyshev, I.V.; Sagatelyan, A.K.; Goltsman, Y.V.; Oleinikova, T.I. Miocene–Pliocene volcanism of Central Armenia: Geochronology and the role of AFC processes in magma petrogenesis. *J. Volcanol. Seismol.* **2018**, *12*, 310–331. [CrossRef]
75. Taylor, S.R.; McLennan, S.M. *The Continental Crust: Its Composition and Evolution*; Blackwell: Oxford, UK, 1985.
76. Aydınçakır, E. Taşlıyayla (Çaykara, Trabzon, KD Türkiye) civarı Geç Kretase yaşlı kalk-alkali volkanik kayaların petrografik ve Jeokimyasal Özellikleri. *Gümüşhane Üniv. Fen Bilim. Derg.* **2017**, *7*, 51–78.
77. Condie, K.C. Chemical composition and evolution of the upper continental crust: Contrasting results from surface samples and shales. *Chem. Geol.* **1993**, *104*, 1–37. [CrossRef]
78. Jahn, B.M.; Wu, F.; Lo, C.H.; Tsai, C.H. Crust–mantle interaction induced by deep subduction of the continental crust: Geochemical and Sr–Nd isotopic evidence from post-collisional mafic–ultramafic intrusions of the northern Dabie complex, central China. *Chem. Geol.* **1999**, *157*, 119–146. [CrossRef]

79. Jahn, B.M.; Zhang, Z.Q. Archean granulite gneisses from eastern Hebei Province, China: Rare earth geochemistry and tectonic implications. *Contrib. Mineral. Petrol.* **1984**, *85*, 224–243. [CrossRef]
80. Alici, P.; Temel, A.; Gourgaud, A.; Kieffer, G.; Gündoğdu, M.N. Petrology and geochemistry of potassic volcanism in the Gölcük area (Isparta, SW Turkey): Genesis of enriched alkaline magmas. *J. Asian Earth Sci.* **2002**, *20*, 867–886.
81. Karaoğlu, Ö.; Helvacı, C.; Sunal, G. Geochemical and Sr–Nd–Pb isotopic constraints on the petrogenesis of Miocene volcanic rocks from western Anatolia: Implications for mantle source characteristics and crustal interaction. *Lithos* **2014**, *184–187*, 63–79.
82. Furman, T.; Rooney, T.O.; Hanan, B.B.; Yücel, C. Isotopic evidence for multi-component mantle sources beneath western Anatolia: Implications for post-collisional magmatism. *Lithos* **2021**, *380–381*, 105871.
83. Romick, J.D.; Kay, S.M.; Kay, R.W. The influence of amphibole fractionation on the evolution of calc-alkaline andesite and dacite tephra from the central Aleutians, Alaska. *Contrib. Mineral. Petrol.* **1992**, *112*, 101–118. [CrossRef]
84. Arth, J.G. Some Trace Elements in Troughs: Their Implication to Magma Genesis and Paleotectonic Setting. In *Developments in Petrology*; U.S. Geological Survey: Denver, CO, USA, 1979; Chapter 3; Volume 6, pp. 123–132.
85. Pang, K.N.; Zhou, M.F.; Qi, L.; Chung, S.L.; Chu, C.H.; Lee, H.Y. Petrology and geochemistry at the Lower zone–Middle zone transition of the Panzhihua intrusion, SW China: Implications for differentiation and oxide ore genesis. *Geosci. Front.* **2013**, *4*, 517–533. [CrossRef]
86. Liu, P.P.; Zhou, M.F.; Luais, B.; Cividini, D.; Rollion-Bard, C. Disequilibrium iron isotopic fractionation during the high-temperature magmatic differentiation of the Baima Fe–Ti oxide-bearing mafic intrusion, SW China. *Earth Planet. Sci. Lett.* **2014**, *399*, 21–29. [CrossRef]
87. Litvak, V.D.; Spagnuolo, M.G.; Folguera, A.; Poma, S.; Jones, R.E.; Ramos, V.A. Late Cenozoic calc-alkaline volcanism over the Payenia shallow subduction zone, South-Central Andean back-arc (34°30′–37°S), Argentina. *J. S. Am. Earth Sci.* **2015**, *64*, 365–380. [CrossRef]
88. Gill, J.B. *Orogenic Andesites and Plate Tectonics*; Earth Sciences Board and Oakes College: Santa Cruz, CA, USA, 1981.
89. Thirlwall, M.F.; Smith, T.E.; Graham, A.M.; Theodorou, N.; Hollings, P.; Davidson, J.P.; Arculus, R.J. High field strength element anomalies in arc lavas: Source or process? *J. Petrol.* **1994**, *35*, 819–838. [CrossRef]
90. Lambert, R.S.J.; Holland, J.G. Yttrium geochemistry applied to petrogenesis utilizing calcium–yttrium relationships in minerals and rocks. *Geochim. Cosmochim. Acta* **1974**, *38*, 1393–1414. [CrossRef]
91. Edwards, C.; Menzies, M.; Thirlwall, M. Evidence from Muriah, Indonesia, for the interplay of supra-subduction zone and intraplate processes in the genesis of potassic alkaline magmas. *J. Petrol.* **1991**, *32*, 555–592. [CrossRef]
92. Aydınçakır, E. Subduction-related Late Cretaceous high-K volcanism in the Central Pontides orogenic belt: Constraints on geodynamic implications. *Geodin. Acta* **2016**, *28*, 379–411. [CrossRef]
93. Tarabi, S.; Emami, M.H.; Modabberi, S.; Zakariaee, S.J.S. Eocene–Oligocene volcanic units of Momen Abad, east of Iran: Petrogenesis and magmatic evolution. *Iran. J. Earth Sci.* **2019**, *11*, 126–140.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Mineralogy and Geochemistry of Jasperoid Veins in Neoproterozoic Metavolcanics: Evidence of Silicification, Pyritization and Hematization

Mohamed Zaki Khedr ^{1,*}, Mahmoud A. Sayed ², Shehata Ali ³, Mokhles K. Azer ⁴, Yuji Ichiyama ⁵, Eiichi Takazawa ⁶, Ali Y. Kahal ⁷, Kamal Abdelrahman ⁷ and Ali M. Mahdi ²

¹ Geology Department, Faculty of Science, Kafrelsheikh University, Kafrelsheikh 33516, Egypt

² Geology Department, Faculty of Science, South Valley University, Qena 83523, Egypt; mahmoud95sayd96@sci.svu.edu.eg (M.A.S.)

³ Geology Department, Faculty of Science, Minia University, El-Minia 61519, Egypt

⁴ Geological Sciences Department, National Research Centre, Cairo 12622, Egypt

⁵ Graduate School of Science, Chiba University, Chiba 263-8522, Japan; ichiyamay@chiba-u.jp

⁶ Geology Department, Faculty of Science, Niigata University, Niigata 950-2181, Japan; takazawa@geo.sc.niigata-u.ac.jp

⁷ Department of Geology and Geophysics, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

* Correspondence: mohamed.khader1@sci.kfs.edu.eg or khedrzm75@gmail.com; Fax: +20-047-264-6545

Abstract: The Wadi Ranga sulfidic jasperoids in the Southern Eastern Desert (SED) of Egypt are hosted within the Neoproterozoic Shadli metavolcanics as an important juvenile crustal section of the Arabian Nubian Shield (ANS). This study deals with remote sensing and geochemical data to understand the mechanism and source of pyritization, silicification, and hematization in the host metavolcanics and to shed light on the genesis of their jasperoids. The host rocks are mainly dacitic to rhyolitic metatuffs, which are proximal to volcanic vents. They show peraluminous calc-alkaline affinity. These felsic metatuffs also exhibit a nearly flat REE pattern with slight LREE enrichment ($\text{La/Yb} = 1.19\text{--}1.25$) that has a nearly negative Eu anomaly ($\text{Eu/Eu}^* = 0.708\text{--}0.776$), while their spider patterns display enrichment in Ba, K, and Pb and depletion in Nb, Ta, P, and Ti, reflecting the role of slab-derived fluid metasomatism during their formation in the island arc setting. The ratios of La/Yb ($1.19\text{--}1.25$) and La/Gd ($1.0\text{--}1.17$) of the studied felsic metatuffs are similar to those of the primitive mantle, suggesting their generation from fractionated melts that were derived from a depleted mantle source. Their Nb and Ti negative anomalies, along with the positive anomalies at Pb, K, Rb, and Ba, are attributed to the influence of fluids/melt derived from the subducted slab. The Wadi Ranga jasperoids are mainly composed of SiO_2 (89.73–90.35 wt.%) and show wide ranges of Fe_2O_3 (2.73–6.63 wt.%) attributed to the significant amount of pyrite (up to 10 vol.%), hematite, goethite, and magnetite. They are also rich in some base metals ($\text{Cu} + \text{Pb} + \text{Zn} = 58.32\text{--}240.68$ ppm), leading to sulfidic jasperoids. Pyrite crystals with a minor concentration of Ag (up to 0.32 wt.%) are partially to completely converted to secondary hematite and goethite, giving the red ochre and forming hematization. Euhedral cubic pyrite is of magmatic origin and was formed in the early stages and accumulated in jasperoid by epigenetic Si-rich magmatic-derived hydrothermal fluids; pyritization is considered a magmatic–hydrothermal stage, followed by silicification and then hematization as post-magmatic stages. The euhedral apatite crystals in jasperoid are used to estimate the saturation temperature of their crystallization from the melt at about 850 °C. The chondrite (C1)-normalized REE pattern of the jasperoids shows slightly U-shaped patterns with a slightly negative Eu anomaly ($\text{Eu/Eu}^* = 0.43\text{--}0.98$) due to slab-derived fluid metasomatism during their origin; these jasperoids are also rich in LILEs (e.g., K, Pb, and Sr) and depleted in HFSEs (e.g., Nb and Ta), reflecting their hydrothermal origin in the island arc tectonic setting. The source of silica in the studied jasperoids is likely derived from the felsic dyke and a nearby volcanic vent, where the resultant Si-rich fluids may circulate along the NW–SE, NE–SW, and E–W major faults and shear zones in the surrounding metavolcanics to leach Fe, S, and Si to form hydrothermal jasperoid lenses and veins.

Keywords: Shadli metavolcanics; Arabian Nubian Shield; pyrite; Fe–Si-rich rocks; ASTER and Landsat-8 OLI; Egypt

1. Introduction

Jasperoids (hematitic cherts) are one of the Fe–Si-rich rocks associated with Neoproterozoic metavolcanics in the Arabian–Nubian Shield (ANS), which is the largest ancient belt on the Earth and was formed during East and West Gondwana collision [1–5]. The famous island arc metavolcanic rocks in Egypt are named Shadli metavolcanics (in this study) that hosted jasperoid lenses and veins and are considered the important crustal component of the ANS [6,7]. These metavolcanics are economically important because they are rich in sulfides, gold, copper, talc, and jasperoid lenses and veins [8–11]; however, there are few studies on the jasperoids in the island arc metavolcanic rocks in Egypt and their genesis is a subject of ongoing debate.

Jasperoids are essentially associated with sulfide deposits (mainly pyrite) [12]. Previous studies of Fe–Si-rich rocks differentiated between those formed in shallow and deep-water environments, as well as the sedimentary and replacement types [13–17]. The ironstone facies in shallow water environments may be classified into oxide, silicate, and carbonate facies with increasing water depth during deposition [18], where sulfidic facies containing pyrite and/or pyrrhotite have been reported in this environment too [19]. The formation of shallow-water ironstones is attributed to subsequent diagenetic processes by incoming fluids seeping from a nearby volcanic source [13,20,21]. On the other hand, the deep-water varieties of Si–Fe-rich rocks are analogical to the shallow ones; however, they are formed by the chemical deposition of Fe–Si-rich fluids exhaled from a direct volcanic vent [22,23] or deep circulating water-carrying rock products [24]. Algoma refers to ironstone with 1 m to 10 m of lenticular types associated with volcanogenic massive sulfide (VMS) mineralization hosted in volcanogenic rocks [25,26]. In addition, disseminated $\text{Fe} \pm \text{Cu} \pm \text{Zn}$ as VMS is encountered within the silica-rich ironstones of Løkken metavolcanics in Norway [27]. These iron and sulfides are related to the rift-related submarine pillow and basalt flows by high-T hydrothermal metal/sulfide-rich vent fluids [28].

Several publications have discussed Fe–Si-rich rocks in the Neoproterozoic island arc metavolcanics in the Eastern Desert of Egypt as banded iron formations (BIFs) [29–32] of sedimentary origin, as exemplified by the Wadi Kariem BIF, and submarine volcanogenic jasperoids or ferruginous chert as those located at Um Anab. The banded or lenticular appearance of jasperoids with the scarce hematite or goethite-staining tricked some researchers into considering them as BIF mineralization; however, they are not consistent with the ideal characteristics of proper BIFs. Geochemically, volcanogenic jasper or ferruginous chert is a Si-rich ore with minor amounts of total Fe_2O_3 not exceeding 10 wt.%, hosted mainly within weakly metamorphosed tuffs of felsic composition instead of those of andesitic and basaltic composition [33,34]. It is also much less spread out laterally, forming structures that look like lenses. This is due to a low-temperature hydrothermal alteration of the ocean's underlying volcanic rocks. Further studies attributed the formation of Umm Ghamis and El Dabbah jasperoids to the syngenetic mixing of Si-rich hydrothermal solutions with iron forming a silica–iron gel, which is subsequently influenced by diagenetic processes, leading to the eventual formation of jasperoids in their ultimate state [35].

The data from fourteen bands of ASTER and seven spectral bands of Landsat-8 OLI were used to distinguish various rock formations and hydrothermal alterations in the Wadi Ranga area, focusing on identifying the location of lenticular jasperoids. The mineral compositions and geochemical data were obtained based on a Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectrometry (EDS), Electron Probe Micro-Analyzer (EPMA), X-ray Fluorescence (XRF), and Inductively Coupled Plasma Mass Spectrometry (ICP–MS). The current study discusses field geology, petrography, remote sensing, and geochemical data to understand silicification, pyritization, and hematization

in the Shadli metavolcanics and sheds light on the genesis of the sulfide-rich jasperoids hosted in these rocks. The aim of this study is also to explain the tectonic setting and sources of high silica and iron in jasperoid lenses or veins in the metavolcanics and whether the occurrence of jasperoids is related to the host rock composition and/or Fe–Si-rich magmatic-derived hydrothermal fluids.

2. Geologic Setting

The studied jasperoids are located around the Wadi Ranga area on the Eastern side of the Shadli metavolcanic belt, at a latitude of $24^{\circ}20'04''$ N and longitude of $35^{\circ}10'54''$ E, about 15 km from the Abu Ghusun area south of Marsa Allam city (Figure 1a). The study area shows distinct features of polyphase extensional and compressional structural events that occurred during the Neoproterozoic Pan-African Orogeny (550–900 Ma; [2,36]). The structural field observations along with aerial photographs demonstrate that the Wadi Ranga is affected mostly by NW–SE and NE–SW structural trends (Figure 1b), which appeared in the form of shear zones, thrusting, and major dykes in the studied metavolcanics. The main NW–SE faults may conjugate with the NE–SW trend, with a subordinate E–W trend (Figure 1b). This is dominant in both the Central Eastern Desert (CED) and the South Eastern Desert (SED) as a structure controlling mineralization [11,37–39]. These structural trends are comparable with their counterparts reported in some areas in the SED of Egypt, such as those at the Wadi Beitan, the Allaqi–Heiani suture zone, and Nugrus [40–43]. The Wadi Ranga area is traversed by many E–W-trending Wadis, including Wadi Mahara, Wadi Sarubi, Wadi Ranga, Wadi Um Sieval, Wadi Dendikan, Wadi Qulan, Wadi El Atshan, and Wadi El Reidi, all primarily flowing towards the Red Sea (Figure 1b).

The Wadi Ranga area is almost entirely covered with Neoproterozoic bimodal metavolcanics, with Hammamat sediments to the east and the metagabbro–diorite complex and granitoid rocks to the west. These bimodal metavolcanics are intruded by the Abu Ghalaga metagabbro–metadiorite pluton and the post-collisional Hamata granitic pluton on the west side [44]; (Figure 1b). The Ranga metavolcanics may be classified into two main categories: intermediate to mafic metavolcanics and felsic to intermediate metavolcanics based on fieldwork and geochemical data. The intermediate to mafic metavolcanics are dominant over the other metavolcanic varieties, forming a rugged hilly, and elevated terrain. They are manifested in two significant belts in the northern and southern parts of the study area. The northern part encompasses Gabel Sarubi and is intersected by Sarubi, Um Sieval, and Ranga Wadis, while the southern part is traversed by Wadi El Reidi and Wadi Atshan. On the other hand, these intermediate to mafic metavolcanics are overlain by the felsic to intermediate metavolcanics that are distributed in the central part of the study area ([45]; Figure 1b). They are composed of andesites, basalts, and andesitic basalts with subordinate pillow lavas. They are dark greenish-gray and suffer from low-grade metamorphism. On the other hand, the felsic to intermediate metavolcanics are light green to buff colors and consist of slightly metamorphosed porphyritic rhyolites and dacites with subordinate dacitic andesites [45,46].

The investigated metavolcanics are associated with metapyroclastics and lapilli metatuffs, mostly of felsic composition (Figure 1b). These felsic rocks are the main host of jasperoids and the target of this study. Wadi Ranga jasperoids appear as red, narrow, discontinuous lenticular bodies of up to 2 m in thickness and as veins of more than 10 m in length hosted within the Neoproterozoic metavolcanics, such as dacitic to rhyolitic metatuffs (Figure 2a–c). Jasperoid lenses are variable in size and enveloped by dacitic and rhyolitic metatuffs, showing sharp, irregular contact with these host rocks (Figure 2c). They are mainly striking N 35° W close to both the shear zones (Figure 2d,e) and the felsic or granitic dyke (Figure 2f). The dacitic to rhyolitic metatuffs, which are the main host of jasperoid lenses and veins, are possibly proximal to the volcanic vents of the Shadli volcano. This is field evidence of the formation and occurrence of jasperoid lenses close to the volcanic vents in the Wadi Ranga area. Not only is the jasperoid occurrence restricted to the proximal volcanic vents, but also spatially associated with sheared zones and sheared metavolcanics,

which are characterized by the intensive fining of grain sizes and appearance of carbonate shreds on the borders (Figure 2d,e). The studied jasperoids are mainly concordant with the shearing and foliation trends of the hosted metavolcanics (Figure 2c). The investigated metavolcanic-hosted jasperoids are also crosscut by a significant felsic dyke, mainly alkali-feldspar granites (Figure 2f). Furthermore, the studied jasperoids are characterized by distinct silica-rich veinlets (Figure 2g) and include visible disseminated pyrite crystals, similar to their host metavolcanics. Pyrite appears as yellow or as black cubic disseminated grains in the presence and absence of reflected light, respectively, and all are distributed in a red matrix of hematite, as shown in the current slabs of Wadi Ranga jasperoids (Figure 2h). The higher percentage of pyrite, which is up to 10 vol.%, implies the sulfidic character of the studied jasperoids. Moreover, the hematitic staining also affects the surrounding metavolcanics, and outcrops appear red in color (Figure 2i).

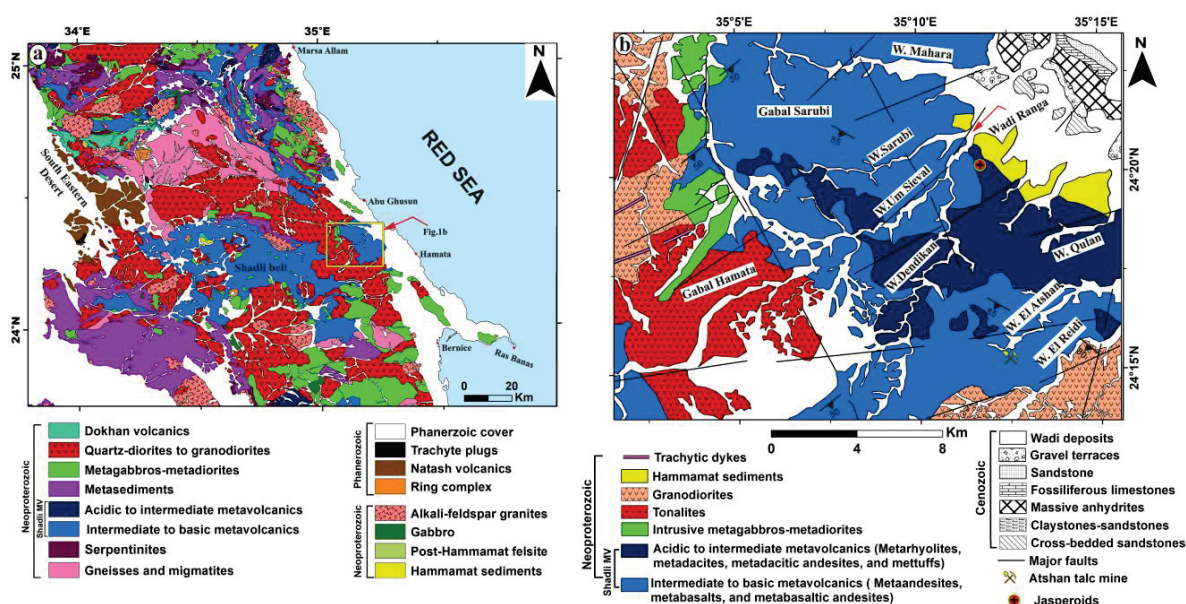


Figure 1. Location of the study area and simplified geologic map. (a) Distribution of the Shadli metavolcanics in the Southern Eastern Desert (SED) of Egypt (modified from [47–50] and related aerial photographs). (b) Detailed geologic map of the Wadi Ranga based on remote sensing data and field verification, showing the different rock units and the studied jasperoids.

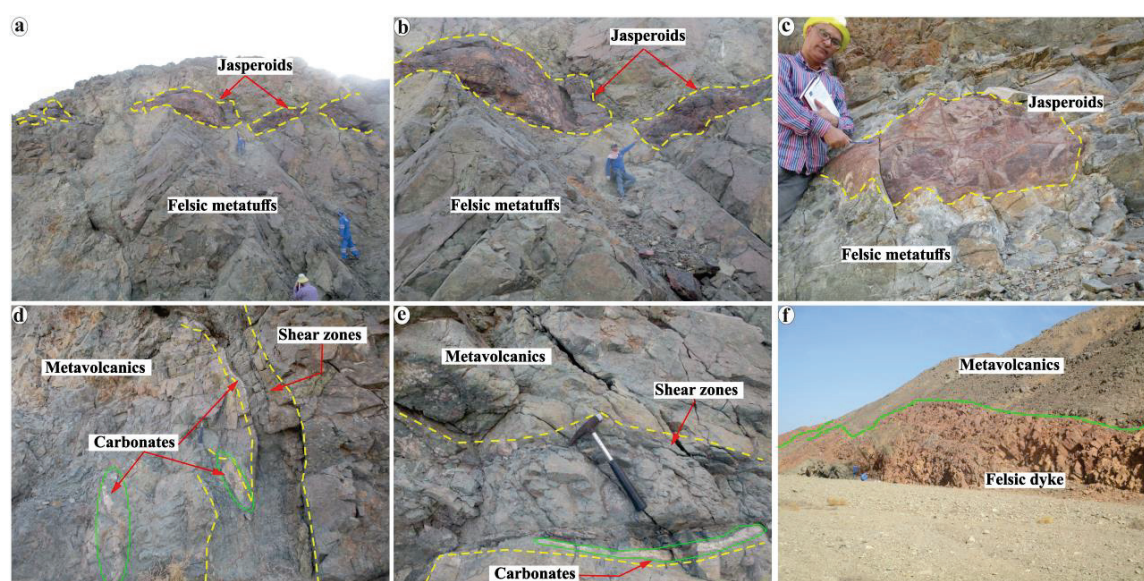


Figure 2. Cont.

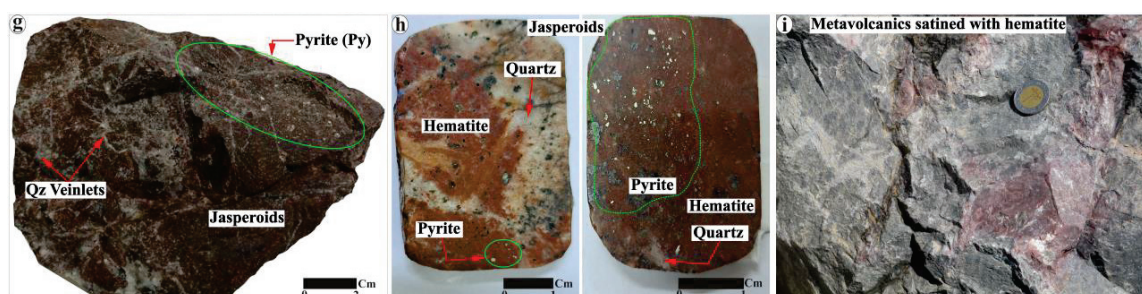


Figure 2. Field photographs and hand specimens of jasperoids and their host metavolcanics. (a) Jasperoid lenses within felsic metatuffs. (b) Close-up view of jasperoid lenses in panel (a). (c) Small jasperoid lens with sharp contact with host metatuffs. (d) Shear zone with carbonate patches cutting through metavolcanics. (e) Shear zone with carbonate bands and cataclastic zone in metavolcanics. (f) Felsic dyke (e.g., alkali-feldspar granite) crosscutting. (g) the studied jasperoids are characterized by distinct silica-rich veinlets. (h) slabs of Wadi Ranga jasperoids. (i) hematitic staining also affects the surrounding metavolcanics.

3. Methodology and Analytical Techniques

A comprehensive geological map of the Wadi Ranga area was developed using satellite images from Landsat-8 Operational Land Imager (OLI) and the Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER). The Landsat-8 OLI images cover a wide spectral range with nine bands, providing a spatial resolution of 30 m for all bands, except for the 15-m panchromatic band [51]; (Table 1). On the other hand, the ASTER data comprise fourteen high-resolution bands offering spatial, spectral, and radiometric capabilities. The visible and near-infrared (VNIR) bands exhibit a spatial resolution of 15 m; the short-wave infrared (SWIR) bands provide a resolution of 30 m; and the bands in the thermal infrared (TIR) regions provide a spatial resolution of 90 m. Each ASTER image scene covers an area of 60 km × 60 km ([51]; Table 1). This study utilized data from 14 bands of ASTER and 7 spectral bands of Landsat-8, acquired in February 2005 and July 2016, respectively [52,53]. The two datasets were processed using ENVI version 5.3 and ERDAS 2015 analytical software with the aid of Arc Map10.8 to produce high-resolution images. Band ratio and constrained energy minimization (CEM) were the more effective remote sensing techniques that aided in creating a detailed geologic map of the Wadi Ranga area and localizing the occurrence of jasperoids. Band ratio transformation proves to be an effective technique for mapping lithology and hydrothermal alteration zones [54–57]. This method entails dividing the digital number (DN) values of a specific band by the corresponding DN values of another band. The resulting DN values are then depicted in a grayscale image, conveying relative band intensities [58]. The technique of CEM has evolved into a widely adopted and efficient approach for target mapping [59]. This technique linearly specifies the preferred target signatures and minimizes less reliable signatures based on the chosen endmembers. The identification of target anomalies is achieved by utilizing a partial unmixing matrix, which relies on the evaluation of target correlations. Emphasizing the distinction between the spectra of the target and the background endmembers is accomplished by maximizing the signatures associated with the desired endmembers, while minimizing other signatures from the composite unknown background.

Table 1. Spectral and spatial characteristics of the Landsat-8 OLI and ASTER bands used in the study.

Characteristics	Imagery System							
	Landsat-8 OLI		ASTER					
	Subsystem	Spectral bands	Wavelength (μm)	Spatial resolution (m)	Subsystem	Spectral bands	Wavelength (μm)	Spatial resolution (m)
Spectral and spatial resolution of bands	Coastal aerosol	1	0.433–0.453	30	VNIR	1	0.52–0.60	15
	Visible	2	0.450–0.515			2	0.63–0.69	
		3	0.525–0.600			3N	0.78–0.86	
		4	0.630–0.680			3B	0.78–0.86	
	NIR	5	0.845–0.885	30	SWIR	4	1.60–1.70	30
	SWIR	6	1.560–0.166			5	2.145–2.185	
		7	2.100–2.300			6	2.185–2.225	
	panchromatic	8	0.500–0.680			7	2.235–2.285	
	Cirrus	9	1.360–1.390	8	2.295–2.365			
				9	2.360–2.430			
						10	8.125–8.475	90
						11	8.475–8.825	
						12	8.925–9.275	
						13	10.25–10.95	
						14	10.95–11.65	

Twenty representative polished thin sections of jasperoids and host rocks from the Ranga area were chosen based on the field relations and hand specimen characteristics. Thin polish and carbon coating were conducted at Chiba University, Chiba, Japan. The prepared thin sections were examined under reflected and transmitted light microscopes to determine the mineralogy and textures of the studied jasperoids and host rocks. Additionally, a set of high-resolution photomicrographs highlighting important features of the jasperoid were captured. The detailed qualitative and quantitative analyses of iron oxides and apatite minerals using a Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectrometry (EDS) were carried out at Niigata University, Niigata, Japan. The operating conditions were 20 kV accelerating voltage and the working distance (WD) was 10 mm. A few analyses of magnetite were made using an Electron Probe Micro-Analyzer (EPMA) (JEOL JXA-8230) at Chiba University. The EMPA analysis conditions were a 15 kV acceleration voltage, a beam current of 2.0×10^{-8} A, and a beam diameter of 3 μ m. Standard materials consisting of natural and synthetic minerals and metals were utilized for calibration purposes. Ferrous and ferric iron contents (Fe_2O_3 and FeO) of iron oxides were calculated assuming spinel stoichiometry.

Seven representative samples (three jasperoids and four felsic metatuffs) were chosen based on petrographic studies for determining the major element compositions using X-ray Fluorescence (XRF) at the Geo Analytical Lab, Washington University, Pullman, WA, USA. The samples underwent crushing and grinding in an agate ball mill to produce a powder. After weighing, the powdered samples were mixed with di-lithium tetraborate flux (in a 2:1 ratio of flux to rock), fused at 1000 °C in a muffle furnace, and then cooled. The resulting bead was then further ground, refused, and polished on diamond laps to attain a flat and smooth surface suitable for analysis. Calibration was conducted utilizing the reference material 650CC sourced from GSP2. The analytical precision for XRF analyses, derived from duplicate samples, was generally better than 1% for most major elements. The loss on ignition (LOI) was determined by measuring the weight difference after firing the samples at 1000 °C. Rare-earth element (REE) and some trace element compositions were determined via Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at the Geo Analytical Lab, Washington University, Washington, USA, where approximately 50 mg of powder from each sample was dissolved in acid-washed Teflon containers by refluxing in a 250 °C hot solution of nitric and hydrofluoric acid at a 3:1 ratio for at least 8 h. A calibration curve for instrument sensitivity was established using a blank fused bead from the same flux batch utilized for preparing the unknown samples, alongside USGS standards AGV-2 and RGM2. Additional USGS standards (DTS-2, BCR-1, G-2) served as references for quality control. The analytical precision for analyzed trace elements was better than 5%, with the exceptions of Ni, Cr, and Sc. The different geochemical data were processed, and various diagrams were plotted using the GCDkit v 3.6.0, Icpet 2010, and CorelDRAW 2017 software.

4. Results

4.1. Remote Sensing Data

The remotely sensed data were used to distinguish various rock formations and hydrothermal alterations in the Wadi Ranga area, focusing on identifying the location of lenticular jasperoids. In the context of Landsat-8, the band ratios b_6/b_7 , $b_6/b_5 \times b_4/5$, and b_5 in RGB were employed to distinguish metavolcanics (AMV) with a dark red color and basic metavolcanics (BMV) with a green color. Granitic rocks were characterized by a greenish-violet color for granodiorites (Gd) and a bluish-violet for tonalites (Tn). Additionally, small bodies of metagabbro–diorite (Mgb) were marked with a reddish-brown color (Figure 3a).

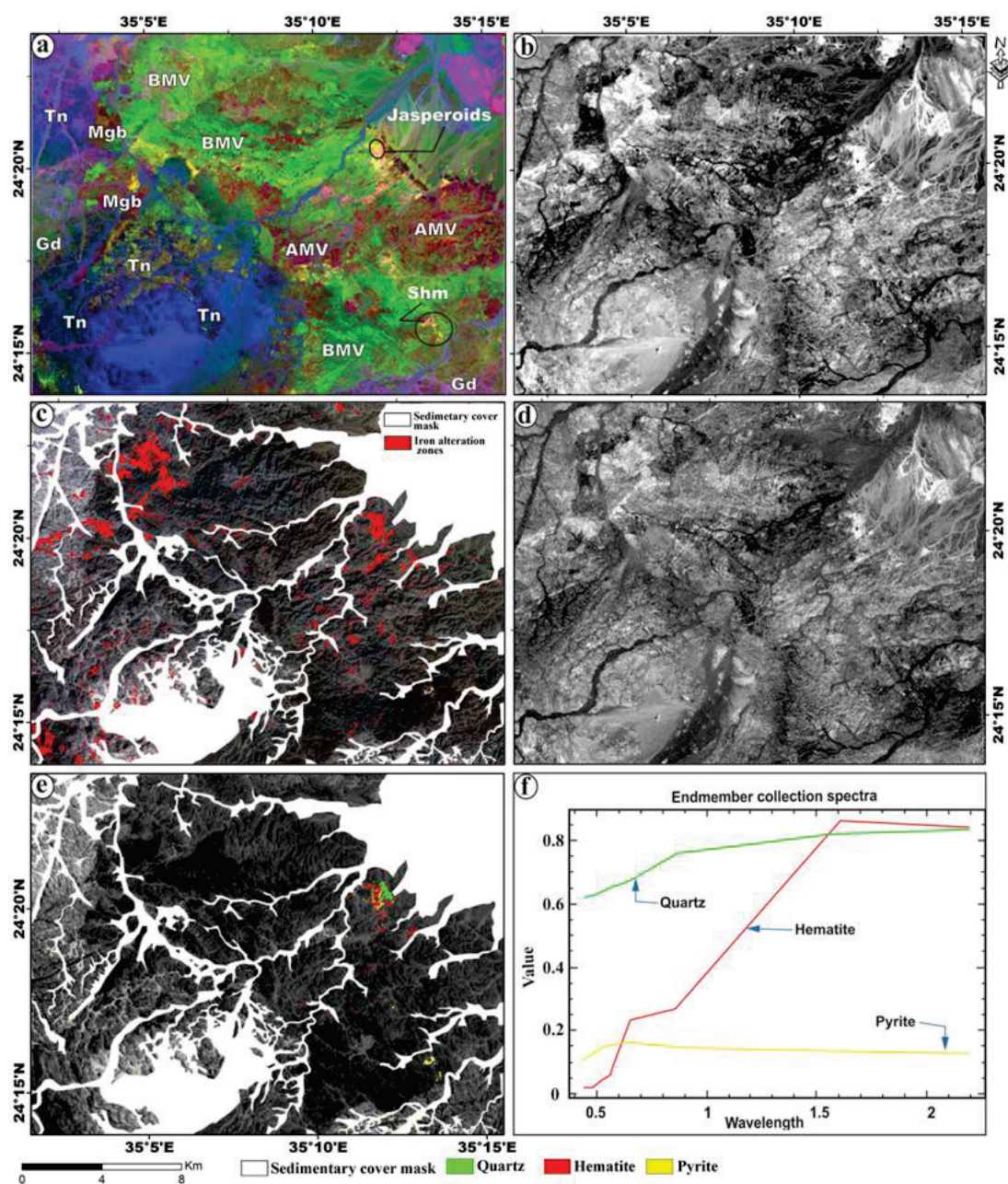


Figure 3. Composite Landsat-8 OLI and grayscale ASTER alteration indices of Shadli metavolcanics. (a) Composite Landsat-8 band ratio (b_6/b_7 , $b_6/b_5 \times b_4/b_5$, and b_5) in RGB. (b) Grayscale Landsat-8 band ratio (b_4/b_2) image. (c) Grayscale density slicing the Landsat-8 band ratio (b_4/b_2) image after building a sedimentary cover mask. (d) Grayscale ASTER band ratio (b_2/b_1). (e) Constrained Energy Minimization (CEM) endmember of the quartz, hematite, and pyrite minerals using VNIR–SWIR Landsat-8 data and the ASTER-resampled spectral library. (f) Endmember collection spectra used in CEM using the ASTER spectral library for the VNIR–SWIR bands. The solid-colored lines symbolize the Landsat-8 bands' wavelengths. Abbreviations: Acidic to intermediate metavolcanics (AMV), intermediate to basic metavolcanics (BMV), Metagabbro–diorite (Mgb), Granodiorite (Gd), Tonalite (Tn), and Atshan talc mine (Shm).

The studied jasperoids appeared in yellow color at the south side of the Wadi Ranga entrance (Figure 3a). The application of the band ratio 4/2 on the Landsat-8 data proved to have a significant capability in distinguishing alteration zones characterized by iron-oxides [54] that led to the red tint of jasperoids. Therefore, these areas were visually represented with a white tone in Figure 3b. The utilization of the density slicing tool further

contributed to enhancing the outcomes obtained from the band ratio of 4/2 with a red tint (Figure 3c). Similarly, Rowan et al. [60] developed the ASTER band 2/1 ratio to detect rocks influenced by significant ferric (Fe^{+3}) alteration, manifested through minerals like hematite and goethite. This band ratio played a crucial role in identifying rocks stained with hematite, such as jasperoids. Consequently, rocks undergoing hematite alteration were visually represented by white pixels, as shown in Figure 3d.

Based on the fact that the studied jasperoids chiefly comprise silica and hematite, the Constrained Energy Minimization (CEM) method proved its worth in identifying the characteristics of these specific endmembers. The ASTER spectral library provides several mineral signatures with specific wavelengths, making the process of mineral identification easier without any need for more field observations; therefore, the CEM along with the ASTER spectral library were employed to identify the two minerals, silica in the form of quartz and hematite, which are associated with disseminated pyrite (Figure 3e,f).

4.2. Petrography

The felsic varieties of Ranga metavolcanic (MV)-hosted jasperoids are classified into porphyritic rhyolites, dacites, and related tuffs (Figure 4), while the basic ones, far away from Fe-Si-rich rocks, are mainly pillow lava flows and agglomerates. The Ranga felsic metatuffs comprise mainly microcrystalline groundmass (15–25 μm) of quartz (80–90 vol.%) associated with plagioclase (0.5–1.0 mm) saussurite phenocrysts (10–15 vol.%) (Figure 4a,b). They show replacement textures of polycrystalline quartz veinlets associated with epidote crosscuts in the examined samples (Figure 4c–e). Quartz veinlets appear in elongated shapes (1–1.5 mm) and intergrow with epidote. In quartz veinlets, there are mosaic-like patches (0.5–2.0 mm) of carbonate (5–10 vol.%), carrying hexagonal apatite between the crystals (Figure 4e). The Ranga felsic metatuffs are rich in disseminated pyrites (5–10 vol.%; Figure 4f), which occur as cubic crystals (0.5–1 mm) of magmatic origin; some pyrite crystals are locally altered to hematite that provides a red tint to the MV fine-grained quartz groundmass, especially at the shear zones around jasperoid lenses (Figure 4).

The jasperoids collected from the Ranga MV consist of quartz with subordinate pyrite and hematite–goethite (Figure 5a–f). Quartz occurs in two generations, either as microcrystalline (Mc-Qz) or polycrystalline quartz (Pc-Qz) of mosaic appearance (Figure 5a,b), including disseminated pyrite grains up to 10 vol.% (Figure 5a–j,l). The polycrystalline quartz grains vary in size from 250 μm to 1 mm in the more recrystallized jasperoid samples (Figure 5a,b). Most of the jasperoids samples include two quartz generations, while few samples include only the microcrystalline quartz phase (Figure 5c). A network of veinlets filled with fine-grained quartz crosscut the whole jasperoids fabric (Figure 5c).

Hematite and goethite (10–15 vol.%) are the main iron oxide phases of jasperoids, manifesting as translucent, red to brown, and fine-grained aggregates. They stain quartz grains and quartz veinlets with a reddish or brownish appearance (Figure 5a–e). Hematite is more abundant than goethite and displays a variety of microscopic textures; it occurs either as a massive reddish-brown tint under the transmitted light and stains quartz spheroids (Figure 5d) or as a channeled-shaped growth over the microcrystalline quartz veinlets (Figure 5e). Hematite is distinguished by a light gray color under reflected light, either intergrown at the rims of the primary pyrite or replacing it completely, while goethite occurs as olive-gray with a colloform appearance. Massive anhedral hematite with a white-gray color was observed individually or intergrown with magnetite and apatite (Figure 5k–l). The existence of interstitial hexagonal apatite grains within hematite resembles those of Tyrone ironstones [61], suggesting its magmatic origin. Some jasperoids preserved some lithic clasts of dacitic composition from the hosted felsic metatuffs of jasperoids. These lithic clasts display an aphyric texture and comprise a very fine-grained quartz groundmass surrounded by coarser recrystallized quartz grains (Figure 5f).

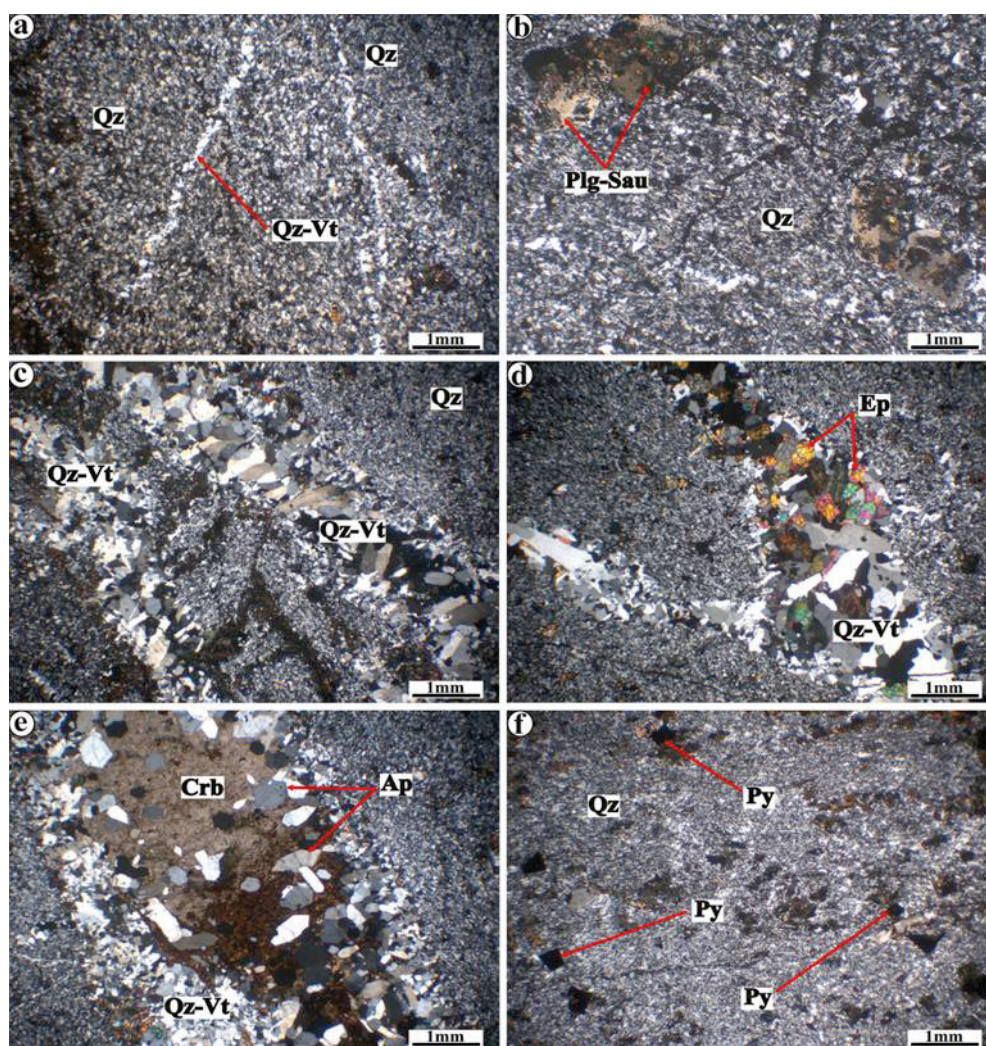


Figure 4. Photomicrographs of Wadi Ranga jasperoid-bearing felsic metatuffs. (a) Microcrystalline quartz veinlets crosscut felsic metatuffs. (b) Plagioclase phenocrysts altered to saussurite in rhyolitic metatuffs. (c) Polycrystalline quartz groundmass cut by two quartz veinlets in felsic metatuffs. (d) Polycrystalline quartz cut by epidote veinlets. (e) Polycrystalline quartz cut by carbonate veinlets that are sieved with coarse quartz in felsic metatuffs. (f) Euhedral pyrite is disseminated within quartz groundmass in the felsic metatuffs. Abbreviations: Quartz (Qz), Quartz Veinlets (Qz-Vts), Plagioclase Saussurite (Plg-Sau), Epidote (Ep), Carbonate (Crb), Apatite (Ap), and Pyrite (Py).

The studied jasperoids in the Ranga area are rich in disseminated sulfides (up to 10 vol.%), similar to Tyrone ironstone hosting sulfides (up to 10 vol.%) in Ireland, where sulfidic jaspers were hosted in the felsic flows and metatuffs [61]. Pyrite is the dominant iron–sulfide mineral in the studied jasperoids (Figure 5e–l) as well as in the host metatuffs (Figure 4h). Pyrite occurs as euhedral to subhedral, light yellow crystals (0.5–1.0 mm) and is disseminated within the quartz groundmass and in quartz veinlets. Most of the studied pyrite crystals are replaced partially or completely with hematite and/or goethite, showing the red ochre (Figure 5g–j).

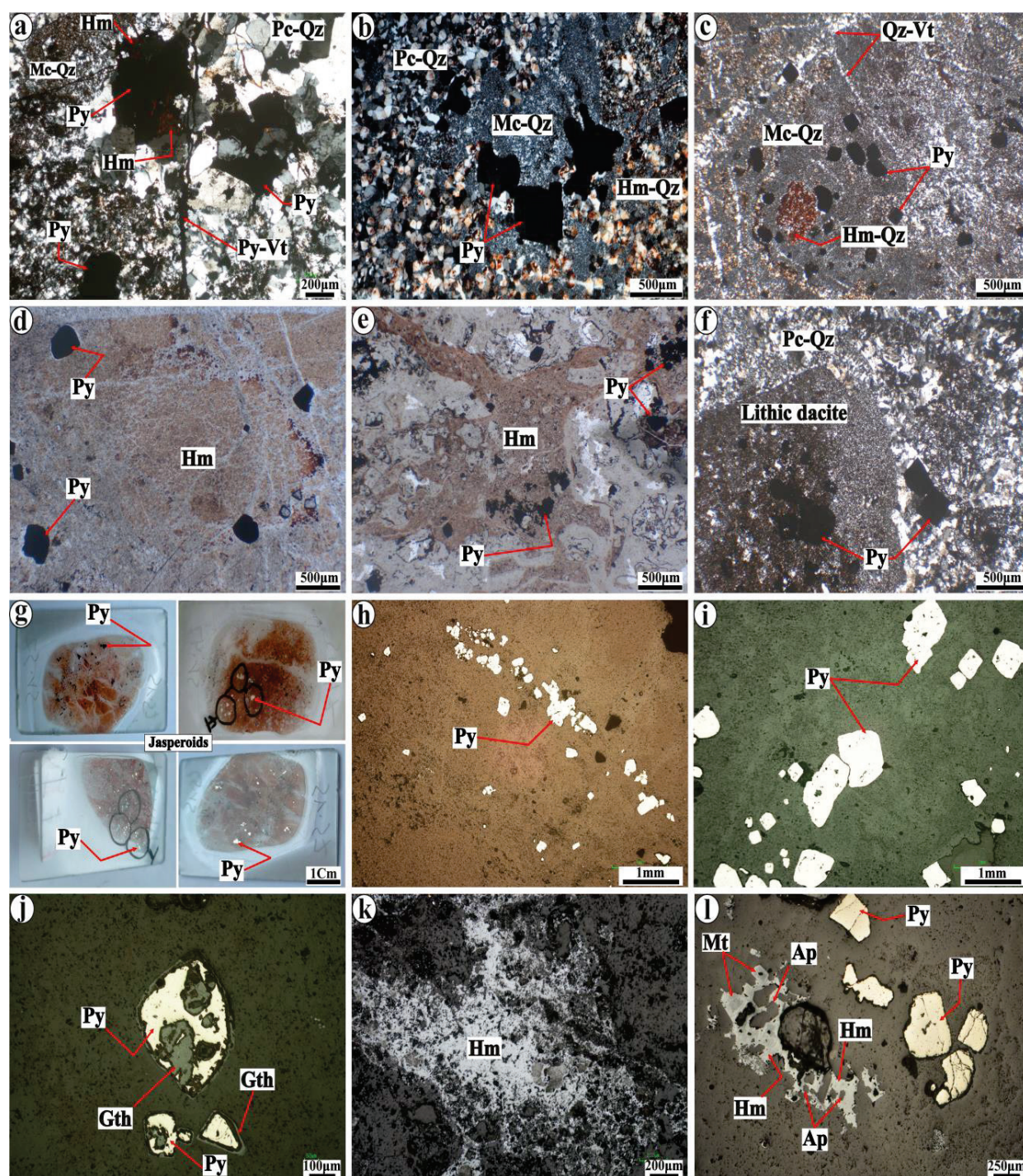


Figure 5. Photomicrographs of Wadi Ranga pyrite-rich jasperoids. (a–c) Jasperoids comprise two quartz-size generations: polycrystalline and microcrystalline quartz associated with hematite and pyrite under transmitted light. (d,e) Massive and channel-shaped reddish-brown hematite textures, respectively, grown over the microcrystalline quartz grains and veinlets. (f) Lithic clast of dacite within jasperoids. (g) Thin polished sections of pyrite-rich jasperoids. Some pyrites appear with yellow color in reflected light, but the upper part of pyrite grains are black due to the absence of reflection of light. (h,i) Disseminated cubic pyrite. (j) Goethite partially replaces pyrite grains. (k) Massive hematite granule. (l) Interstitial apatite hosted within a hematite mosaic in the presence of pyrite and magnetite. Abbreviations: Microcrystalline Quartz (Mc-Qz), Polycrystalline Quartz (Pc-Qz), Hematite (Hm), Goethite (Gth), Hematite Growth over Quartz Grains (Hm-Qzs), Pyrite Veinlets (Py-Vts), Pyrite (Py), Magnetite (Mt), and Apatite (Ap).

4.3. SEM-EDS Data and Mineral Chemistry

More than 50 photomicrographs were captured by Scanning Electron Microscopy (SEM) for the desired polished thin sections, revealing that hematite and goethite with subordinate magnetite are the iron oxides found in jasperoids, while pyrite is the sole sulfide mineral (Figure 6). The SEM microphotographs show the crystal forms and different relationships of the studied minerals, such as hematite and goethite, which occur either as sparse dissemination or replacement rims around the primary pyrite (Figure 6a–d). Most pyrites are partial to completely converted to secondary hematite and goethite pseudomorph after their cubic crystals (Figure 6a–d).

The colloform texture of goethite was recognized easily from SEM images and this texture can differentiate it from the massive hematite (Figure 6a–d). Hematite appears in two generations: the first-generation (Hm₁) type is formed after pyrite, as evidenced by its cubic forms, while the second generation (Hm₂) appears as coarse massive crystals carrying both the former cubic pyrite shape and the hexagonal apatite crystals (Figure 6e,f). The hematite generation (Hm₁) was oxidized after the darker gray magnetite that only appears as sparse shapes within Hm₁ (Figure 6e). Some pyrites appear to be fresh without any iron oxide replacements (Figure 6g,h).

A representative sampling of 32 analyzed points within minerals of jasperoids was conducted using EDS to determine their major oxide compositions (Supplementary Figure S1). The analyzed points were five points in hematite, two in goethite, eight in magnetite, two in apatite, and fifteen points in pyrites (Tables 2 and 3). The repartition of Fe⁺³ (Fe₂O₃) and Fe⁺² (FeO) wt.% contents from the EDS-normalized total iron (FeO total) was conducted using Droop's [62] method (Table 2). Hematite is often considered an endmember of all other iron oxide transformations and mainly constitutes Fe₂O₃ ranging from 79.8 to 85.3 wt.% compared to goethite, which contains a lower Fe₂O₃ content (74–77.3 wt.%; Table 2). Both hematite and goethite have higher SiO₂ (up to 6.97 wt.%) and Al₂O₃ contents (up to 1.59 wt.%) compared to magnetite (wt.%), i.e., SiO₂ (up to 2.37 wt.%) and Al₂O₃ (up to 0.84 wt.%) (Table 2).

The low content of CuO (1.0 wt.%) that appeared in hematite may be due to the presence of micrometer-sized inclusions of Cu-rich sulfides. Magnetite is rich in FeO (61.76–67.32 wt.%) relative to Fe₂O₃ (27.87–30.29 wt.%), as shown in Table 2. The contents of SiO₂ (up to 2.37 wt.%) and Al₂O₃ (up to 0.84 wt.%) in magnetite are lower than those in hematite and goethite. Magnetite also includes minor contents of Na₂O, K₂O, CaO, and MgO (<0.4 wt.%). The appearance of Co⁺² (less than 1.0 wt.%) in the chemical structures of the studied iron oxides may be attributed to the substitution of Fe⁺² by Co⁺² (Table 2).

Apatite is used as a mineral indicator for interpreting geological environments since it can incorporate various ions into its structure [63]; this explains the minor contents of FeO (1.29–1.34 wt.%) and Na₂O (0.36 wt.%) observed in the studied apatite (Table 2). CaO and P₂O₅ are considered the dominant oxides in the analyzed apatite with averages of 54.14 and 37.2 wt.%, respectively (Table 2). The saturation temperature at which apatite begins to recrystallize from the melt is about 850 °C based on Equation (1) of Piccoli and Candela [64].

$$\text{Apatite (T)} = ((26,400 \times C^{\text{I}}\text{SiO}_2 - 4800) / (12.4 \times C^{\text{I}}\text{SiO}_2 - \ln(C^{\text{I}}\text{P}_2\text{O}_5) - 3.97)) \quad (1)$$

where T is the apatite saturation temperature (in Kelvin), and C^ISiO₂ and C^IP₂O₅ represent the concentration of silica and phosphorus in the melt (see Table 2), respectively; they are expressed as weight fractions (wt.%/100).

Pyrite has an average of 46.4 wt.% Fe and 52.9 wt.% S (Table 3). A trace amount (<0.2 wt.%) of Si was detected and could be attributed to the association of pyrite in a Si-rich groundmass (jasperoids). A minor concentration of Ag (up to 0.32 wt.%) was observed in some pyrites.

Table 2. Representative EDS analyses of hematite, goethite, magnetite, and apatite in the Wadi Ranga jasperoids.

Sample No.	Sr44	Sr47				Sr57				Sr44	Sr47	Sr57				Sr46				Sr47	
Point No.	18	153	167	163	102	139	141	17	104	138	140	145	146	8	9	160	164				
Mineral	Hematite								Goethite				Magnetite				Apatite				
SiO ₂	1.86	1.69	6.82	6.97	1.60	3.19	3.35	2.37	1.68	1.73	2.00	0.42	0.30	2.33	2.15	-	-				
TiO ₂	-	-	-	-	-	-	-	-	-	-	-	-	-	0.05	0.03	-	-				
Al ₂ O ₃	1.59	0.24	0.49	0.61	0.26	0.40	0.44	0.19	0.84	0.31	0.33	0.34	0.00	0.24	0.09	-	-				
Cr ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
FeO*	85.38	79.89	83.22	82.88	85.03	77.30	73.98	94.41	93.25	90.26	89.78	96.67	97.61	89.83	91.17	1.34	1.29				
MnO	-	-	-	-	-	-	-	-	-	-	-	-	-	0.03	-	-	-				
MgO	0.12	0.33	0.21	-	0.46	-	-	0.15	0.44	-	-	-	-	0.10	0.09	-	-				
CaO	0.14	-	0.19	-	-	-	-	0.12	0.00	-	-	-	-	0.22	0.27	53.88	54.39				
Na ₂ O	0.22	-	-	-	0.22	-	-	0.28	0.15	-	-	-	-	0.06	0.07	0.36	-				
K ₂ O	0.12	-	-	-	-	-	-	-	-	-	-	-	-	0.03	0.01	-	-				
P ₂ O ₅	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	36.34	38.05				
CoO	-	0.96	0.87	-	-	0.99	-	-	-	-	-	0.83	0.93	-	-	-	-				
CuO	1.04	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
Total	90.46	83.11	91.80	90.46	87.58	81.88	77.77	97.52	96.36	92.30	92.11	98.26	98.84	92.89	93.87	91.92	93.73				
Mg#	0.01	0.02	0.01	-	0.03	-	-	0.01	0.03	-	-	-	-	0.01	0.01	-	-				
FeO	-	-	-	-	-	-	-	65.21	64.45	62.10	61.76	66.51	67.32	61.96	62.94	-	-				
Fe ₂ O ₃	85.38	79.89	83.22	82.88	85.03	77.30	73.98	29.20	28.80	28.16	28.02	30.16	30.29	27.87	28.23	-	-				
C ^I SiO ₂	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.9	0.9				
C ^I P ₂ O ₅	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.0	0.0				
T (°C)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	885.3	885.3				

Total iron as FeO*; Mg# = Mg/(Mg + Fe) atomic ratio; C^ISiO₂ and C^IP₂O₅ are the concentrations of silica and phosphorus in the melt.

Table 3. Representative EDS analyses of pyrite in the Wadi Ranga jasperoids.

Sample No.	Sr44					Sr47					Sr57				
	16	19	20	151	152	154	157	158	98	101	103	142	143	148	149
Point No.															
Si	0.15	0.09	0.08	-	4.42	-	-	-	0.08	0.11	0.08	-	-	-	-
Al	0.06	-	-	-	1.39	-	-	-	-	-	0.07	-	-	-	-
Ca	-	-	-	-	0.13	-	-	-	-	0.07	0.05	-	-	-	-
Na	-	-	-	-	0.36	-	-	-	-	0.18	-	-	-	-	-
K	-	-	-	-	0.13	-	-	-	-	-	-	-	-	-	-
Ti	-	-	-	-	0.16	-	-	-	-	-	-	-	-	-	-
Mg	-	-	-	-	0.35	-	-	-	-	-	-	-	-	-	-
Fe	46.33	46.12	46.26	40.61	49.37	47.2	45.84	46.26	45.89	45.44	46.33	47.36	47.56	48.63	47.15
S	53.46	53.61	53.38	59.39	43.7	52.8	54.16	53.74	53.72	53.2	53.28	52.64	52.44	51.37	52.85
Ni	-	-	0.16	-	-	-	-	-	-	-	-	-	-	-	-
Cr	-	-	0.12	-	-	-	-	-	-	-	-	-	-	-	-
Ag	-	0.17	-	-	-	-	-	-	0.32	-	0.19	-	-	-	-
La	-	-	-	-	-	-	-	-	-	1	-	-	-	-	-
Total	100	100	100	100	100	100	100	100	100.01	100	100	100	100	100	100

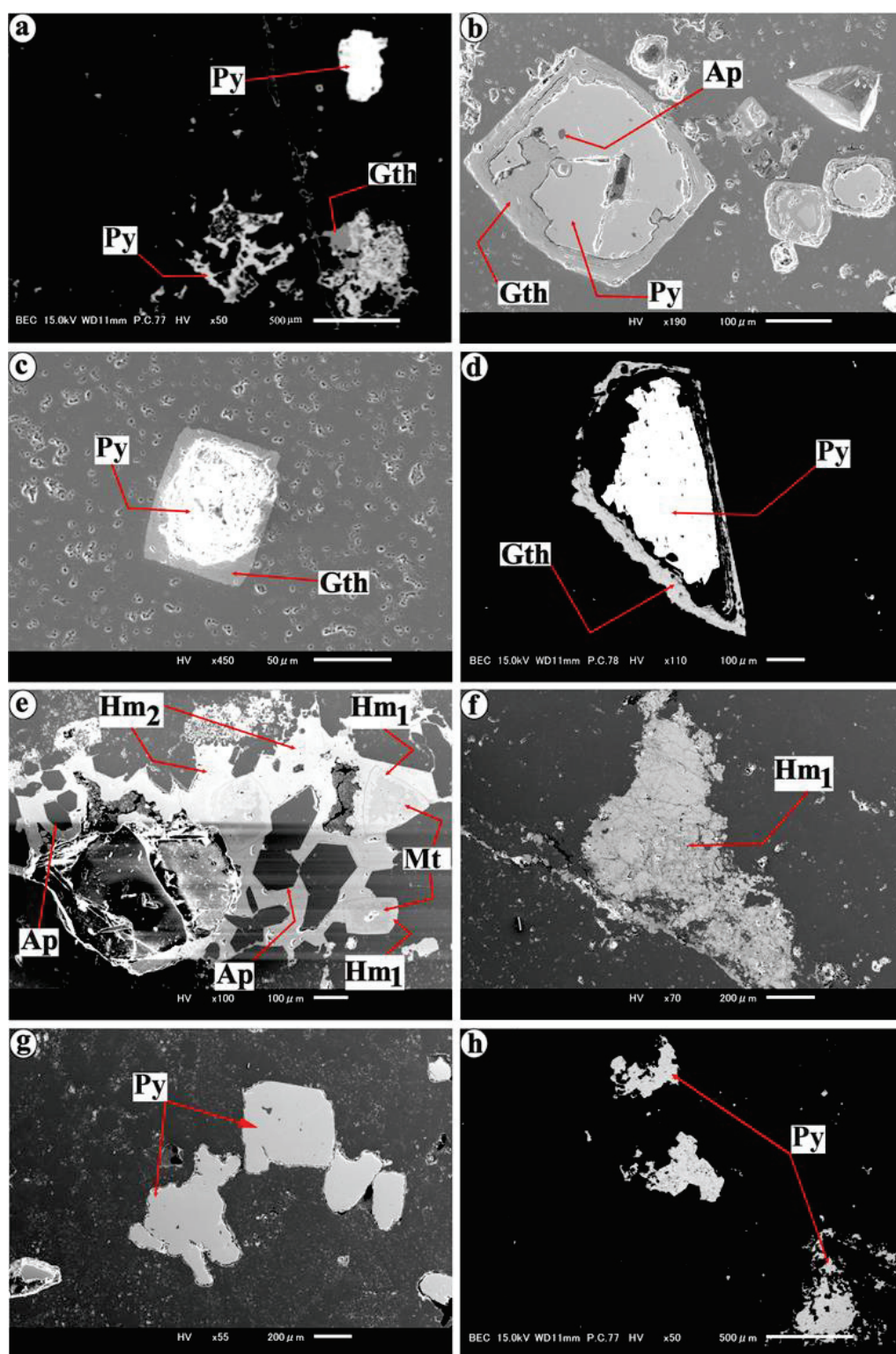


Figure 6. Scanning Electron Microscope (SEM) photomicrographs of Wadi Ranga pyrite-rich jasperoids. (a–d) Goethite pseudomorphed former cubic pyrites. (e,f) Two generations of hematite (Hm₁, Hm₂) carrying hexagonal apatite with minor magnetite. (g,h) Fresh cubic pyrite.

4.4. Bulk Compositions of Jasperoids and Host Rocks

The major and trace element compositions of some representative samples of both jasperoids and Ranga metavolcanics (MV) are shown in Table 4. The major element data of the Ranga MV hosted-jasperoids (Table 4) comprise mainly SiO₂ (74.19 wt.% on average)

for the more felsic samples (dacitic to rhyolitic metatuffs), except for one sample (Sr.53) that exhibited a lower SiO_2 content (55.89 wt.%) and was plotted between dacites and andesites (named andesitic dacitic metatuffs). The more felsic metatuffs show small variations in Al_2O_3 (9.56–12.85 wt.%), Fe_2O_3 (≈ 3.53 wt.%), MgO (0.83–1.81 wt.%), CaO (0.88–2.05 wt.%), K_2O (0.03–1.0 wt.%), and Na_2O (2.95–5.19 wt.%) compared to andesitic dacitic samples (Sr.53) that consist of higher Al_2O_3 (18.62 wt.%), Fe_2O_3 (≈ 6.27 wt.%), and CaO (9.52 wt.%). All analyzed samples have a low loss on ignition (LOI; 1.32–2.12 wt.%) reflecting the fresh nature of these rocks. The studied Ranga MV consisted primarily of felsic metatuffs with a subalkaline composition range from dacites to rhyolites according to Winchester and Floyd's [65] classification diagram using the relationship between Nb/Y and Zr/Ti (Figure 7a).

Table 4. Major (wt.%) and trace element (ppm) contents of Ranga MV (felsic metatuffs) and jasperoids.

Rock Name.	Felsic Metatuffs					Jasperoids	
Sample No.	Sr52	Sr55	Sr53	Sr58	Sr47	Sr56	Sr57
SiO_2	76.49	74.04	55.89	72.04	90.32	89.73	93.35
TiO_2	0.17	0.23	0.32	0.28	0	<d.l.	0.01
Al_2O_3	9.56	12.39	18.62	12.85	0.17	0.21	0.25
Fe_2O_3	3.84	3.28	6.27	3.46	5.1	6.63	2.73
MgO	1.58	1.61	1.81	0.83	0.01	0.17	0.06
CaO	1.90	0.88	9.52	2.05	0.05	0.32	0.14
Na_2O	2.95	5.19	4.01	4.56	<d.l.	<d.l.	<d.l.
K_2O	0.05	0.03	0.03	1.00	<d.l.	<d.l.	0
P_2O_5	0.05	0.07	0.09	0.06	0.01	0.04	0.02
MnO	0.13	0.08	0.16	0.08	0.01	0.01	0.01
LOI	1.77	1.32	2.12	1.39	1.12	1.49	1.08
Total	98.50	99.13	98.85	98.61	96.78	98.59	97.66
A/CNK	1.95	2.03	1.37	1.69	-	-	-
A/NK	3.19	2.37	4.61	2.31	-	-	-
Mg#	44.92	49.31	36.39	32.22	0.39	4.83	4.17
Trace elements (ppm)							
Rb	1.78	0.89	2.31	13.78	2.36	3.14	1.56
Ba	39.52	67.91	47.23	232.27	20.95	14.79	16.42
Sr	80.54	84.74	276.89	103.42	12.14	23.66	36.13
Nb	1.13	1.61	1.36	1.90	0.61	0.79	0.91
Zr	82.57	107.83	150.01	81.15	8.25	8.13	8.24
Y	33.94	43.24	49.61	23.54	1	0.61	1.21
Zn	110	65.08	102.36	31.35	15.64	62.84	14.29
Cu	1333	19.55	93.18	9.35	53.53	138.1	40.02
Ni	59.44	31.77	38.48	30.07	4.27	9.67	1.03
Co	2.97	1.95	7.62	3.77	2.12	0.52	1.39
Cr	<d.l.	<d.l.	32.55	<d.l.	<d.l.	<d.l.	<d.l.
V	33.09	15.55	158.70	34.28	18.71	30.97	12.66
Sc	6.53	6.81	11.08	10.26	<d.l.	0.31	1.03

Table 4. Cont.

Rock Name.	Felsic Metatuffs				Jasperoids		
Sample No.	Sr52	Sr55	Sr53	Sr58	Sr47	Sr56	Sr57
Ga	5.91	5.66	14.21	5.65	<d.l.	<d.l.	<d.l.
Mo	1.34	1.80	1.47	0.30	5.13	9.68	5.51
Sn	<d.l.	<d.l.	12.05	<d.l.	<d.l.	<d.l.	<d.l.
Cs	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
La	4.91	6.01	7.72	3.35	0.22	0.43	0.66
Ce	13.97	17.08	21.75	9.24	0.41	0.86	1.33
Pr	2.33	2.69	3.53	1.44	0.05	0.1	0.16
Nd	11.16	14.51	17.91	6.93	0.22	0.37	0.63
Sm	3.87	4.49	5.64	2.18	0.05	0.07	0.12
Eu	1.06	1.17	1.56	0.58	0.01	0.02	0.04
Gd	4.51	5.68	6.86	2.87	0.1	0.07	0.13
Tb	0.81	0.99	1.21	0.53	0.02	0.01	0.02
Dy	5.64	6.81	8.16	3.49	0.13	0.09	0.15
Ho	1.21	1.51	1.81	0.79	0.03	0.02	0.04
Er	3.72	4.65	5.52	2.44	0.1	0.06	0.11
Tm	0.57	0.73	0.88	0.40	0.02	0.01	0.02
Yb	3.94	5.07	6.17	2.67	0.12	0.07	0.16
Lu	0.59	0.74	0.94	0.41	0.02	0.01	0.03
Hf	3.17	4.03	4.86	2.83	0.42	0.12	0.11
Ta	<d.l.	<d.l.	0.03	0.00	<d.l.	<d.l.	<d.l.
Pb	54.69	5.16	1.25	3.26	36.03	39.74	4.01
Th	2.00	2.22	3.02	2.33	0.37	0.37	0.34
U	0.45	0.38	0.34	0.56	0.29	0.17	0.27
ΣREE	58.29	72.13	89.66	37.32	1.5	2.19	3.6
Eu/Eu*	0.776	0.708	0.767	0.709	0.43	0.87	0.98
(Nb/La) _N	0.23	0.27	0.18	0.57	-	-	-
(La/Yb) _N	1.25	1.19	1.25	1.25	1.83	6.14	4.13
(La/Gd) _N	1.09	1.06	1.13	1.17	2.20	6.14	5.08
(Lu/Gd) _N	0.13	0.13	0.14	0.14	0.20	0.14	0.23
(Cu + Pb + Zn)	1498.43	89.79	196.79	43.96	105.2	240.68	58.32
[Fe + Mn]/Ti	-	-	-	-	39,742	51,635	3,557,323
Al/[Al + Fe + Mn]	-	-	-	-	221	211	585

Total iron as Fe₂O₃; Mg# = Mg/(Mg + Fe) atomic ratio; A/CNK = (Al₂O₃/[CaO + Na₂O + K₂O]); A/NK = (Al₂O₃/[Na₂O + K₂O]). <d.l.: below the detection limit.

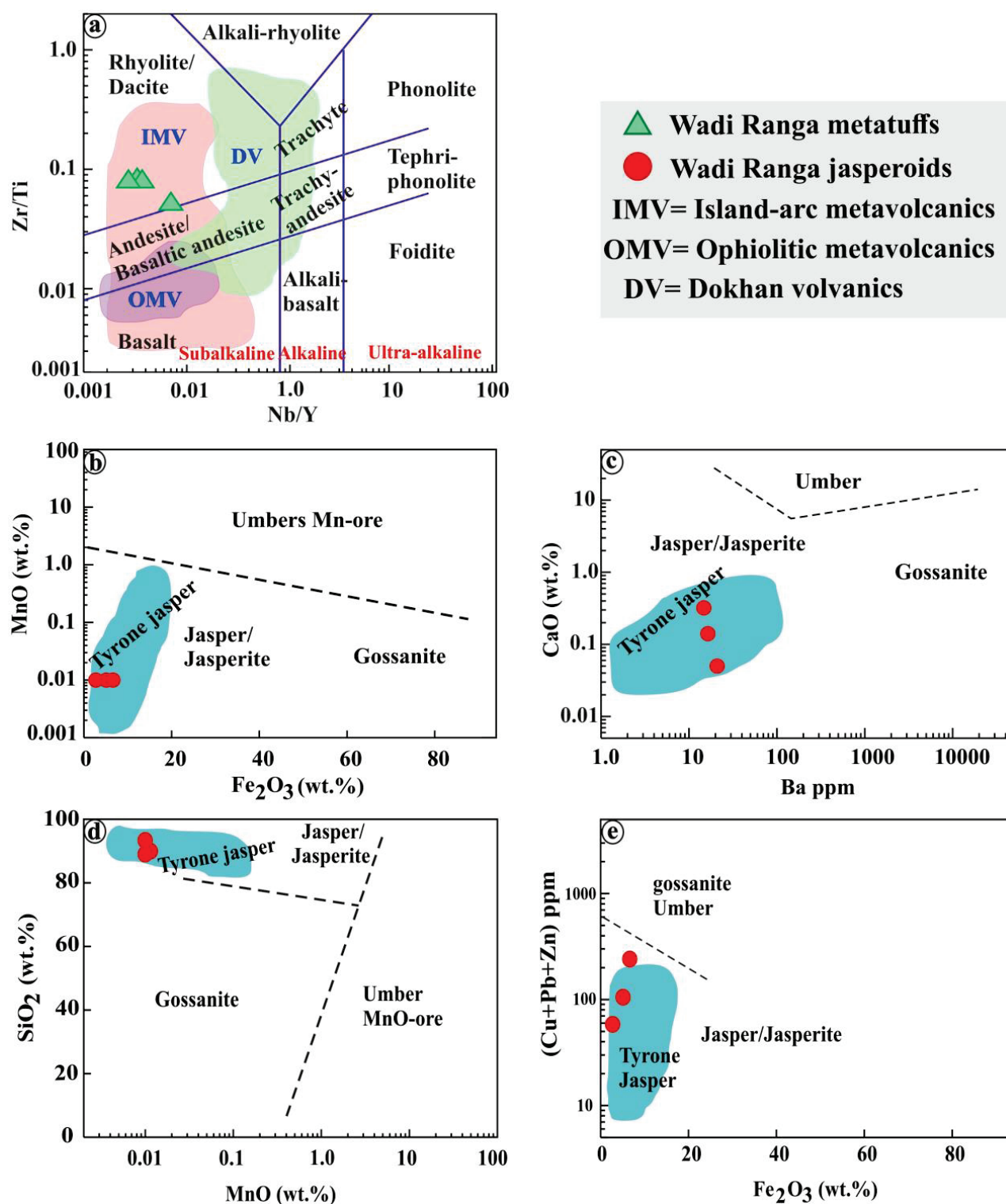


Figure 7. Whole-rock chemistry of Wadi Ranga metatuffs and their sulfidic jasperoids. (a) Zr/Ti vs. Nb/Y diagram [65]. (b–e) Bivariate geochemical plots of Wadi Ranga jasperoids show that jasperoids samples from Wadi Ranga are most like jaspers and jasperites from the Urals and Tyrone complex (data from [61,66,67]). The fields of Dokhan MV (DV) were drawn according to available data from Moghazi [68], Eliwa et al. [69], Abdel Wahed et al. [70], Dessouky et al. [71], ophiolitic MV (OMV) field from Stern [72], Abd El-Rahman et al. [73], island arc MV (IMV) field from Stern, et al. [6], Faisal et al. [9], and Abdelkareem [74]. The field of Tyrone jaspers in the bivariate geochemical plots was after Hollis et al. [61]. The studied felsic metatuffs show enrichment in base metals (Cu, Pb, and Zn),

especially Cu (9.35–1333 ppm; Table 4) and Zn (31.35–110 ppm), because of the existence of sulfides observed during petrographical observation (Figure 4f). After comparing the chemical data of Ranga MV alongside their counterparts of island arc MV (IMV or Shadli MV; Figure 7a) and ophiolitic MV varieties (OMV; Figure 7a) distributed in the Centre and South Eastern Desert (SED), we concluded that the studied Ranga MV rocks resemble in composition the Shadli island arc MV [6,9,74]. The studied Ranga metavolcanics differ in chemical composition from OMV [72,73]. The incompatible trace element ratios of La/Yb (1.19–1.25; Table 4) and La/Gd (1.06–1.17; Table 4) of the studied felsic metatuffs are consistent with those of both chondrite (1.47 and 1.190 [75]) and the primitive mantle (1.46 and 1.191 [75]), but are lower than their averages in the upper continental crust (15.5 and 7.75 [76]). Moreover, the Lu/Gd ratio (0.13–0.14; Table 4) is higher than its average in the upper crust (0.078 [76]) and also consistent with chondrite and the primitive mantle (0.123 and 0.124 [75]).

The Wadi Ranga jasperoids are mainly composed of SiO₂ (89.73–90.35 wt.%) due to the abundance of quartz and its microcrystalline forms and show wide ranges of Fe₂O_{3t} (2.73–6.63 wt.%) attributed to the significant amount of hematite, goethite, pyrite, and magnetite (Table 4). The Al₂O₃, CaO, and MgO concentrations are typically less than 0.4 wt.% on average, with minor contents of MnO and P₂O₅ (<0.04 wt.% on average) (Table 4). The remaining major elements (TiO₂, Na₂O, and K₂O) are not detected in the analyzed jasperoids. A low loss on ignition (LOI) ranging from 1.08% to 1.49% (Table 4) reflects less H₂O and alterations in the jasperoid and its host metatuffs. Bivariate geochemical plots of some major oxides and base metals for the studied jasperoids were conducted and compared to the literature data from Urals and Tyrone Si-rich ironstones associated with volcanogenic massive sulfide (VMS) deposits in Russia and Ireland, respectively [61,66,67]. Ferruginous deposits from the Urals are subdivided into jaspers/jasperites, gossanites, and Umbers [66,67]; however, their counterparts of the Tyrone igneous complex are mainly jaspers/jasperites [61]. The studied jasperoids are mainly plotted within jaspers/jasperites of Urals and coexist with the sulfidic jaspers of the Tyrone igneous complex that has a low total Fe₂O₃, MnO, CaO, and moderate base metals (Cu = 77.2 ppm, Pb = 26.6 ppm, and Zn = 30.9 ppm on average) alongside higher SiO₂ (up to 93 wt.%) concentrations (Figure 7b–e and Table 4). The base metal contents of our jasperoids (Cu + Pb + Zn = 58.32–240.68 ppm) are generally lower than those of their host rocks (Cu + Pb + Zn = 43.96–1498.43 ppm), as shown in Table 4.

The Wadi Ranga felsic metatuffs have relatively high rare-earth element (REE) contents, varying from 37.32 to 89.66 ppm (Table 4). The chondrite (C1)-normalized REE pattern of the Ranga felsic metatuffs is flat in shape (La/Yb)_N = 1.19–1.25; it also displays a nearly negative Eu anomaly (Eu/Eu* = 0.708–0.776; Table 4 and Figure 8a) and resembles REE patterns of the Shadli felsic MV [6,45,74]. The primitive mantle (PM)-normalized pattern of the Ranga felsic metatuffs generally shows enrichment in large-ion lithophile elements (LILEs; Ba, K, and Pb) and depletion in high-field strength elements (HFSEs: Nb, Ta, P, and Ti) (Figure 8b).

Moreover, the spider pattern is similar to that of the felsic metatuffs recorded in the Um Samuiki and the Wadi Ranga ([45,74]; Figure 8b). The Wadi Ranga jasperoids show a chondrite-normalized U-shaped REE pattern similar to Tyrone jaspers with a moderate (La/Yb)_N ratio (1.8–6.1; Figure 8c) and are lower than both of their hosted calc-alkaline felsic metatuffs (1.19–1.25; Figure 8c) and the felsic Shadli MV after Maurice et al. [45] (1.3–1.9; Figure 8c). Furthermore, they display a slightly negative Eu anomaly (Eu/Eu* = 0.43–0.98; Table 4), which resembles that of both the hosted felsic metatuffs and Shadli MV after Maurice et al. [45] (Eu/Eu* = 0.708–0.776, 0.77–0.80, respectively). The primitive mantle-normalized patterns of the Ranga jasperoids exhibit enrichment in U and Zr, but depletion in Ti and Nb, similar to those of the Tyrone jasper PM patterns after Hollis et al. [61] (Figure 8d). The REE and trace element patterns of the Wadi Ranga jasperoids are considerably like those of the host MV rocks (Figure 8c,d), as both are high in LILEs and low in HFSEs. They have negative Eu, Nb, and Ti anomalies and positive K, Pb, and Sr anomalies resembling the Tyrone jasper and its host rhyolitic rocks [61] and Shadli MV [6,45,74].

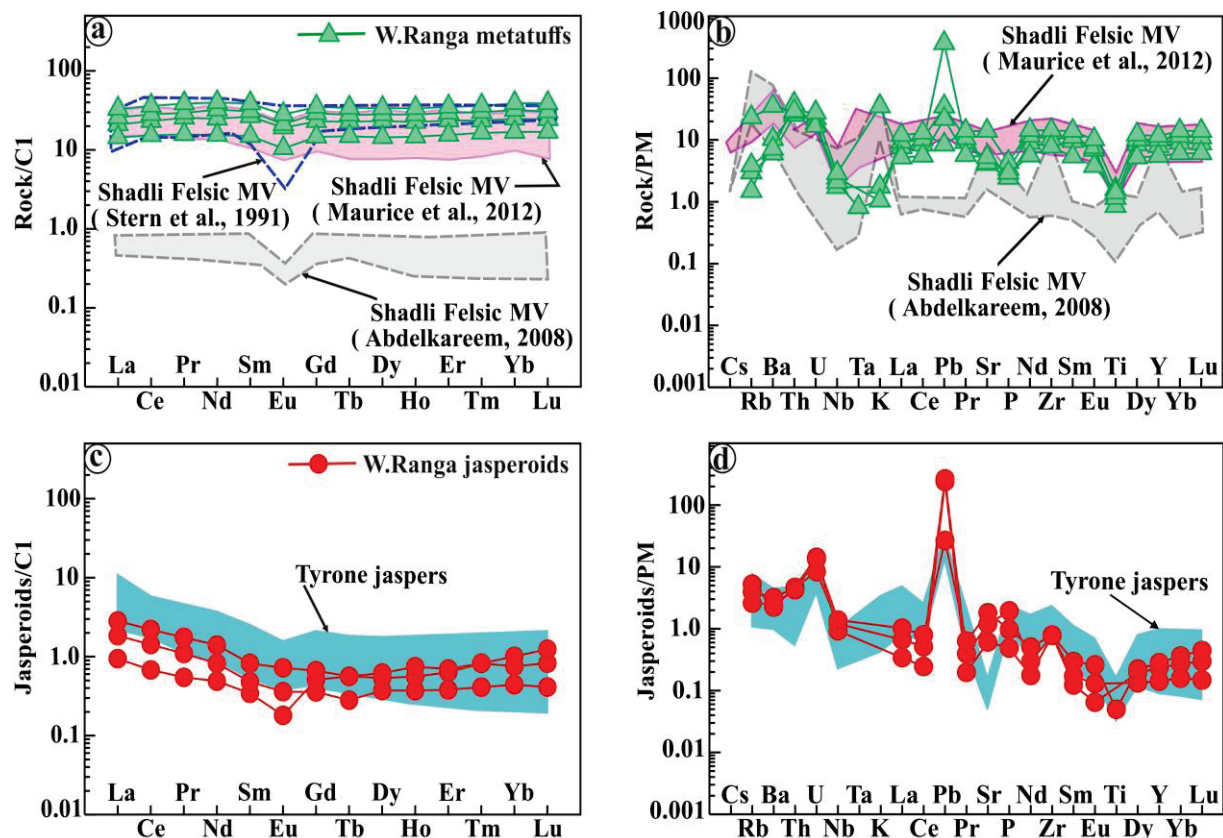


Figure 8. Trace element chemistry of Wadi Ranga metatuffs and their sulfidic jasperoids. (a) Chondrite (C1)-normalized REE pattern of Wadi Ranga metatuffs [75]. (b) The primitive mantle (PM)-normalized trace element patterns of Wadi Ranga metatuffs [75]. (c) Chondrite (C1)-normalized REE pattern of Wadi Ranga sulfidic jasperoids [75]. (d) The primitive mantle (PM)-normalized trace element patterns of Wadi Ranga sulfidic jasperoids [75]. The felsic metavolcanics fields used in the spider patterns (a,b) were adapted from Stern et al. [6], Maurice et al. [45], and Abdelkareem [74], while the field of Tyrone jaspers is after Hollis et al. [61].

5. Discussion

5.1. Petrogenesis and Tectonic Setting of Jasperoid-Bearing Metavolcanics

5.1.1. Magma Source and Affinity

The low loss on ignition values (LOI; 1.32–2.12 wt.%) and the absence of Ce anomalies (Table 4 and Figure 8a) of the Wadi Ranga felsic metatuffs support the fresh nature of these rocks and exclude the effect of any post-magmatic alteration [77]. The Wadi Ranga felsic metatuffs are classified as subalkaline metavolcanics by using the $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ vs. SiO_2 diagram (Figure 9a; [78]). Based on the AFM diagram [78], the Wadi Ranga felsic metatuffs fall in the calc-alkaline category and are far away from the tholeiitic rock field (Figure 9b), suggesting their generation in the island arc setting.

Similarly, the studied felsic metatuffs show calc-alkaline affinity in the Co vs. Th discrimination diagram (Figure 9c; [79]). This is consistent with the island arc metavolcanics (IMV or Shadli MV; Figure 9b) field, but different from the ophiolitic metavolcanics (OMV) based on the available chemical data from the SED of Egypt [6,9,72–74]. The felsic metatuffs of the Wadi Ranga can be classified as peraluminous types [80], exhibiting A/CNK values $(\text{Al}_2\text{O}_3/[\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}])$ ranging from 1.37 to 2.03 (Figure 9d). Moreover, they show a magnesian character (Figure 9e) and some hydrous minerals, reflecting the origin from hydrous and oxidizing magmatic sources that likely originated in a subduction-related environment [81].

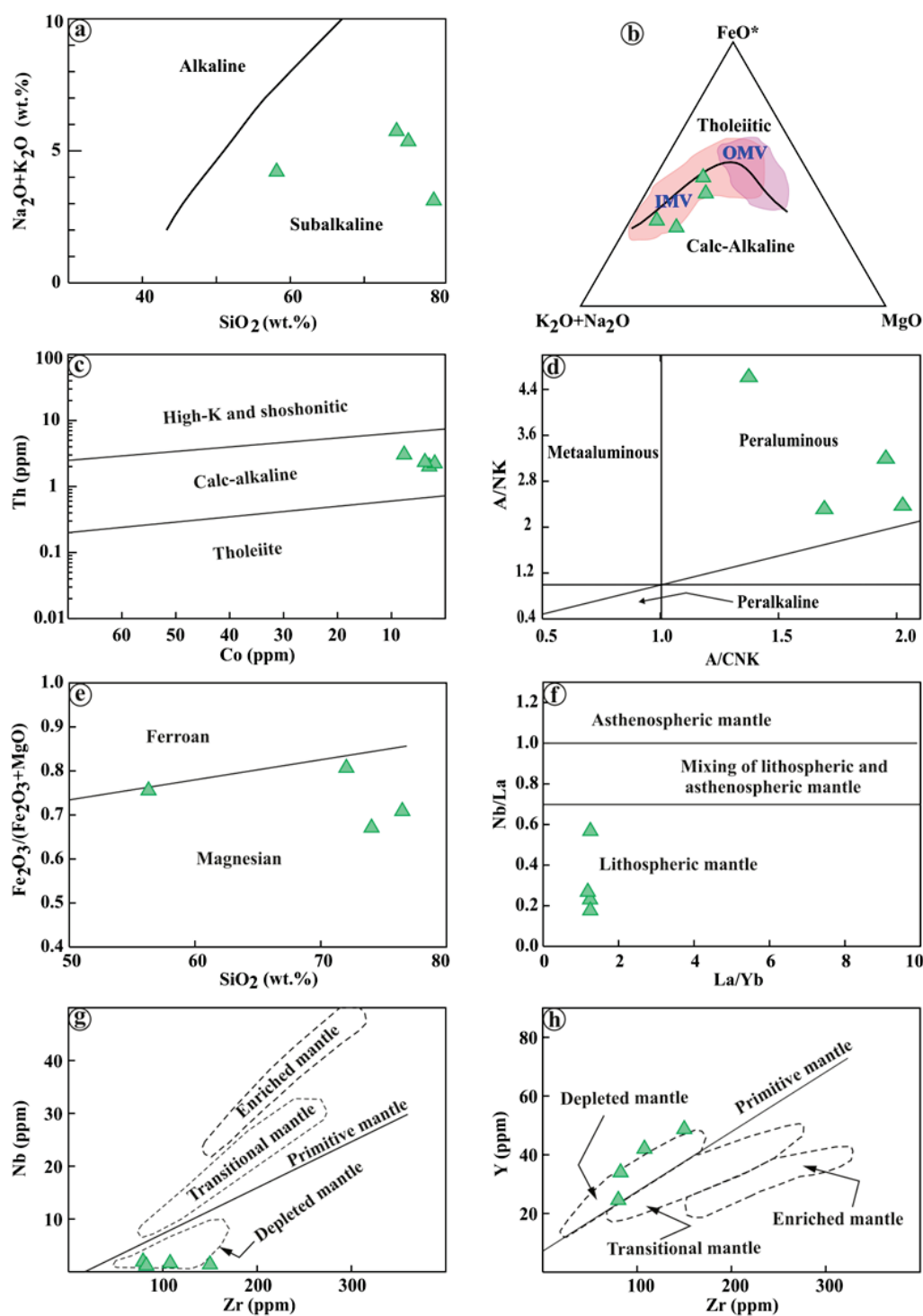


Figure 9. Magma type and source of Wadi Ranga metatuffs. (a) $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ vs. SiO_2 diagram [78]. (b) AFM diagram of Irvine and Baragar [78], showing a tholeiitic to calc-alkaline trend. (c) Co vs. Th diagram [79]. (d) A/CNK $[\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})]$ vs. A/NK $[\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O})]$ diagram [80]. (e) SiO_2 vs. $\text{Fe}_2\text{O}_3/(\text{Fe}_2\text{O}_3 + \text{MgO})$ diagram for magnesian character discrimination [81]. (f) La/Yb vs. Nb/La [82]. (g,h) Zr vs. Nb and Y diagrams, respectively. The field of ophiolitic MV (OMV) from Stern [72] and Abd El-Rahman et al. [73], while the island arc MV (IMV) field from Stern et al. [6], Faisal et al. [9], and Abdelkareem [74].

The Wadi Ranga felsic metatuffs show negative P and Ti anomalies that are likely attributed to the fractional crystallization of apatite and ilmenite, respectively (Figure 8b).

This euhedral magmatic apatite in felsic metatuffs (Figure 4e) and jasperoids (Figure 5l) crystallized at a temperature of 850 °C [64]; this suggests the crystallization of metatuffs from the felsic melts at 850 °C, where some apatite crystals from the host rocks leached to the jasperoids (Figure 5l) that were generated after metatuffs at <850 °C. It is well known that the lithospheric magma is depleted in the HFSE relative to the LREE, and the HFSE/LREE ratio $(\text{Nb/La})_N$ is useful for distinguishing the mantle sources of different rocks either lithospheric or asthenospheric mantle sources [82]. For example, low $(\text{Nb/La})_N$ ratios (<0.7) suggest that the source is the lithospheric mantle, whereas higher ratios (>1.0) indicate an origin from the asthenospheric mantle; in addition, rocks have moderate $(\text{Nb/La})_N$ ratios (0.7–1.0) derived from the mix of lithospheric and asthenospheric magma (Figure 9f). The Wadi Ranga metatuffs show a low $(\text{Nb/La})_N$ ratio (0.27–0.23; Table 4), reflecting their magma source being the lithospheric mantle (Figure 9f).

There were lower $(\text{La/Yb})_N$ (1.19–1.25; Table 4) and $(\text{La/Gd})_N$ (1.06–1.17; Table 4) and the higher $(\text{Lu/Gd})_N$ (0.13–0.14; Table 4) ratios of the studied metatuffs, excluding any contamination with continental crustal materials [76]. In addition, the Wadi Ranga felsic metatuffs possibly crystallized from fractionated melts that were derived from a depleted mantle source (Figure 9g,h) based on the Zr versus Nb and Y diagrams [83]. The negative anomalies of Nb and Ti, along with the positive anomalies at Pb, K, Rb, and Ba (Figure 8b), are attributed to the influence of fluids/melt derived from the subducted slab (oceanic crust) in a subduction-related setting [84–87]. Consequently, the influence of fluids/melts derived from the subducted slab on the lithospheric-derived melts (primary melts) and fractionation (by fractional crystallization) of these melts can yield more silicic rocks than those of andesitic composition, like the Wadi Ranga felsic metatuffs (55.89–76.49 wt.%; Table 4). The higher REE contents (ΣREE : 37.32–89.66 ppm; Table 4) of the Wadi Ranga felsic metatuffs relative to other mafic rocks in the area (ΣREE : 15.14–33.54 ppm [45]) suggest an origin during the late stage of the former fractionated basaltic rocks [11]. Therefore, the Wadi Ranga felsic metatuffs are thought to be derived from the partial melting of the calc-alkaline, peraluminous basaltic melts by fractional crystallization.

5.1.2. Tectonic Setting and Evolution

The HFSE and HREE are conservative elements that can be used for discriminating the tectonic environments of volcanic rocks [65,88,89]. The studied MV rocks and their jasperoids are rich in LILEs relative to HFSEs (Figure 8b,c), reflecting a supra-subduction zone (SSZ) setting [90]. The LILE enrichment relative to the HFSE one is attributed to the addition of fluids and/or melts derived from the subducted slab to the lithospheric mantle [91–93]. The Wadi Ranga felsic metatuffs plot in the field of volcanic arc granites (VAGs) and syn-collisional granites (Syn-COIGs) are close to oceanic ridge granites on the Nb vs. Y diagram (Figure 10a; [94]).

This is evidence of the island arc tectonic setting proposed for the generation of the Wadi Ranga MV rocks and their jasperoids, where these arc-related granites are considered the plutonic equivalent of the island arc metavolcanics.

The Wadi Ranga felsic metatuffs show characteristics similar to the arc magmatic rocks based on Y vs. Sr/Y discrimination diagram (Figure 10b; [95]). They also plot within the island arc basalts by using the Hf/3–Th–Nb/16 triangular diagram (Figure 10c; [96]). The arc-related signature of MV samples is proved by falling within the volcanic arc tholeiites field (VAT) and close to the back arc basin in the Y/15–La/10–Nb/8 diagram (Figure 10d; [97]). Based on the Th/Yb versus Nb/Yb diagram (Figure 10e; [98]), the Ranga felsic metatuffs have been likely formed from an N-MORB-depleted mantle source and are similar to those found in volcanic arcs of the SSZ setting [90]. Similarly, all studied samples plot on the field of arc volcanics are based on the Nb versus Ba/Nb diagram (Figure 10f), with a tendency for subduction enrichment [94,99–101]. The REE and trace element-normalized patterns of the Wadi Ranga MV closely resemble those of the Shadli MV (Figure 8a,b) [6,45,74], suggesting that they were likely formed in the island arc tectonic setting (Figure 11).

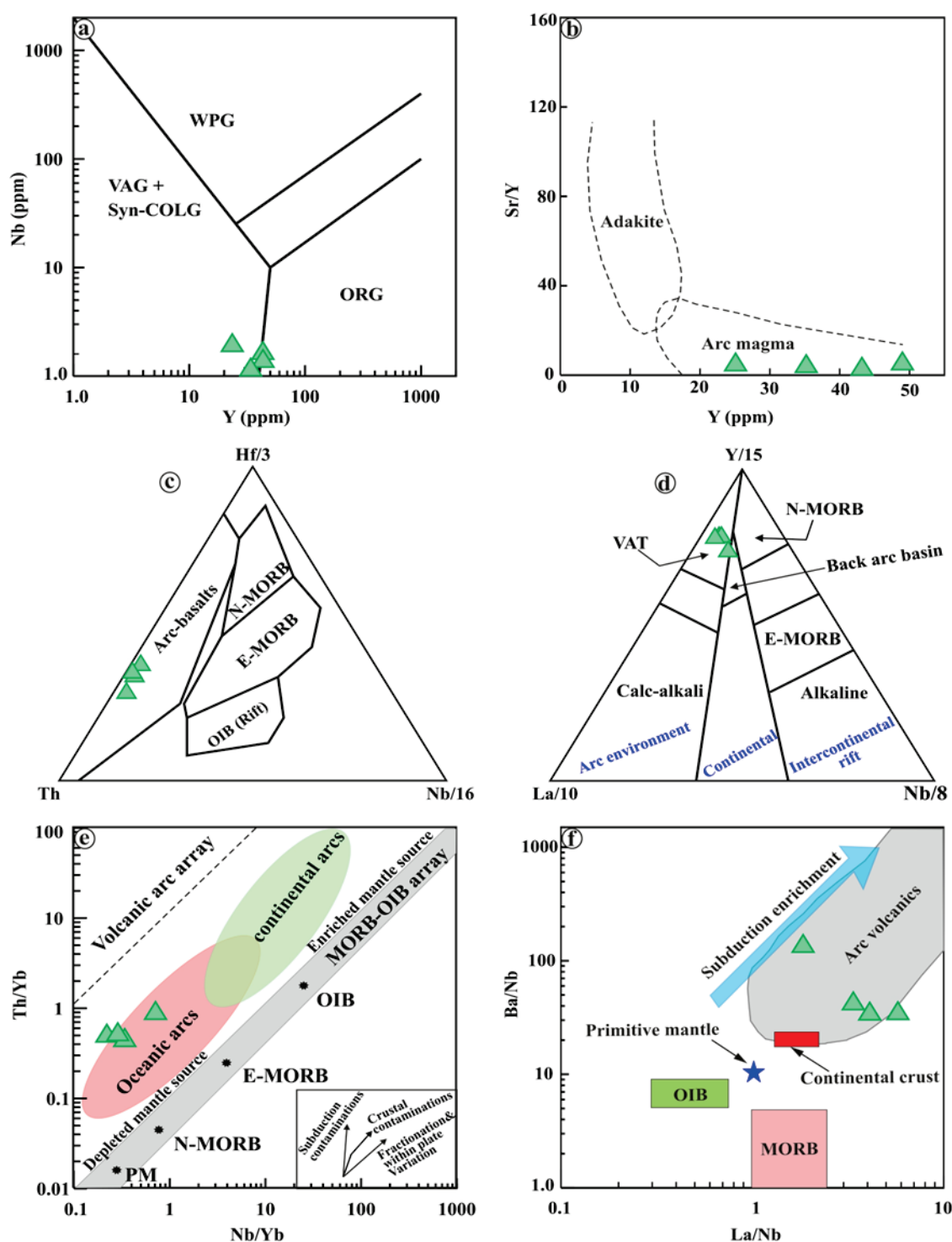


Figure 10. The tectomagmatic discrimination diagrams of Wadi Ranga metatuffs. (a) Y vs. Nb diagram [94]. (b) Y vs. Sr/Y discrimination diagram [95]. (c) Hf/3–Th–Nb/16 ternary diagram [96]. (d) Y/15–La/10–Nb/8 ternary diagram [97]. (e) Nb/Yb vs. Th/Yb [98]. (f) Nb vs. Ba/Nb; fields of MORB, OIB, continental crust, and arc volcanics are after Pearce et al. [94], Taylor and McLennan [99], Sun and McDonough [100], and Condie [101]. Abbreviations: Volcanic Arc Granites (VAGs), Syn-Collisional Granites (Syn-COLGs), Within-Plate Granites (WPGs), Orogenic Granites (ORGs), Ocean Island Basalt (OIB), Normal Mid-Ocean Ridge Basalts (N-MORBs), Enriched Mid-Ocean Ridge Basalts (E-MORBs), Primitive Mantle (PM), and Volcanic Arc Tholeiites (VATs).

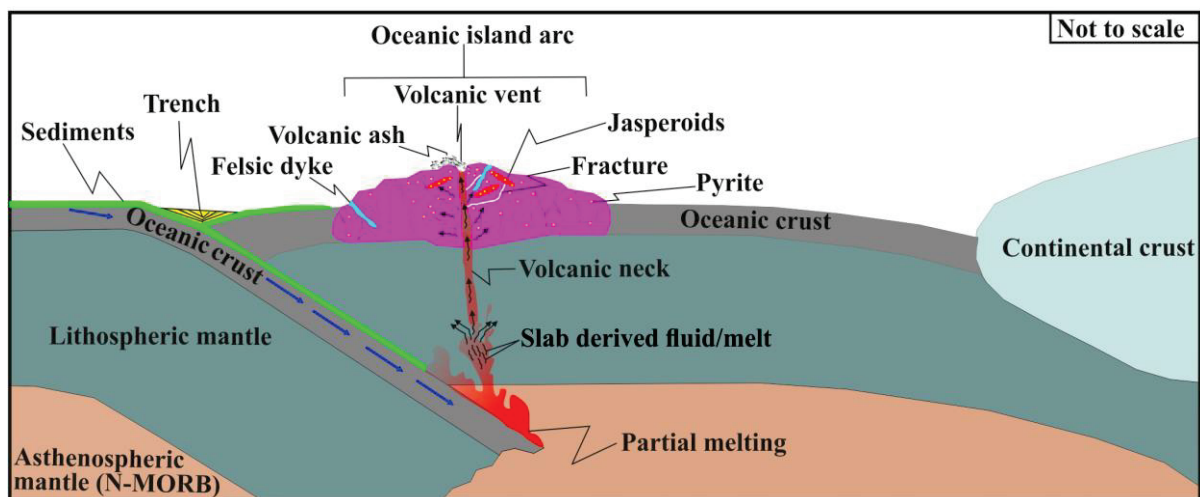


Figure 11. Simplified tectonic sketch and ore genetic model of the Wadi Ranga jasperoids-bearing metavolcanics in an island arc setting.

The sketch in Figure 11 summarizes the tectonic setting of the jasperoid lenses and their host metatuffs, where the subduction between two oceanic crusts produces an island arc volcano, such as the Shadli one. The volcanic vent of the Shadli volcano as a source of hydrothermal Si-rich fluids is surrounded by the felsic tuffs (later metamorphosed) as the host of the jasperoid lenses (Figure 11). Not only the volcanic vent but also the felsic dyke (Figure 2f) is the possible source of these fluids, where the felsic dyke is close to the shear zone and volcanic vent (Figure 11). Finally, the Ranga sulfidic jasperoids are hosted in Shadli metavolcanic rocks, which crystallized from peraluminous calc-alkaline magma.

5.2. Genesis of Jasperoid and Its Silica and Iron Sources

The sources of silica are various, but the most important sources are biogenic, detrital, and hydrothermal potential sources [102–104]. The remote sensing (Figure 3e,f), fieldwork (Figure 2g,h), textural (Figure 5), and geochemical characteristics (Figure 7b–e) suggest that the high silica (SiO_2 up to 93.4 wt.%; Table 4) and iron (Fe_2O_3 up to 6.63 wt.%; Table 4) required for the formation of the studied sulfidic jasperoids are likely magmatic-derived hydrothermal fluids, circulated from a nearby volcanic vent [105–107] (Figure 11) and granitic dykes. For example, the existence of lithic clasts (Figure 5f) in the examined jasperoids is due to the nearby volcanic vent in the study area. The fieldwork demonstrates that the Hamata granitoid that intrudes the studied MV on the western side of the study area (Figure 1b) may be another source of Si-rich hydrothermal fluids, causing the hydrothermal alteration of the Shadli metavolcanics. For example, the investigated metavolcanic-hosted jasperoids are mainly crosscut by the felsic dyke, mainly alkali-feldspar granite related to the Hamata granitoid (Figure 2f).

The remote sensing data delineated the jasperoid areas and the highly enriched quartz and hematite bands in the Wadi Ranga metavolcanics based on the wavelength characteristics of the desired minerals (see Section 4.1; Figure 3e,f). The studied MV rocks around jasperoid lenses and veins (Figure 2d,e) are highly sheared and deformed due to fractures or faults, besides the occurrence of felsic dykes (Figure 2f). These sheared and fractured MV rocks reflect the occurrence of the shear zone that acts as pathways for the hydrothermal fluids possibly derived from the volcanic vent [61]; this was confirmed by the dominant major NW–SE faults conjugated with the NE–SW trend and the subordinate E–W trend in the Ranga MV rocks (Figure 1b). The magmatic-derived hydrothermal fluids are mainly of the Si-rich-type, circulating within the hosted sulfide-bearing MV (Figure 4f), leading to the leaching of Si, Fe, and S from the hosted MV (Figure 11) as sources of sulfidic jasperoids in the shear zones [108–111] (Figures 2h and 5g), forming pyritization. The occurrence of a network of quartz veinlets within both jasperoids and their host rocks (Figures 4c–e and 5c,d)

supports that the Si-rich fluids are the main source of Si, while supergene fluids can leach Fe and S from the MV, forming silicification (Figure 11).

This explanation can elucidate the limited Fe content in the studied jasperoids (up to 6.63 wt.%; Table 4) relative to silica (up to 93.4 wt.%; Table 4). Additionally, the euhedral and compositionally homogeneous pyrites found in both jasperoids and their host felsic metatuffs (Table 3) suggest the same source and origin (Figures 4f and 5h,i). Therefore, pyrite is of magmatic origin and formed in the early stage before the epigenetic Si-rich hydrothermal fluids derived from the nearby volcanic vent ([17]; Figure 2g,h). Under oxidizing conditions, the hydrothermal fluids altered primary pyrite, leaching S and adding OH. This leads to extensive silicification and hematization, as testified by goethite and hematite pseudomorphs after pyrite (Figure 6a–f). So, we think that pyritization is considered a magmatic–hydrothermal stage, where pyrite is of magmatic origin in the host metavolcanics, but its accumulation of up to 10 vol.% is attributed to magmatic-derived hydrothermal fluids. The second stage is silicification and then hematization, and these two processes are considered post-magmatic stages. So, euhedral hematite and goethite pseudomorph crystals after cubic pyrite are dominant in the Ranga jasperoid (Figure 6b,c,e).

Moreover, the variation diagrams of SiO₂ contents (Figure 12a–c) in the Wadi Ranga jasperoids versus some representative mobile fluid elements (Rb, Th, Pb, Sr, Ba, and P) reflect that SiO₂ (up to 93 wt.% in jasperoids) and these mobile elements come from an external source compared to the Fe₂O₃ (up to 6.63 wt.% in jasperoids; Table 4) that resulted from the internal leaching of Fe from the surrounding Shadli metavolcanics (Fe₂O₃: 3.28–6.27 wt.% in the host rocks; Table 4). The red staining of the Wadi Ranga jasperoids may be attributed to the secondary formation of iron oxides resulting from the oxidation of Fe⁺² in pyrites to Fe⁺³, implying the red staining of the jasperoids in the form of hematite and goethite [12,108,112]. The increase in SiO₂ (up to 6.97 wt.%) and Al₂O₃ (up to 1.59 wt.%) in hematite and goethite (Table 2) may be ascribed to the latter substitutions during high-grade metamorphism [34]. The trace contents of both TiO₂ (up to 0.05 wt.%; Table 2) and MgO (up to 0.1 wt.%) in magnetite indicate its secondary origin at low-temperature conditions [113,114]. Magnetite is possibly formed after pyrite and then altered into hematite in two stages, hematite I and hematite II (Hm₁ and Hm₂; Figure 6e). These iron oxides are of secondary origin and are considered a post-magmatic stage. The occurrence of apatite in the host rocks and jasperoids (Figures 4e and 5l) reflects the possibility of apatite within the Si-rich sulfide ores, similar to that in the quartz–sulfide ores of Gaolong, China [115].

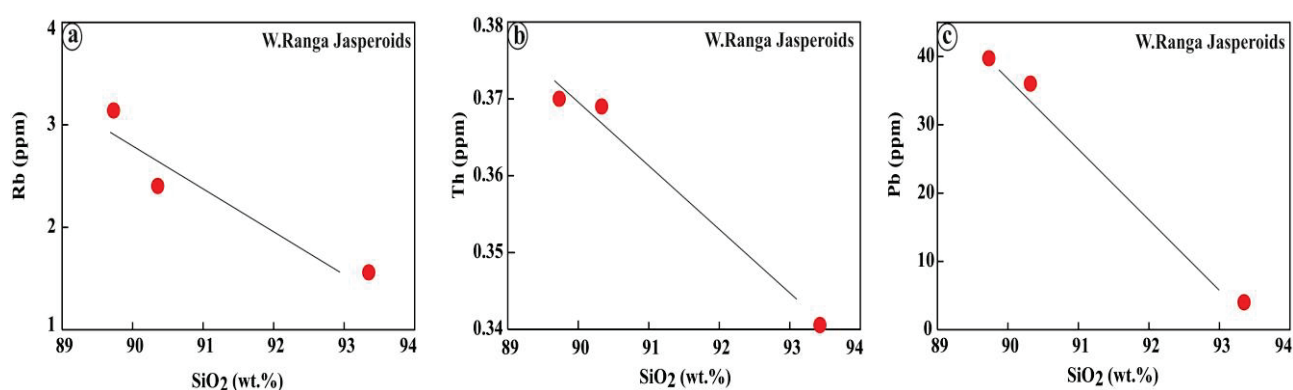


Figure 12. Variation diagrams of SiO₂ and Fe₂O₃ versus some fluid mobile elements for the Wadi Ranga jasperoids, South Eastern Desert, Egypt. (a) SiO₂ versus Rb. (b) SiO₂ versus Th. (c) SiO₂ versus Pb.

The Wadi Ranga jasperoids have geochemical characteristics that resemble sulfide-bearing jasperoids in the Pitcairn Islands. Both of them are rich in opaline silica (>35 wt. %) but are lower in Fe content (<10 wt.%) and base metals [116].

The Wadi Ranga jasperoids show enrichment in concentrations of typically mobile elements (like LILEs), such as Sr (up to 276.89 ppm), Ba (up to 232.27 ppm), Pb^{+2} (up to 54.7 ppm), and Rb (up to 13.78 ppm), in addition to Cu (up to 1333 ppm), Zr (up to 150 ppm), and Zn (up to 62.84 ppm) (Table 4 and Figure 8d), suggesting the role of hydrothermal sources. Moreover, the depletion of Al_2O_3 and TiO_2 (immobile Ti) and the enrichment of Fe_2O_3 (mobile Fe) (Table 4) supports the role of hydrothermal fluids in the formation of the Ranga jasperoids [103,117,118]. The higher values of $([Fe + Mn]/Ti = 39,742\text{--}3,557,323 \text{ ppm})$ for the investigated jasperoids accompanied with lower values of $(Al/[Al + Fe + Mn] = 211\text{--}585 \text{ ppm})$ are remarkable for the hydrothermal formation of jasperoids, in contrast with jasperoids after metalliferous sediments (clastic and biogenic materials) accumulated distally from the hydrothermal source [66,119–121]. The elemental ratios of Al, Fe, Mn, $(Ni + Cu + Co)$, Si, and Co/Zn (Figure 13) are used in the classification diagrams to distinguish between hydrothermal, hydrogenous, and diagenetic Si-rich deposits. Based on the ternary diagram Fe–Mn–Al [122,123], the studied jasperoids plot within the hydrothermal field (Figure 13a). Moreover, the relation between Fe, Mn, and some base metals $(Ni\text{--}Cu\text{--}Co)$ was used [124,125] to confirm the hydrothermal source of the studied jasperoids (Figure 13b). The relationship between Si and Al (Figure 13c) also supported the hydrothermal origin of the Ranga jasperoids and excluded the hydrogenous or diagenetic origin [126]. Additionally, the studied jasperoids fall within the hydrothermal field on the binary diagram of $(Cu + Co + Ni)$ vs. (Co/Zn) (Figure 13d; [121,122]). In addition, the Ranga jasperoid U-shaped REE patterns (Figure 8c) are similar to those of Tyrone jasper in Northern Ireland, which formed in a similar island arc tectonic setting and is hosted in calc-alkaline tuffaceous rocks (Tanderagee member); these chemical characteristics (U-shaped REE patterns) confirm the arc-like setting and metasomatism by the slab-derived fluids [61,127].

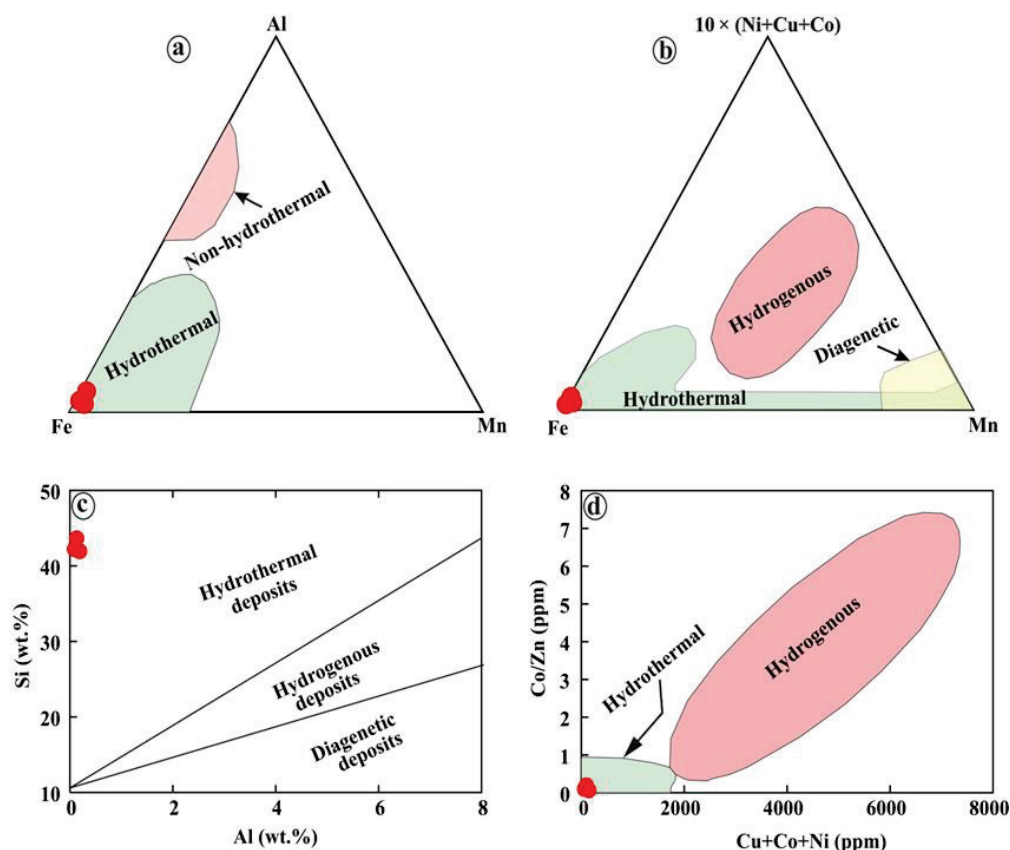


Figure 13. Discriminating diagrams of the Wadi Ranga jasperoid samples. (a) Fe–Mn–Al ternary diagram [122,123]. (b) Fe–Mn– $10 \times (Ni + Cu + Co)$ ternary diagram [124,125]. (c) Al vs. Si diagram [126]. (d) $(Cu + Co + Ni)$ vs. Co/Zn [124,125].

5.3. Why Are Jasperoids Limited to a Specific Region within the Shadli Metavolcanics?

It is well known that Shadli metavolcanics are dominant in the SED of Egypt, and some of them are highly mineralized with copper, gold, talc, BIFs, and Ni-Fe-Co-sulfide deposits [8–11,29,31–33,72,128–130]. Shadli metavolcanics are completely free of jasperoids in most parts; however, a few places around the volcanic vent include jasperoids (Figure 11). The occurrence of jasperoids close to the volcanic vent is related to the source of Si, S, and gases from volcanoes [22,23]. In addition, the felsic dyke, mainly alkali-feldspar granites (Figure 2f), intruded into jasperoid-bearing metavolcanics. This is another possible source of highly Si-rich fluids. The source of Fe may be an internal source from the host metavolcanics ($\text{Fe}_2\text{O}_3 \approx 3.53$; Table 4).

Structural features such as faults and shear zones represent localized regions of higher strain relative to the adjacent wall rocks [131]. They are characterized by intense deformation along specific planes; therefore, they often serve as pathways (Figure 11) for the migration and concentration of mineralizing fluids [132]. It is commonly accepted that shear zones play significant roles in the localization and evolution of hydrothermal flow on several scales. They control the transportation of magmatic, hydrothermal, and meteoric fluids during the mineralization process [131–133]. Shear zones or fractures enhance the permeability of rocks, thereby facilitating the transportation and precipitation of ore-forming fluids. This explains why the Ranga jasperoids are localized in the sheared and fractured MV rocks along the NW–SE, NE–SW, and E–W shear zones (Figure 1b) that acted as pathways for the circulation of the hydrothermal fluids from the volcanic vent and felsic dyke (Figure 2f). The distribution of jasperoid in a specific area of Shadli metavolcanics may have been influenced by the composition of the host metavolcanics, specifically the acidic type with high Si and Fe. The Ranga sulfidic jasperoids are hosted in Shadli metavolcanic rocks, which crystallized from the peraluminous calc-alkaline magma as a possible composition. These results may open the door for the future exploration of sulfide-rich jasperoids.

6. Conclusions

1. The Wadi Ranga jasperoids are hosted in Shadli metavolcanic rocks, which are mainly composed of rhyolitic and dacitic metatuffs.
2. The studied metavolcanics (e.g., felsic metatuffs) crystallized from fractionated peraluminous calc-alkaline melts that were derived from a depleted lithospheric mantle source (N–MORB) in the island arc setting. They are rich in LILEs relative to HFSEs with a low (Nb/La)_N ratio (<0.7), reflecting a high addition of fluids/melts from the subducted slab (oceanic crust) to the mantle-derived parent melts.
3. The Ranga jasperoids (SiO_2 : 89.73–90.35 wt.%; Fe_2O_3 : 2.73–6.63 wt.%) are considered the first documented Si–Fe-rich deposits hosted in the island arc metavolcanics. They are different from other jasperoids recorded in the Egyptian Nubian Shield as they are rich in pyrite (up to 10 vol.%), hematite, and goethite, with subordinate magnetite and Zn–Pb–Cu base metal sulfides. Their base metal content ($\text{Cu} + \text{Pb} + \text{Zn} = 58.32\text{--}240.68$ ppm) is generally lower than that of their host rocks ($\text{Cu} + \text{Pb} + \text{Zn} = 43.96\text{--}1498.43$ ppm).
4. The euhedral shape of pyrite associated with Wadi Ranga jasperoids reflects its magmatic origin and was accumulated by Si-rich fluids derived from the felsic dyke and volcanic vent. The low contents of iron within the studied jasperoids compared to silica reveal that the internal iron source (goethite and hematite) is a result of the secondary oxidation of the primary pyrite. So, massive pyritization occurred after the remobilization and accumulation of primary magmatic pyrite. Pyritization was followed by silicification and hematization, as suggested by hematite and goethite pseudomorphs.
5. The granitic dyke (felsic type) and volcanic vent likely represent the source of high silica in the Wadi Ranga jasperoids. The Si-rich hydrothermal fluids circulated along the NW–SE, NE–SW, and E–W major faults and shear zones in the Wadi Ranga

MV rocks, forming the Ranga hydrothermal jasperoid veins and lenses. This is also evidenced by the existence of lithic clasts within the host metatuffs of jasperoids and the dominant major NW–SE faults conjugated with NE–SW and E–W trends in the Ranga MV rocks.

6. The enrichment in mobile elements (Rb, Ba, Th, Pb^{+2} , Sr, P, Zn, Cu, and Mn) relative to the immobile elements (Ti, Nb, Zr, Hf, and Ta) alongside the relative abundance of Fe_2O_3 over Al_2O_3 and TiO_2 supported the magmatic-derived hydrothermal Si-rich fluids that formed jasperoids. These fluids are rich in mobile elements (Rb, Ba, Th, Pb^{+2} , Sr, Fe, P, Zn, Cu, and Mn) relative to immobile elements.
7. The Ranga jasperoids plot within the hydrothermal field supports their hydrothermal origin in the island arc setting and excludes the hydrogenous or diagenetic origin. This is confirmed by the jasperoid slightly U-shaped REE patterns, which are enriched in LILEs (e.g., K, Pb, and Sr) and depleted in HFSEs (e.g., Nb, Ta).

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14070647/s1>. Supplementary Figure S1. SEM images with EDS spectrum analyses of the dominant iron oxides, pyrite, and apatite in Wadi Ranga jasperoids. (a) Cubic pyrite. (b) Colloform goethite partially replaces cubic pyrite. (c) The first generation of hematite (Hm_1) at the rims of former cubic pyrite. (d) The second generation of the massive hematite (Hm_2). (e) Darker gray magnetite disperses within the former cubic pyrite and is intergrown with hematite (Hm_1). (f) Hexagonal apatite. Abbreviations: Pyrite (Py), Goethite (Gth), Hematite1 (Hm_1), Hematite2 (Hm_2), Magnetite (Mt), and Apatite (Ap).

Author Contributions: Conceptualization, M.Z.K.; data curation, M.Z.K. and M.A.S.; formal analysis, M.Z.K., M.K.A., Y.I. and E.T.; funding acquisition, A.Y.K. and K.A.; investigation, M.Z.K., M.K.A., Y.I. and E.T.; methodology, M.Z.K. and M.A.S.; project administration, M.Z.K., M.A.S., S.A. and A.M.M.; resources, A.Y.K. and K.A.; supervision, M.Z.K., S.A. and A.M.M.; validation and visualization, M.Z.K. and M.A.S.; writing—original draft preparation, M.Z.K. and M.A.S.; and writing—review and editing, M.Z.K., S.A. and A.M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Researchers Supporting Project number (RSPD2024R546) at King Saud University in Riyadh, Saudi Arabia.

Data Availability Statement: All data derived from this research are presented in the enclosed figures and tables and Supplementary Figure S1, which can be downloaded at: <https://www.mdpi.com/article/10.3390/min14070647/s1>.

Acknowledgments: The first author is grateful to all colleagues in the Geology Department at both Niigata and Chiba Universities, Japan, for their support during his stay in August 2022 and December 2023, to polish thin sections, take petrographical photos, EDS–SEM, and conduct mineral chemistry (EPMA). We are grateful to the anonymous reviewers for their careful reading of our manuscript and their many insightful comments. The authors extend their sincere appreciation to the Researchers Supporting Project number (RSPD2024R546) at King Saud University in Riyadh, Saudi Arabia.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Stern, R.J.; Kröner, A. Late Precambrian crustal evolution in NE Sudan: Isotopic and geochronologic constraints. *J. Geol.* **1993**, *101*, 555–574. [CrossRef]
2. Stern, R.J. Crustal evolution in the East African Orogen: A neodymium isotopic perspective. *J. Afr. Earth Sci.* **2002**, *34*, 109–117. [CrossRef]
3. Stern, R.; Ali, K.; Liégeois, J.-P.; Johnson, P.; Kozdroj, W.; Kattan, F. Distribution and significance of pre-Neoproterozoic zircons in juvenile Neoproterozoic igneous rocks of the Arabian–Nubian Shield. *Am. J. Sci.* **2010**, *310*, 791–811. [CrossRef]
4. Johnson, P.; Andresen, A.; Collins, A.; Fowler, A.; Fritz, H.; Ghebreab, W.; Kusky, T.; Stern, R. Late Cryogenian–Ediacaran history of the Arabian–Nubian Shield: A review of depositional, plutonic, structural, and tectonic events in the closing stages of the northern East African Orogen. *J. Afr. Earth Sci.* **2011**, *61*, 167–232. [CrossRef]
5. Meredith, A.S.; Williams, S.E.; Müller, R.D.; Collins, A.S. Kinematic constraints on the Rodinia to Gondwana transition. *Precambrian Res.* **2017**, *299*, 132–150. [CrossRef]

6. Stern, R.J.; Kröner, A.; Rashwan, A.A. A late Precambrian (~710 Ma) high volcanicity rift in the southern Eastern Desert of Egypt. *Geol. Rundsch.* **1991**, *80*, 155–170. [CrossRef]
7. Shukri, N.; Mansour, M.S. Lithostratigraphy of Um Samuiki District, Eastern Desert, Egypt. *Evol. Miner. Arab. Nubian Shield* **1980**, *4*, 83–93.
8. Johnson, P.; Zoheir, B.; Ghebreab, W.; Stern, R.; Barrie, C.; Hamer, R. Gold-bearing volcanogenic massive sulfides and orogenic-gold deposits in the Nubian Shield. *South Afr. J. Geol.* **2017**, *120*, 63–76. [CrossRef]
9. Faisal, M.; Yang, X.; Khalifa, I.H.; Amuda, A.K.; Sun, C. Geochronology and geochemistry of Neoproterozoic Hamamid metavolcanics hosting largest volcanogenic massive sulfide deposits in Eastern Desert of Egypt: Implications for petrogenesis and tectonic evolution. *Precambrian Res.* **2020**, *344*, 105751. [CrossRef]
10. Abdel-Karim, A.-A.M.; El-Awady, A.; Khedr, M.Z.; El-Afandy, A.H.; Elwan, W.; Tamura, A.; Ali, S. Genesis of sulfide mineralization, Atshan and Darhib Areas, South Eastern Desert of Egypt: Evidence of fluid pathway effects along shear zones. *Arab. J. Sci. Eng.* **2022**, *47*, 641–665. [CrossRef]
11. Khedr, M.Z.; Kamh, S.; Al Desouky, A.A.; Takazawa, E.; Hauzenberger, C.; Whattam, S.A.; El-Awady, A. Remote sensing and geochemical investigations of sulfide-bearing metavolcanic and gabbroic rocks (Egypt): Constraints on host-rock petrogenesis and sulfide genesis. *Gondwana Res.* **2023**, *119*, 282–312. [CrossRef]
12. Cline, J.S.; Hofstra, A.H.; Muntean, J.L.; Tosdal, R.M.; Hickey, K.A. *Carlin-Type Gold Deposits in Nevada: Critical Geologic Characteristics and Viable Models*. Economic Geology 2005, 100th Anniversary Volume. Available online: <https://pubs.geoscienceworld.org/segweb/books/edited-volume/1940/chapter-abstract/107715257/Carlin-Type-Gold-Deposits-in-NevadaCritical?redirectedFrom=fulltext> (accessed on 21 January 2024).
13. Kimberley, M.M. Geochemical distinctions among environmental types of iron formations. *Chem. Geol.* **1979**, *25*, 185–212. [CrossRef]
14. Kimberley, M.M. Exhalative origins of iron formations. *Ore Geol. Rev.* **1989**, *5*, 13–145. [CrossRef]
15. Fyon, J.; Breaks, F.; Heather, K.; Jackson, S.; Muir, T.; Stott, G.; Thurston, P.; Williams, H.; Sutcliffe, R. Metallogeny of metallic mineral deposits in the Superior Province of Ontario. *Geology of Ontario*. Edited by PC Thurston, HR Williams, RH Sutcliffe, and GM Stott. *Ont. Geol. Surv. Spec.* **1992**, *4*, 1091–1176.
16. Simonson, B.M. Sedimentological constraints on the origins of Precambrian iron-formations. *Geol. Soc. Am. Bull.* **1985**, *96*, 244–252. [CrossRef]
17. Phillips, G.; Groves, D.; Martyn, J. An epigenetic origin for Archean banded iron-formation-hosted gold deposits. *Econ. Geol.* **1984**, *79*, 162–171. [CrossRef]
18. James, H.L. Sedimentary facies of iron-formation. *Econ. Geol.* **1954**, *49*, 235–293. [CrossRef]
19. Fripp, R. Stratabound gold deposits in Archean banded iron-formation, Rhodesia. *Econ. Geol.* **1976**, *71*, 58–75. [CrossRef]
20. Dimroth, E.; Chauvel, J.-J. Petrography of the Sokoman iron formation in part of the central Labrador trough, Quebec, Canada. *Geol. Soc. Am. Bull.* **1973**, *84*, 111–134. [CrossRef]
21. Dimroth, E. Depositional environments and tectonic settings of the cherty iron-formations of the Canadian Shield. *Geol. Soc. India* **1986**, *28*, 239–250.
22. Gross, G.A. A classification of iron formations based on depositional environments. *Can. Mineral.* **1980**, *18*, 215–222.
23. Lydon, J.W. Ore deposit Models-8. Volcanogenic massive sulphide deposits Part I: A descriptive model. *Geoscience Canada* **1984**, *11*, 1–8.
24. Kimberley, M.M. Debate about ironstone: Has solute supply been surficial weathering, hydrothermal convection, or exhalation of deep fluids? *Terra Nova* **1994**, *6*, 116–132. [CrossRef]
25. Slack, J.; Grenne, T.; Bekker, A.; Rouxel, O.; Lindberg, P. Suboxic deep seawater in the late Paleoproterozoic: Evidence from hematitic chert and iron formation related to seafloor-hydrothermal sulfide deposits, central Arizona, USA. *Earth Planet. Sci. Lett.* **2007**, *255*, 243–256. [CrossRef]
26. Bekker, A.; Slack, J.F.; Planavsky, N.; Krapez, B.; Hofmann, A.; Konhauser, K.O.; Rouxel, O.J. Iron formation: The sedimentary product of a complex interplay among mantle, tectonic, oceanic, and biospheric processes. *Econ. Geol.* **2010**, *105*, 467–508. [CrossRef]
27. Grenne, T.; Slack, J.F. Mineralogy and geochemistry of silicate, sulfide, and oxide iron formations in Norway: Evidence for fluctuating redox states of early Paleozoic marine basins. *Miner. Depos.* **2019**, *54*, 829–848. [CrossRef]
28. German, C.; Von Damm, K. Hydrothermal processes. In *The Oceans and Marine Geochemistry*; Elderfield, H., Ed.; Elsevier: Amsterdam, The Netherlands, 2003; Treatise on Geochemistry 6; pp. 181–222.
29. El Habaak, G.H. Geology of Banded Iron Formation and Associated Metavolcanics at Wadi Kareim Area, Eastern Desert, Egypt. Ph.D. Thesis, Faculty of Science, Assiut University, Assiut, Egypt, 1992.
30. El Habaak, G.H.; Mahmoud, M.S. Carbonaceous bodies of debatable organic provenance in the Banded Iron Formation of the Wadi Kareim area, Eastern Desert, Egypt. *J. Afr. Earth Sci.* **1994**, *19*, 125–133. [CrossRef]
31. El Habaak, G.H.; Soliman, M. Rare earth element geochemistry of the Egyptian banded iron formations and the evolution of the Precambrian atmosphere and ocean. In *Proceedings of the 4th International Conference on Geochemistry*, Alexandria, Egypt, 1999; pp. 149–160.
32. El Habaak, G.H. Pan-African skarn deposits related to banded iron formation, Um Nar area, central Eastern Desert, Egypt. *J. Afr. Earth Sci.* **2004**, *38*, 199–221. [CrossRef]

33. Khudeir, A.; Ali, M.; El Habaak, G. The metavolcanics at Um Samiuki area, Egypt. *Bull. Fac. Sci. Assiut. Univ.* **1988**, *17*, 73–101.
34. El Habaak, G.H. Ferruginous jasper and chert deposits associated with island-arc metavolcanics, Eastern Desert, Egypt. *Acad. J. Sci.* **2012**, *1*, 347–381.
35. Aly, S.; Salem, I. Mineralogy and Chemistry of Jasper from Um Ghamis and El-Dabbah Metamorphic Iron Deposits, Central Eastern Desert, Egypt. *Ann. Geol. Surv. Egypt* **1985**, *15*, 223–232.
36. Stern, R.J. Arc-assembly and continental collision in the Neoproterozoic African orogen: Implications for the consolidation of Gondwanaland. *Annu. Rev. Earth Planet. Sci.* **1994**, *22*, 319–351. [CrossRef]
37. Khedr, M.Z.; Khashaba, S.M.A.; El-Shibiny, N.; Takazawa, E.; Hassan, S.M.; Azer, M.K.; Whattam, S.A.; El-Arafy, R.A.; Ichiyama, Y. Integration of remote sensing and geochemical data to characterize mineralized A-type granites, Egypt: Implications for origin and concentration of rare metals. *Int. J. Earth Sci.* **2023**, *112*, 1717–1745. [CrossRef]
38. Hamimi, Z.; Abd El-Wahed, M.A. Suture (s) and major shear zones in the Neoproterozoic basement of Egypt. In *The Geology of Egypt Book*; Springer: Berlin/Heidelberg, Germany, 2020; pp. 153–189.
39. Heikal, M.T.S.; Khedr, M.Z.; Abd El Monsef, M.; Gomaa, S.R. Petrogenesis and geodynamic evolution of neoproterozoic Abu Dabbab albite granite, central Eastern Desert of Egypt: Petrological and geochemical constraints. *J. Afr. Earth Sci.* **2019**, *158*, 103518. [CrossRef]
40. Abdel-Khalek, M.; Takla, M.; Sehim, A.; Hamimi, Z.; El Manawi, A. Geology and tectonic evolution of Wadi Beitan area, southeastern Desert, Egypt. In Proceedings of the International Conference on Geology of the Arab World, Cairo, Egypt, 27–30 September 1992; pp. 369–394.
41. Abdelsalam, M.G.; Abdeen, M.M.; Dowaidar, H.M.; Stern, R.J.; Abdelghaffar, A.A. Structural evolution of the Neoproterozoic western Allaqi–Heiani suture, southeastern Egypt. *Precambrian Res.* **2003**, *124*, 87–104. [CrossRef]
42. Hagag, W.; Moustafa, R.; Hamimi, Z. Neoproterozoic Evolution and Najd-Related Transpressive Shear Deformations Along Nugrus Shear Zone, South Eastern Desert, Egypt (Implications from Field-Structural Data and AMS-Technique). *Geotectonics* **2018**, *52*, 114–133. [CrossRef]
43. Hamimi, Z.; El-Fakharani, A.; Emam, A.; Barreiro, J.G.; Abdelrahman, E.; Abo-Soliman, M.Y. Reappraisal of the kinematic history of Nugrus shear zone using PALSAR and microstructural data: Implications for the tectonic evolution of the Eastern Desert tectonic terrane, northern Nubian Shield. *Arab. J. Geosci.* **2018**, *11*, 1–29. [CrossRef]
44. Hussein, A.A.A.; Ali, M.M.; El Ramly, M. A proposed new classification of the granites of Egypt. *J. Volcanol. Geotherm. Res.* **1982**, *14*, 187–198. [CrossRef]
45. Maurice, A.E.; Basta, F.F.; Khiamy, A.A. Neoproterozoic nascent island arc volcanism from the Nubian Shield of Egypt: Magma genesis and generation of continental crust in intra-oceanic arcs. *Lithos* **2012**, *132*, 1–20. [CrossRef]
46. Gharib, M.E.; Ahmed, A.H. Late Neoproterozoic volcanics and associated granitoids at Wadi Ranga, south Eastern Desert, Egypt: A transition from subduction-related to intra-arc magmatism. *Lithos* **2012**, *155*, 236–255. [CrossRef]
47. Conoco. *Geological Maps of Egypt*, NF 36 NE Bernice, Egypt, Scale 1: 500,000. 1987. Conoco Coral; Institut für Angewandte Geodäsie: Berlin, Germany, 1987.
48. Conoco. *Geological Maps of Egypt*, NG 36 SE Gebel Hamata, Egypt, Scale 1: 500,000. 1987. Conoco Coral; Institut für Angewandte Geodäsie: Berlin, Germany, 1987.
49. EGSMa. *Geologic Map of Berence Quadrangle, Egypt*, Scale 1:250,000; The Egyptian Geologic Survey and Mining Authority (EGSMa): Cairo, Egypt, 1997.
50. EGSMa. *Geologic Map of Hamata Quadrangle, Egypt*, Scale 1:250,000; The Egyptian Geologic Survey and Mining Authority (EGSMa): Cairo, Egypt, 1997.
51. Abrams, M.; Hook, S.; Ramachandran, B. *ASTER User Handbook, Version 2: Advanced Spaceborne Thermal Emission and Reflection Radiometer*; Jet Propulsion Laboratory: Pasadena, CA, USA, 2002. Available online: https://lpdaac.usgs.gov/documents/262/ASTER_User_Handbook_v2.pdf (accessed on 21 January 2024).
52. NASA/METI/AIST. ASTER Level 1B Data Set Registered Radiance at the Sensor, NASA EOSDIS Land Processes Distributed Active Archive Center (LP DAAC), Japan Space Systems & U.S./Japan ASTER Science Team, 2001. Available online: https://lpdaac.usgs.gov/products/ast_l1bv003 (accessed on 21 January 2024).
53. U.S. Geological Survey Distribution of European Space Agency’s Landsat-8 OLI data; Path = 173 and Row = 43, Collection Number 1, US. 2013. Available online: <https://earthexplorer.usgs.gov/> (accessed on 21 January 2024).
54. Sabins, F.F. Remote sensing for mineral exploration. *Ore Geol. Rev.* **1999**, *14*, 157–183. [CrossRef]
55. Di Tommaso, I.; Rubinstein, N. Hydrothermal alteration mapping using ASTER data in the Infiernillo porphyry deposit, Argentina. *Ore Geol. Rev.* **2007**, *32*, 275–290. [CrossRef]
56. Rockwell, B.W.; Hofstra, A.H. Identification of quartz and carbonate minerals across northern Nevada using ASTER thermal infrared emissivity data—Implications for geologic mapping and mineral resource investigations in well-studied and frontier areas. *Geosphere* **2008**, *4*, 218–246. [CrossRef]
57. Amin, B.P.; Mazlan, H. Spectral transformation of ASTER data and the discrimination of hydrothermal alteration minerals in a semi-arid region, SE Iran. *Int. J. Phys. Sci.* **2011**, *6*, 2037–2059.
58. Sabins, F.F. *Remote Sensing. Principles and Interpretation*; W. H. Freeman and Company: New York, NY, USA, 1997; pp. 366–371.
59. Harsanyi, J.C. *Detection and Classification of Subpixel Spectral Signatures in Hyperspectral Image Sequences*; University of Maryland: Baltimore County, MD, USA, 1993.

60. Rowan, L.C.; Hook, S.J.; Abrams, M.J.; Mars, J.C.J.E.G. Mapping hydrothermally altered rocks at Cuprite, Nevada, using the Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER), a new satellite-imaging system. *Econ. Geol.* **2003**, *98*, 1019–1027. [CrossRef]
61. Hollis, S.P.; Cooper, M.R.; Herrington, R.J.; Roberts, S.; Earls, G.; Verbeeten, A.; Piercey, S.J.; Archibald, S.M. Distribution, mineralogy and geochemistry of silica-iron exhalites and related rocks from the Tyrone Igneous Complex: Implications for VMS mineralization in Northern Ireland. *J. Geochem. Explor.* **2015**, *159*, 148–168. [CrossRef]
62. Droop, G. A general equation for estimating Fe³⁺ concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. *Mineral. Mag.* **1987**, *51*, 431–435. [CrossRef]
63. Taman, Z. Mineralogical and Geochemical Studies on Some Banded Iron Formations from the Eastern Desert of Egypt, and Their Industrial Uses. Ph.D. Thesis, Ain Shams University, Cairo, Egypt, 2005; p. 166.
64. Piccoli, P.M.; Candela, P.A. Apatite in igneous systems. Reviews in Mineralogy and Geochemistry. *Rev. Mineral. Geochem.* **2002**, *48*, 255–292. [CrossRef]
65. Winchester, J.A.; Floyd, P.A. Geochemical discrimination of different magma series and their differentiation products using immobile elements. *Chem. Geol.* **1977**, *20*, 325–343. [CrossRef]
66. Brusnitsyn, A.; Zhukov, I. Manganese deposits of the Devonian Magnitogorsk palaeovolcanic belt (Southern Urals, Russia). *Ore Geol. Rev.* **2012**, *47*, 42–58. [CrossRef]
67. Maslennikov, V.V.; Ayupova, N.; Herrington, R.; Danyushevskiy, L.; Large, R. Ferruginous and manganiferous haloes around massive sulphide deposits of the Urals. *Ore Geol. Rev.* **2012**, *47*, 5–41. [CrossRef]
68. Moghazi, A. Geochemistry and petrogenesis of a high-K calc-alkaline Dokhan Volcanic suite, South Safaga area, Egypt: The role of late Neoproterozoic crustal extension. *Precambrian Res.* **2003**, *125*, 161–178. [CrossRef]
69. Eliwa, H.; Kimura, J.-I.; Itaya, T. Late Neoproterozoic Dokhan Volcanics, North Eastern Desert, Egypt: Geochemistry and petrogenesis. *Precambrian Res.* **2006**, *151*, 31–52. [CrossRef]
70. Abdel Wahed, A.A.; Ali, K.G.; Khalil, M.M.; Abdel Gawad, A.E. Dokhan volcanics of Gabal Monqul area, North Eastern Desert, Egypt: Geochemistry and petrogenesis. *Arab. J. Geosci.* **2012**, *5*, 29–44. [CrossRef]
71. Dessouky, O.K.; Cai, M.; Ali, H.H.; Dardier, A.M.; Fowler, A.-R.; Ali, K.A.; Santosh, M.; Stüwe, K.; Hassan, M.M. A newly recorded Cryogenian-Ediacaran Dokhan Volcanic caldera with resurgent uplift in the Arabian-Nubian Shield, southwest Safaga, Egypt. *Precambrian Res.* **2023**, *387*, 106993. [CrossRef]
72. Stern, R.J. Petrogenesis and tectonic setting of Late Precambrian ensimatic volcanic rocks, Central Eastern Desert of Egypt. *Precambrian Res.* **1981**, *16*, 195–230. [CrossRef]
73. Abd El-Rahman, Y.; Polat, A.; Dilek, Y.; Fryer, B.J.; El-Sharkawy, M.; Sakran, S. Geochemistry and tectonic evolution of the Neoproterozoic incipient arc–forearc crust in the Fawakhir area, Central Eastern Desert of Egypt. *Precambrian Res.* **2009**, *175*, 116–134. [CrossRef]
74. Abdelkareem, M. Massive Sulfide Deposit, and Associated Metavolcanics, Um Samuiki Area, South Eastern Desert, Egypt. Master’s Thesis, South Valley University, Qena, Egypt, 2008.
75. McDonough, W.F.; Sun, S.-S. The composition of the Earth. *Chem. Geol.* **1995**, *120*, 223–253. [CrossRef]
76. Rudnick, R.; Gao, S. Composition of the Continental Crust. *Treatise Geochem.* **2014**, *4*, 1–51. [CrossRef]
77. Polat, A.; Hofmann, A. Alteration and geochemical patterns in the 3.7–3.8 Ga Isua greenstone belt, West Greenland. *Precambrian Res.* **2003**, *126*, 197–218. [CrossRef]
78. Irvine, T.N.; Baragar, W. A guide to the chemical classification of the common volcanic rocks. *Can. J. Earth Sci.* **1971**, *8*, 523–548. [CrossRef]
79. Hastie, A.R.; Kerr, A.C.; Pearce, J.A.; Mitchell, S. Classification of altered volcanic island arc rocks using immobile trace elements: Development of the Th–Co discrimination diagram. *J. Petrol.* **2007**, *48*, 2341–2357. [CrossRef]
80. Maniar, P.D.; Piccoli, P.M. Tectonic discrimination of granitoids. *Geological society of America bulletin* **1989**, *101*, 635–643. [CrossRef]
81. Frost, B.R.; Barnes, C.G.; Collins, W.J.; Arculus, R.J.; Ellis, D.J.; Frost, C.D. A geochemical classification for granitic rocks. *J. Petrol.* **2001**, *42*, 2033–2048. [CrossRef]
82. Smith, E.I.; Sanchez, A.; Walker, J.D.; Wang, K. Geochemistry of mafic magmas in the Hurricane Volcanic field, Utah: Implications for small-and large-scale chemical variability of the lithospheric mantle. *J. Geol.* **1999**, *107*, 433–448. [CrossRef]
83. Zhao, Z. *Principles of Trace Element Geochemistry*; Science Press: Beijing, China, 1997; pp. 1–495.
84. Wilson, M. *Igneous Petrogenesis: A Global Tectonic Approach*; Unwin Hyman: London, UK, 1989; pp. 1–466.
85. Rudnick, R.L.; Fountain, D.M. Nature and composition of the continental crust: A lower crustal perspective. *Rev. Geophys.* **1995**, *33*, 267–309. [CrossRef]
86. Atherton, M.; Ghani, A. Slab breakoff: A model for Caledonian, Late Granite syn-collisional magmatism in the orthotectonic (metamorphic) zone of Scotland and Donegal, Ireland. *Lithos* **2002**, *62*, 65–85. [CrossRef]
87. Kamber, B.S.; Ewart, A.; Collerson, K.D.; Bruce, M.C.; McDonald, G.D. Fluid-mobile trace element constraints on the role of slab melting and implications for Archaean crustal growth models. *Contrib. Mineral. Petrol.* **2002**, *144*, 38–56. [CrossRef]
88. Pearce, J.A. Geochemical fingerprinting of oceanic basalts with applications to ophiolite classification and the search for Archean oceanic crust. *Lithos* **2008**, *100*, 14–48. [CrossRef]
89. Pearce, J.A.; Peate, D.W. Tectonic implications of the composition of volcanic arc magmas. *Annu. Rev. Earth Planet. Sci.* **1995**, *23*, 251–285. [CrossRef]

90. Pearce, J.A.; Lippard, S.; Roberts, S. Characteristics and tectonic significance of supra-subduction zone ophiolites. *Geol. Soc. Lond. Spec. Publ.* **1984**, *16*, 77–94. [CrossRef]
91. Best, M. Amphibole-bearing cumulate inclusions, Grand Canyon, Arizona and their bearing on silica-undersaturated hydrous magmas in the upper mantle. *J. Petrol.* **1975**, *16*, 212–236. [CrossRef]
92. Hawkesworth, C.; O’Nions, R.; Pankhurst, R.; Hamilton, P.; Evensen, N. A geochemical study of island-arc and back-arc tholeiites from the Scotia Sea. *Earth Planet. Sci. Lett.* **1977**, *36*, 253–262. [CrossRef]
93. Tarney, J.; Wood, D.; Saunders, A.; Cann, J.; Varet, J. Nature of mantle heterogeneity in the North Atlantic: Evidence from deep sea drilling. *Philosophical Transactions of the Royal Society of London. Ser. A Math. Phys. Sci.* **1980**, *297*, 179–202.
94. Pearce, J.A.; Harris, N.B.; Tindle, A.G. Trace element discrimination diagrams for the tectonic interpretation of granitic rocks. *J. Petrol.* **1984**, *25*, 956–983. [CrossRef]
95. Hou, Z.-Q.; Gao, Y.-F.; Qu, X.-M.; Rui, Z.-Y.; Mo, X.-X. Origin of adakitic intrusives generated during mid-Miocene east–west extension in southern Tibet. *Earth Planet. Sci. Lett.* **2004**, *220*, 139–155. [CrossRef]
96. Wood, D.A. The application of a ThHfTa diagram to problems of tectonomagmatic classification and to establishing the nature of crustal contamination of basaltic lavas of the British Tertiary Volcanic Province. *Earth Planet. Sci. Lett.* **1980**, *50*, 11–30. [CrossRef]
97. Cabanis, B. The La/10-Y/15-Nb/8 diagram-A tool for discriminating volcanic series and evidencing continental-crust magmatic mixtures and/or contamination. *Comptes Rendus L’Académie Sci.* **1989**, *309*, 2023–2029.
98. Pearce, J.A. Immobile element fingerprinting of ophiolites. *Elements* **2014**, *10*, 101–108. [CrossRef]
99. Taylor, S.R.; McLennan, S.M. *The Continental Crust: Its Composition and Evolution*; Blackwell Scientific Publications: Oxford, MA, USA, 1985; pp. 1–349.
100. Sun, S.-S.; McDonough, W.F. Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes. *Geol. Soc. Lond. Spec. Publ.* **1989**, *42*, 313–345. [CrossRef]
101. Condie, K.C. Chemical composition and evolution of the upper continental crust: Contrasting results from surface samples and shales. *Chem. Geol.* **1993**, *104*, 1–37. [CrossRef]
102. Sugisaki, R.; Yamamoto, K.; Adachi, M. Triassic bedded cherts in central Japan are not pelagic. *Nature* **1982**, *298*, 644–647. [CrossRef]
103. Adachi, M.; Yamamoto, K.; Sugisaki, R. Hydrothermal chert and associated siliceous rocks from the northern Pacific their geological significance as indication of ocean ridge activity. *Sediment. Geol.* **1986**, *47*, 125–148. [CrossRef]
104. Yamamoto, S. Correlation between iron and magnesium and its significance on the distribution of heavy metals in deep-sea cherts. *Sediment. Geol.* **1986**, *49*, 261–280. [CrossRef]
105. Grenne, T.; Slack, J.F. Geochemistry of jasper beds from the Ordovician Løkken ophiolite, Norway: Origin of proximal and distal siliceous exhalites. *Econ. Geol.* **2005**, *100*, 1511–1527. [CrossRef]
106. Grenne, T.; Slack, J.F. Paleozoic and Mesozoic silica-rich seawater: Evidence from hematitic chert (jasper) deposits. *Geology* **2003**, *31*, 319–322. [CrossRef]
107. Davidson, G.J.; Stolz, A.; Eggins, S. Geochemical anatomy of silica iron exhalites: Evidence for hydrothermal oxyanion cycling in response to vent fluid redox and thermal evolution (Mt. Windsor Subprovince, Australia). *Econ. Geol.* **2001**, *96*, 1201–1226. [CrossRef]
108. Lovering, T.G. *Jasperoid in the United States; Its Characteristics, Origin, and economic Significance*; U.S. Geological Survey Professional Paper; USGS: Washington, DC, USA, 1972; pp. 1–176. [CrossRef]
109. Binns, R.; Barriga, F.; Miller, D. Leg 193 synthesis: Anatomy of an active felsic-hosted hydrothermal system, eastern Manus Basin, Papua New Guinea. In *Ocean Drilling Program, Scientific Results*; ODP: College Station, TX, USA, 2007.
110. Binns, R. Data report: Petrography and geochemistry of jasperoids from Site 1189. In *Ocean Drilling Program, Scientific Results*; ODP: College Station, TX, USA, 2006.
111. Saitoh, M.; Shibuya, T.; Saito, T.; Torimoto, J.; Ueda, H.; Sato, T.; Suzuki, K. Experimental Hydrothermal Alteration of Rhyolite and Andesite at 325 °C and 300 Bar: Implications for a Potential Role of Volcanic Glass in the Fluid Composition in the Okinawa Trough. *Minerals* **2024**, *14*, 259. [CrossRef]
112. Cline, J.S.; Hofstra, A.A. Ore-fluid evolution at the Getchell Carlin-type gold deposit, Nevada, USA. *Eur. J. Mineral.* **2000**, *12*, 195–212. [CrossRef]
113. Buddington, A.F.; Lindsley, D. Iron-titanium oxide minerals and synthetic equivalents. *J. Petrol.* **1964**, *5*, 310–357. [CrossRef]
114. Khedr, M.Z.; Arai, S. Composite origin of magnetite deposits hosted in Oman peridotites: Evidence for iron mobility during serpentinization. *Ore Geol. Rev.* **2018**, *101*, 180–198. [CrossRef]
115. Lin, S.; Hu, K.; Cao, J.; Liu, Y.; Liu, S.; Zhang, B. Geochemistry and origin of hydrothermal apatite in Carlin-type Au ore deposits, southwestern China (Gaolong deposit). *Ore Geol. Rev.* **2023**, *154*, 105312. [CrossRef]
116. Hekinian, R.; Hoffert, M.; Larque, P.; Cheminee, J.-L.; Stoffers, P.; Bideau, D. Hydrothermal Fe and Si oxyhydroxide deposits from South Pacific intraplate volcanoes and East Pacific Rise axial and off-axial regions. *Econ. Geol.* **1993**, *88*, 2099. [CrossRef]
117. Yongzhang, Z.; Guangchi, T.; Chown, E.H.; Guha, J.; Huanzhang, L. Petrologic and geochemical characteristics and origin of Gusui cherts, Guangdong Province, China. *Chin. J. Geochem.* **1994**, *13*, 118–131. [CrossRef]
118. Jim, P.; Haisheng, Y.; Wenjie, X. Geochemical Indication of Sinian Bedded Siliceous Rocks in the Hunan-Guizhou-Guangxi Area and Their Environmental Significance. *Acta Geol. Sin. -Engl. Ed.* **2000**, *74*, 46–53. [CrossRef]

119. Boström, K.; Kraemer, T.; Gartner, S. Provenance and accumulation rates of opaline silica, Al, Ti, Fe, Mn, Cu, Ni and Co in Pacific pelagic sediments. *Chem. Geol.* **1973**, *11*, 123–148. [CrossRef]
120. Brusnitsyn, A.; Zhukov, I. Geochemistry and formation model of manganese rocks in jaspers of the South Urals. *Lithol. Miner. Resour.* **2018**, *53*, 14–35. [CrossRef]
121. Cronan, D.S. Metallogenesis at oceanic spreading centres. *J. Geol. Soc.* **1979**, *136*, 621–626. [CrossRef]
122. Yamamoto, K. Geochemical study of Triassic bedded cherts from Kamiasso, Gifu Prefecture. *J. Geol. Soc. Jpn* **1983**, *89*, 143–162. [CrossRef]
123. Sugisaki, R. Major element chemistry of the sediments on the central Pacific transect, Wake to Tahiti, GH80-1 cruise. *Geol. Surv. Jpn. Cruise Rept.* **1982**, *18*, 293–312.
124. Toth, J.R. Deposition of submarine crusts rich in manganese and iron. *Geol. Soc. Am. Bull.* **1980**, *91*, 44–54. [CrossRef]
125. Khan, M.A.; Kakar, M.I.; Ulrich, T.; Ali, L.; Kerr, A.C.; Mahmood, K.; Siddiqui, R.H. Genesis of manganese deposits in the Ali Khanzai block of the Zhob ophiolite, Pakistan: Inferences from geochemistry and mineralogy. *J. Earth Sci.* **2020**, *31*, 884–895. [CrossRef]
126. Choi, J.H.; Hariya, Y. Geochemistry and depositional environment of Mn oxide deposits in the Tokoro Belt, northeastern Hokkaido, Japan. *Econ. Geol.* **1992**, *87*, 1265–1274. [CrossRef]
127. Hollis, S.P.; Roberts, S.; Cooper, M.R.; Earls, G.; Herrington, R.; Condon, D.J.; Cooper, M.J.; Archibald, S.M.; Piercey, S.J. Episodic arc-ophiolite emplacement and the growth of continental margins: Late accretion in the Northern Irish sector of the Grampian-Taconic orogeny. *Bulletin* **2012**, *124*, 1702–1723. [CrossRef]
128. Khedr, M.Z.; Abo Khashaba, S.M.; Takazawa, E.; Hassan, S.M.; Azer, M.K.; El-Shibiny, N.; Abdelrahman, K.; Ichiyama, Y. Genesis of Rare Metal Granites in the Nubian Shield: Tectonic Control and Magmatic and Metasomatic Processes. *Minerals* **2024**, *14*, 522. [CrossRef]
129. Abdel-Karim, A.-A.M.; Ali, S.; El-Afandy, A.H.; El-Awady, A.; Khedr, M.Z.; Tamura, A.; Elwan, W. Hamama volcanogenic massive sulfide deposits, central Eastern Desert, Egypt: Mineralogical and tectonic implications. *Euro-Mediterr. J. Environ. Integr.* **2024**, *9*, 235–254. [CrossRef]
130. Ghoneim, M.; Lebda, E.; Nasr, B.; Khedr, M. Geology and tectonic evolution of the area around Wadi Arais, Southeastern Desert, Egypt. In Proceedings of the 6th International Conference on Geology of the Arab World, Cairo, Egypt, 10–14 February 2002; Volume 1, pp. 45–66.
131. Fossen, H.; Cavalcante, G.C.G. Shear zones—A review. *Earth-Sci. Rev.* **2017**, *171*, 434–455. [CrossRef]
132. Tian, Z.; Liu, F.; Xiao, W.; Wang, H.; Zhu, Z.; Wang, D. Structure-controlled mineralization resulted from Paleoproterozoic orogenesis in the Dahenglu Cu-Co deposit, NE China. *Ore Geol. Rev.* **2024**, *165*, 105893. [CrossRef]
133. Pirajno, F. *Hydrothermal Processes, and Mineral Systems*; Springer Science & Business Media: Berlin/Heidelberg, Germany, 2008.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Genesis of Fe-Ti-(V) Oxide-Rich Rocks by Open-System Evolution of Mafic Alkaline Magmas: The Case of the Ponte Nova Massif, SE Brazil

Amanda Andrade de Souza ^{1,2,*}, Rogério Guitarrari Azzone ^{1,*}, Luanna Chmyz ¹, Lina Maria Cetina Tarazona ^{1,2}, Fábio Ramos Dias de Andrade ¹, José Vinicius Martins ¹, Excelso Ruberti ¹ and Celso de Barros Gomes ¹

¹ Department of Mineralogy and Geotectonics, Institute of Geosciences (IGc), University of São Paulo (USP), São Paulo 05508-080, Brazil; chmyz@usp.br (L.C.); linacetina0526@usp.br (L.M.C.T.); dias@usp.br (F.R.D.d.A.); viniciusmartins@usp.br (J.V.M.); exrubert@usp.br (E.R.); cgomes@usp.br (C.d.B.G.)

² Postgraduate Program for Geosciences (Mineralogy and Petrology), Institute of Geosciences (IGc), University of São Paulo (USP), São Paulo 05508-080, Brazil

* Correspondence: amandaandrade@usp.br (A.A.d.S.); rgazzone@usp.br (R.G.A.)

Abstract: The formation of Fe-Ti oxides-rich layers is commonly associated with open-system magma chamber dynamics. These processes are widely discussed due to the economic importance of Fe-Ti-(V) deposits, although an alkaline-system approach to the matter is still scarce. In this study, we use petrography, mineral chemistry, X-ray diffraction and elemental geochemical analyses (whole-rock and Sr isotopes) to discuss the process associated with the formation of Fe-Ti-(V) oxide-rich clinopyroxenite (OCP, 7–15 vol.%) and magnetitite (MTT, 85 vol.%) from the Ponte Nova alkaline mafic-ultramafic massif (PN, K-Ar 87.6 Ma). Ilmenite and Ti-magnetite from both OCP and MTT exhibit higher MgO contents (MgO > 5.0 wt%) than other PN rocks. OCP shows high ⁸⁷Sr/⁸⁶Sr_i ratios, equivalent to crustal-contaminated lithotypes of the PN Central Intrusion, while MTTs are less radiogenic. The oxide supersaturation in silicate mafic magmas is typically associated with the dislocation of the liquid cotectic evolution line, shifting to Fe-Ti-(V) oxide minerals stability field, mainly Ti-magnetite. Different magmatic processes can lead to these changes such as crustal contamination and magma recharge. For the PN massif, the OCP was formed by the assimilation of crustal contaminants in a mush region, near the magma chamber upper walls, which was associated with the evolution of the main pulse. Differently, the MTT would have its origin related to the interaction between magma chamber evolved liquids and more primitive liquids during a new episode of magma recharge. Lastly, post-magmatic events were superimposed on these rocks, generating sulfides.

Keywords: Fe-Ti oxides; crustal assimilation; magma recharge; open-system; alkaline rocks

1. Introduction

Fe-Ti-(V) oxides-rich layers in mafic-ultramafic igneous complexes are widely discussed in the literature (e.g., [1,2]) mainly due to their significant economic importance as ore deposits [3]. These layers are usually hosted in layered intrusions of tholeiitic filiation such as the Bushveld Complex in South Africa [4], the Sept Iles intrusion in Canada [5], the Bjerkreim-Sokndal intrusion in Norway [6] and the Emeishan Large Igneous Province intrusions in SW China [7,8]. For such oxide-rich layers to crystallize from a silicate magma, the crystallization of silicate minerals must temporally halt, allowing a short period of time that only the oxide phase crystallizes [9]. The main petrological models to explain oxide minerals as the sole liquidus phase in the magmatic system include the assimilation of a crustal contaminant [10], magma mixing (e.g., [9,11]) and/or liquid immiscibility [12,13]. Fractional crystallization by in situ and/or the crystal settling of oxides is also invoked to explain the origin of oxide layers in those intrusions [14].

The records of rocks with abnormal concentrations of Fe-Ti oxide minerals are scarce for alkaline systems and usually relate to associated carbonatite rocks. Several carbonatite bodies from tropical regions were initially described as iron ore occurrences due to residual concentrations of magnetite after the extensive weathering of carbonate (e.g., [15]). Primary concentrations of Fe-Ti oxides in alkaline intrusions are mostly found associated with phoscorites, rare plutonic ultramafic rocks formed by magnetite, apatite and forsterite and sometimes forming near monomineralic layers of magnetite [16,17]. Primary Fe-Ti oxide concentrations directly related to silicate alkaline rocks remain unknown.

The Ponte Nova alkaline mafic-ultramafic massif (PN, Upper Cretaceous; [18]) is part of the extensive Meso-Cenozoic continental alkaline-carbonatite magmatism in the central and southeastern regions of the South American Platform [19]. PN corresponds to a lithologically varied intrusive body with a predominance of cumulate rocks representative of successive magmatic pulses. In its central-western domain, the massif presents a restricted level particularly enriched in Ti-magnetite, ilmenite and, subordinately, sulfides [18], whose origin is still poorly understood.

Several processes previously mentioned, such as fractional crystallization [18], crustal assimilation [20,21] and magma recharge [22], played an important role in the Ponte Nova evolution. Considering that, this study aims to investigate the magmatic processes that may have contributed to the formation and accumulation of Fe-Ti(V) oxides in oxide-rich clinopyroxenites (OCPs, 7–15 vol.%) and magnetitites (MTTs, 85 vol.%) in the PN massif. We present new petrographic, mineral chemistry, as well as X-ray diffraction and elemental geochemistry analyses (whole-rock and Sr isotopes) of the studied rocks to be compared with the other PN intrusions and worldwide Fe-Ti-V deposits. This work proposes a model for the origin of OCP and MTT facies looking to encourage and expand discussions related to the origin of Fe-Ti(V) oxides-rich layers associated with alkaline occurrences, which are considerably less common in the literature, in an open-transcrustal system context. From an economic perspective, OCP and MTT are pointed as potential exploratory targets for Fe, Ti and V [23].

2. Geologic Setting

The Meso-Cenozoic tectono-magmatic reactivation on the South American Platform [24,25] has resulted in intense episodes of magmatic activity, including a restricted, yet notable, manifestation of alkaline and carbonatite magmatism [19,24]. In general, alkaline occurrences in the Brazilian territory are predominantly suites (<100 km²) of evolved lithotypes, usually SiO₂-undersaturated to saturated syenites [26]. Mafic occurrences are generally small intrusions (dikes, veins, stocks, plugs and pipes) or cumulates associated with carbonatitic complexes, such as Juquiá [27] and Jacupiranga [28].

Accounting for petrographic and geochronological characteristics [29,30], as well as regional tectonics [19,24], the Brazilian alkaline occurrences are grouped into provinces. The Serra do Mar Alkaline Province (Figure 1a,b; [24,30]) covers most of the coastline of Rio de Janeiro and São Paulo states, extending to the Serra da Mantiqueira in its continental domain. The province is composed of about 20 main alkaline occurrences, mostly plutonic, along with many mafic-ultramafic and felsic dikes, all formed between the Upper Cretaceous and the Lower Paleocene. Most intrusions are syenitic in nature, such as the Passa Quatro [31], Itatiaia [32] and Poços de Caldas [33] occurrences. Syenitic intrusions associated with small mafic-ultramafic cumulate bodies are described in São Sebastião [34] and the Monte de Trigo [35] islands. Exceptionally, the Ponte Nova alkaline mafic-ultramafic massif [18] is the only area with a predominance of mafic-ultramafic rocks in the region.

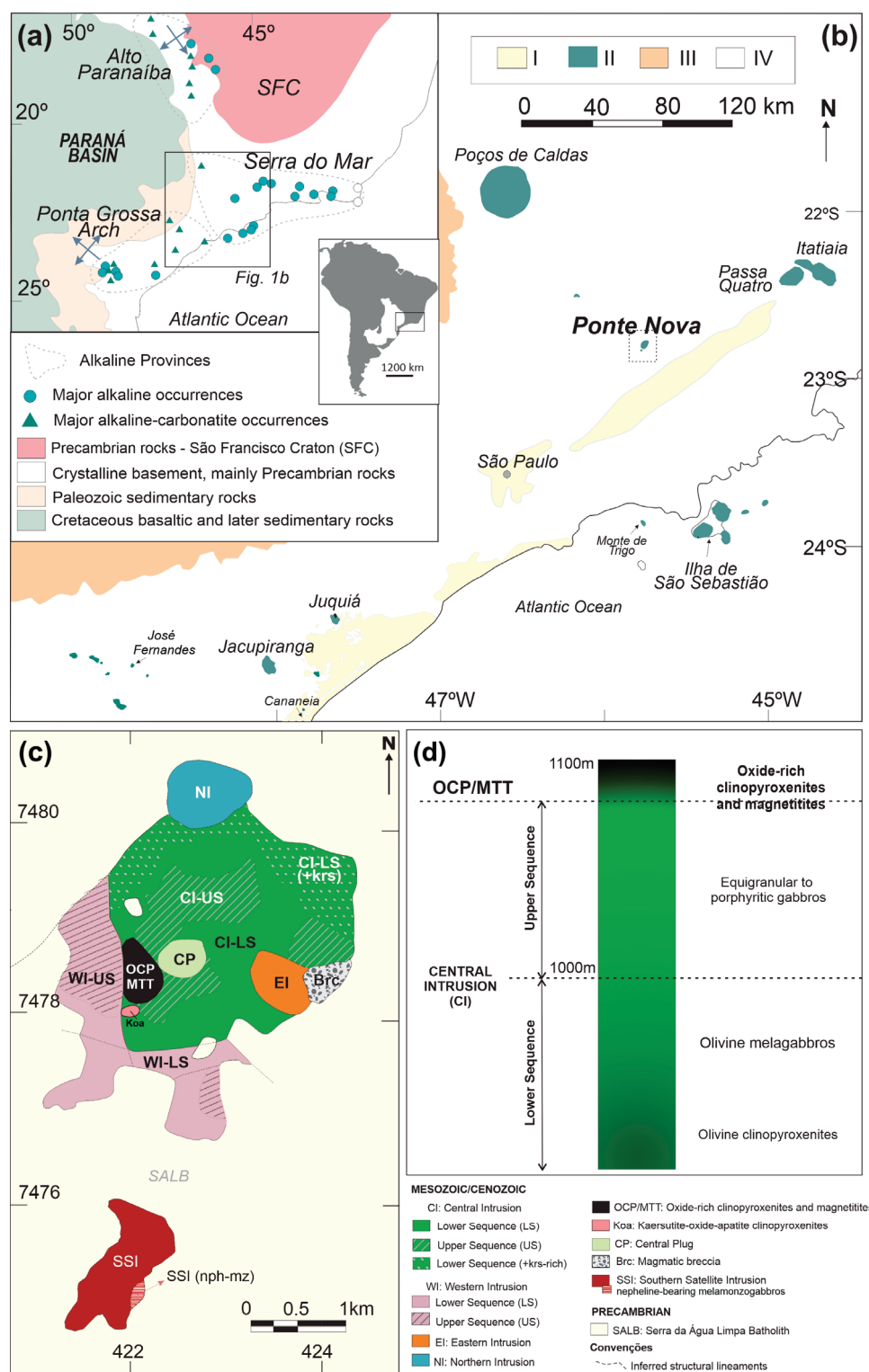


Figure 1. (a) Geological setting of alkaline intrusions of Cretaceous magmatism in the southeastern part of the South American Platform showing the distribution of major alkaline occurrences of Alto Paranaíba, Serra do Mar and Ponta Grossa Arch alkaline provinces (modified after [20]). (b) Detail of (a), with the location of the main occurrences. Legend: I—Sediments or sedimentary rocks (Cenozoic); II—Alkaline complexes (Meso-Cenozoic); III—Sedimentary rocks of the Paraná Basin (Ordovician-Silurian); IV—Crystalline Basement, Brasília and Ribeira orogenic belts (Precambrian). (c) Simplified geological map of the Ponte Nova alkaline mafic-ultramafic massif (modified after [20]). (d) Schematic model of the lithostratigraphy of the studied rocks, after [36].

The PN massif (Figure 1c, K-Ar 87.6 Ma; [18]) is composed of an alkaline gabbroic association representative of successive magmatic pulses in a shallow-level chamber environment [20]. Its parental magma has basanitic composition as well as the mafic dikes that intruded the crystalline basement and the massif itself. The massif is originated from a heterogeneous mantle-derived partial melting, which was enriched by metasomatic events [20].

PN has two exposure areas, with a larger one (5.5 km²) encompassing the massif main intrusions, along with a smaller one (1 km²), constituted by a satellite body to the south of the main occurrence. Following geological and petrographic descriptions [18,20,21,36–38], the Central (CI) and Western (WI) intrusions comprise most of the occurrence and are divided into lower and upper sequences. The lower sequences are cumulates composed of clinopyroxenites and melagabbros with variable amounts of olivine and kaersutite-bearing layers. Nepheline monzogabbros exhibiting varied textural features (i.e., massive, banded, equigranular, porphyritic) are present in the upper sequences. The Northern Intrusion (NI), also cumulatic, contains melamonzogabbros with variable amounts of olivine. The Eastern Intrusion (EI) includes more evolved lithotypes, such as inequigranular to porphyritic monzodiorites with variable amounts of nepheline. A small plug (CP) composed of equigranular to porphyritic microgabbros occupies the massif central part. Separated from the rest of the massif by crystalline basement rocks, the Southern Satellite Intrusion (SSI) is formed by porphyritic nepheline-bearing melamonzonites and monzogabbros. Three other subordinate facies in the PN massif correspond to the magmatic breccia facies (Brc), kaersutite-oxide-apatite clinopyroxenites (Koa) and, finally, the oxide-rich clinopyroxenites (OCPs) and magnetitites (MTTs) facies, which are the focus of this study. Covering the massif highest altitude hill (1100 m) are the restricted outcrops of oxide-rich clinopyroxenites and magnetitites (Figure 1d). Both lithotypes are found close to each other, forming isolated blocks with less than 1 m² and exposed in an area less than 1 km². Primarily characterized by [18], the OCP facies was described as cumulates where clinopyroxene is the predominant cumulus phase in addition to subordinate ilmenite. Close to that facies, there is a horizon enriched in Fe-Ti oxides (85% vol.) such as Ti-magnetite (95%) and ilmenite (5%), which is classified as magnetitite [18].

3. Analytical Methods

Seven polished sections (6 from OCP, 1 from MTT) were selected for electron microprobe analyses (EPMA) of the main cumulus phases (clinopyroxene, Ti-magnetite and ilmenite). The analyses were performed by wavelength-dispersive spectroscopy (WDS) using JEOL JXA-8530F equipment at the GeoAnalitica (GeoAnalitica, Phoenix, AZ, USA) facilities of the Institute of Geosciences, University of São Paulo, São Paulo, Brazil. Backscattered electron images via energy-dispersive X-ray spectroscopy (EDS) were also obtained. Operating conditions were 15 kV for accelerating potential, 20 nA for probe current and 5 µm for beam diameter. Peak counting times ranged from 10 to 40 s for Fe-Ti oxides and 10 to 60 s for clinopyroxene. Standards included silicate minerals and synthetic oxides with data correction using the PROZA program [39]. Structural formulae were calculated in accordance with [40] and [41]. Fe³⁺/Fe²⁺ ratios for clinopyroxene were calculated by stoichiometry following the method of [42], while Fe³⁺/Fe²⁺ ratios for Fe-Ti oxides were calculated by stoichiometry, as described by [43]. Standard details and other analytical parameters, as well as the obtained data, are presented in the Supplementary Materials S1.

Four thin sections (3 from OCP, 1 from MTT) were selected for in situ minor and trace elements analyses in Ti-magnetite and ilmenite. The measurements were carried out by laser ablation in a CETAC LSX-213 G2+ laser coupled (Teledyne CETAC Technologies, Omaha, NE, USA) to a Thermo Scientific iCap Q-ICP-MS instrument (Thermo Fisher, Waltham, MA, USA) at the Chemistry and ICP Laboratory of the GeoAnalitica. Analytical time was 70 s with background acquisition of 30 s (gas blank) followed by 40 s of sample data acquisition. Operating conditions included 50 to 100 µm for a beam diameter through a 15 Hz repetition rate and energy fluence of 7.11 J/cm². Element contents were calibrated

utilizing the following international glass standards: BCR-2G for quantification and drift control, and BIR-1G for quality control (see Supplementary Materials S2). Data integration and the determination of concentrations, detection limits and analytical errors were conducted using the software Glitter Version 2008 [44]. The mean of $\text{FeO}_{(\text{T})}$ contents from the electron microprobe analyses was employed as internal standard with a standard deviation of 1.10% for Ti-magnetite (MTT) and 0.79% and 1.59% for ilmenite in the MTT and OCP facies, respectively.

Whole-rock major, minor and trace elements (see Supplementary Materials S3) were analyzed in fused glass discs and pressed powder pellets using a Panalytical Axios Max Advanced X-ray fluorescence spectrometer (XRF) (Malvern Panalytical, Malvern, Worcestershire, UK) at the GeoAnalitica core facility with standard methods described by [45]. Whole-rock trace elements, including rare earth elements, were also obtained by inductively coupled plasma mass spectrometry (ICP-MS), utilizing a Thermo Scientific iCap Q-ICP-MS instrument (Thermo Fisher, Waltham, MA, USA) at the same laboratory. Analytical procedures followed the routines described by [46]. Whole-rock Sr isotope analyses were carried out at the Centro de Pesquisas Geocronológicas (CPGeo) of the Institute of Geosciences with equipment and procedures as described in [47] and [48].

X-ray diffraction analyses (powder method) were conducted on 3 samples (2 from MTT, 1 from OCP) using a Panalytical Empyrean diffractometer (Malvern Panalytical, Malvern, Worcestershire, UK) at the Laboratório de Caracterização Tecnológica (LCT) of the Department of Mining and Petroleum Engineering, Polytechnic School of the University of São Paulo. The instrumental parameters included $\text{CoK}\alpha$ radiation, 40 mA, 45 kV, an angular range from 5° to 80° 2-theta, an angular step of 0.02° 2-theta and 300 s per step. Data interpretation and quantitative phase analysis (Rietveld method) were performed using the software tools Match! Version 5.0.2 (Crystal Impact), Profex [49] and High Score Plus Version 4.0 (Panalytical) (Malvern Panalytical, Malvern, Worcestershire, UK). Crystallographic information files from the Crystallography Open Database [50] were utilized for this analysis.

4. Results

4.1. OCP and MTT Petrography

The OCP facies corresponds to coarse-grained ultramafic cumulates constituted predominantly by clinopyroxene and ilmenite (Figure 2a,c) in addition to sulfides, apatite, biotite and, locally, kaersutite (Table 1). Clinopyroxene is the dominant phase in the cumulus assemblage (85–90%), forming micro to macrocrystals oriented grains up to 1 cm, euhedral to subhedral, often zoned (diopside cores and Ti-augite rims). Ilmenite is secondary in the cumulus assemblage, occurring as rounded, small inclusions in clinopyroxene or homogeneous aggregates of polygonal habit and typical triple-junctions (Figure 2g) within the clinopyroxene framework. Ilmenite also constitutes the main intercumulus assemblage as homogeneous, subhedral to anhedral crystals (Figure 2b,c), occasionally replaced by hematite (Figure 2h). Sulfides are represented by pyrite chalcopyrite, mostly found with ilmenite or in veins (Figure 2e,f), but they can be present as euhedral microcrystals dispersed in the intercumulus association.

Hydrothermal and weathering alteration processes are present at the edges and along fractures of clinopyroxene grains, but they are also evident in some crystals of Fe-Ti oxides. Due to these alterations, ilmenite crystals frequently exhibit corroded edges (Figure 2h). Ilmenite in acicular shapes (Figure 2e,f) are specifically attributed to previous ilmenite exsolution lamellae of Ti-magnetite pseudomorphs, the latter replaced by sulfides. Apatite occurs as an accessory phase, as acicular inclusions in clinopyroxene or matrix-disseminated granular microcrystals (Figure 2b). Exceptionally, a restricted apatite-rich domain was recognized with euhedral apatite associated with intercumulus kaersutite and ilmenite (Figure 2d). Kaersutite is only identified in the apatite-rich domain. Biotite is generally secondary and found along clinopyroxene fractures, in veins or enclave rims. OCP presents mafic microgranular enclaves of gabbroic composition, similar to the ones

found at the CI upper sequence, as well as enclaves of OCP's of similar composition but of fine grain texture.

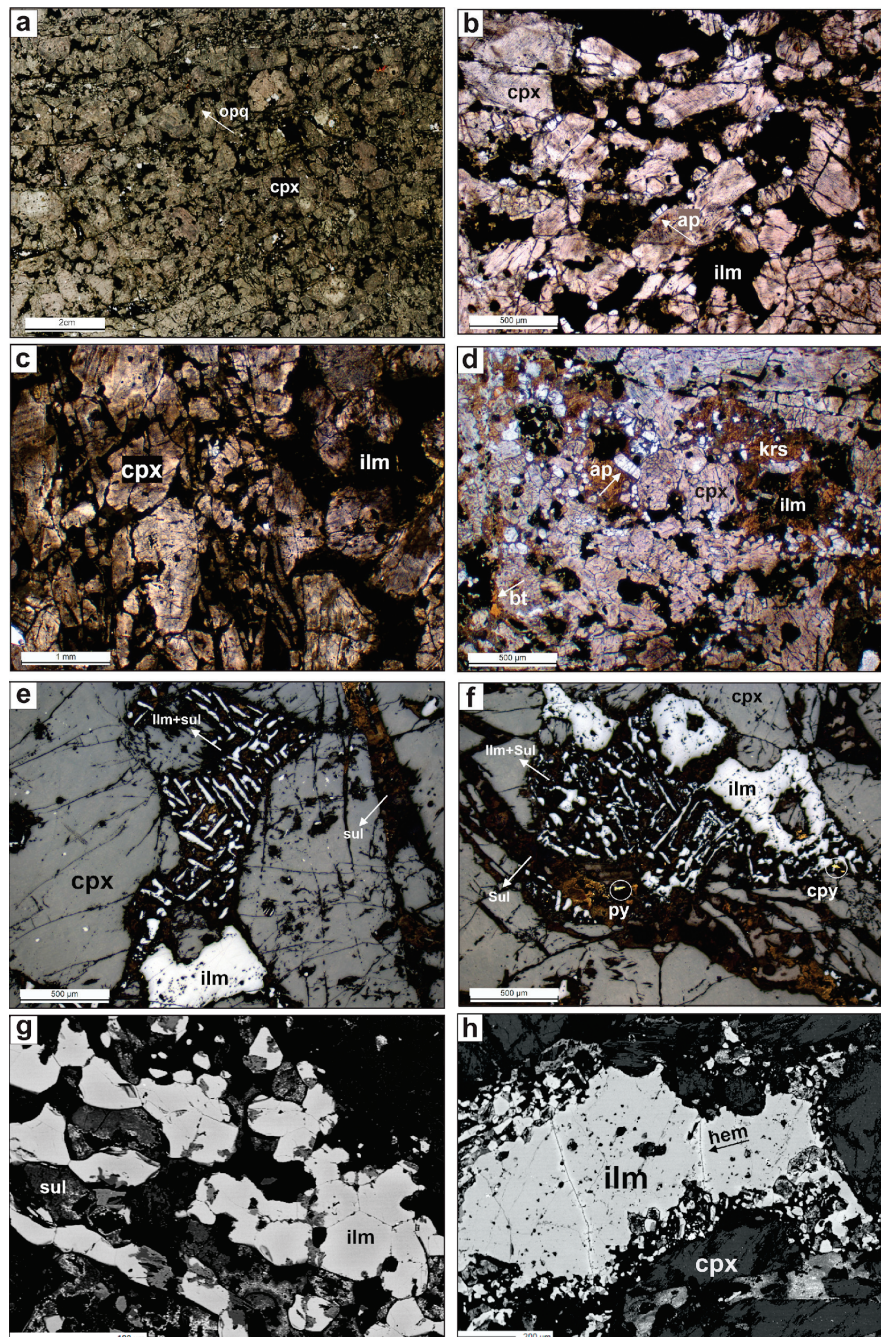


Figure 2. Petrographic aspects of the OCP facies. (a) OCP scanned thin section. Transmitted and plane-polarized light: (b) Photomicrograph of OCP cumulate texture and mineral assemblage constituted of clinopyroxene, ilmenite and apatite (granular and acicular) disseminated through the matrix. (c) Orientation and compaction structures. (d) Apatite-rich domain with subordinate kaersutite, ilmenite and biotite. Reflected and plane-polarized light: (e,f) Anhedral and acicular ilmenite associated with cumulus clinopyroxene and weathered sulfides along fractured zones. Backscattered electron image (BSE): (g) Ilmenite (in triple-junction contacts) and sulfides; and (h) Ilmenite corroded rims and substitution by hematite along fractures. Abbreviations: bt—biotite, cpx—clinopyroxene, cpy—chalcopyrite, hem—hematite, ilm—ilmenite, py—pyrite, sul—weathered sulfide, opq—opaque minerals.

Table 1. Summary of petrographic features of intrusions of the Ponte Nova massif (after [38]). CI, central intrusion; WI, western intrusion; NI, northern intrusion; EI, eastern intrusion; SSI, southern satellite intrusion; OCP, oxide-rich clinopyroxenite; MTT, magnetitite; Brc, magmatic breccia; LS, lower sequence; US, upper sequence; Krs-rich, kaersutite-rich cumulates; Nph, nepheline-bearing monzonite.

Intrusion	Lithologies	Color Index	Crystallization Stages			
			Early-Magmatic (Primocrysts)	Principal	Late-Magmatic	Post-Magmatic
CI	(coarse- to medium-grained) (cumulatic) Olivine clinopyroxenites, Olivinel-bearing clinopyroxenites, Olivine melagabbros, Olivine-bearing melagabbros	97–70	Di, Ti-Aug, Ol, $\pm$ Ti-Mgt, $\pm$ Ap, $\pm$ Pl	Ti-Aug, Pl, Krs, Ti-Mgt, Ap, $\pm$ Ilm, $\pm$ Bdy	Ti-rich Bt, $\pm$ Afs, $\pm$ Nph	
	(coarse- to medium-grained) (cumulatic) Olivine kaersutite clinopyroxenites, Kaersutite melagabbros	95–80	Di, Ti-Aug, Ol, $\pm$ Ti-Mgt, $\pm$ Ap, $\pm$ Pl	Krs, Ti-Aug, Pl, Ti-rich Bt, Ti-Mgt, Ap, $\pm$ Ilm, $\pm$ Bdy	Ti-rich Bt, $\pm$ Afs, $\pm$ Nph	
	(coarse- to medium-grained) (inequigranular to macrocrystic) Nepheline-bearing monzogabbros	62–50	Di, Ti-Aug, Pl, $\pm$ Ol	Pl, Ti-Aug, Bt, Ti-Mgt, Ti-rich Bt, Ap	Intergrowth of Afs + Nph + Pl	(incipient levels) Anl, Ab, Ms, Cb, Ep/Czo, Chl, Bt, Act, Ttn, Py, $\pm$ Po, $\pm$ Cpy, $\pm$ Sp
WI	(coarse- to medium-grained) (cumulatic) Olivine melagabbros, Olivine-bearing melagabbros, Olivine-bearing clinopyroxenites	99–75	Di, Ti-Aug, Ol, $\pm$ Ti-Mgt, $\pm$ Ap, $\pm$ Pl	Ti-Aug, Pl, Krs, Ti-rich Bt, Ti-Mgt, Ap, $\pm$ Ilm, $\pm$ Bdy	Ti-rich Bt, $\pm$ Afs, $\pm$ Nph	
	(coarse- to medium-grained) (inequigranular to equigranular, banded to massive) Nepheline-bearing monzogabbros	52–36	Pl, Ti-Aug, $\pm$ Ti-Mgt, $\pm$ Ap, $\pm$ Ol	Pl, Ti-Aug, Ti-Mgt, Ap, Ti-rich Bt, Afs, Nph, Ba-rich Afs	Intergrowth of Afs + Nph + Pl	
NI	(coarse- to medium-grained) (cumulatic) Olivine melamonzogabbros, Olivine-bearing melamonzogabbros	76–67	Di, Ti-Aug, Ol, $\pm$ Ti-Mgt, $\pm$ Ap, $\pm$ Pl	Ti-Aug, Pl, Ti-Mgt, Ap, Afs, Ilm, $\pm$ Bdy	Ti-rich Bt, $\pm$ Krs, intergrowth of Afs + Nph	--
EI	(medium- to fine-grained) (seriate to porphyritic) Nepheline monzodiorites, Nepheline-bearing monzodiorites	58–51	Di, Ol, Pl, $\pm$ Ap	Ti-Aug, Pl, Ba-Ti-rich Bt, Ti-Mgt, Ilm, Ap, $\pm$ Zrc	Afs, Ba-rich Afs, Nph, $\pm$ Sdl	(incipient levels) Anl, Ab, Prh, Cb, Ep/Czo, Chl, Bt, Py, $\pm$ Cpy, $\pm$ Sp
CP	(medium-grained) (porphyritic to equigranular) microgabbros	56–50	Ti-Aug, Ol	Ti-Aug, Pl, Ti-Mgt, Bt, Ap	Bt, Afs, Nph	--
SSI	(porphyritic, medium-grained matrix) Nepheline-bearing melamonzogabbros	67–60	Di, Ti-Aug, Ol	Pl, Ti-Aug, Ti-Mgt, Ilm, Ap	Ti-rich Bt, Afs, Ba-rich Afs, Nph	
	(porphyritic, medium-grained matrix) Nepheline-bearing melamonzonites	64–62	Di, Ti-Aug	Pl, Ti-Aug, Ba-Ti-rich Bt, Afs, Ba-rich Afs, Ti-Mgt, Ilm, Ap $\pm$ Zrc	Nph	(incipient levels) Cb, Anl, Ab, Ms, Ep/Czo, Chl, Bt, Ttn, Py, Fl
	coarse- to medium-grained (inequigranular, porphyritic) Nepheline-bearing monzonites	46–40	Pl, Afs, Ba-rich Afs, Ti-Aug	Ba-Ti-rich Bt, Ap, Prg, Hst, Ti-Mgt, Nph	Nph	
OCP MTT	(coarse- to medium-grained) (cumulatic) Oxide-rich clinopyroxenites	100	Ti-Aug, Di, Ilm ($\pm$ Ti-Mgt)	Ti-Aug, Ilm, ($\pm$ Ti-Mgt), Ap,	Ti-rich Bt, $\pm$ Py, Ap, Krs	(low-levels) Ti-rich Bt, Hem, Py, $\pm$ Cpy, Mlnt, Rmb
	(coarse- to medium-grained) (cumulatic) Magnetitites	100	Ti-Mgt, Ilm, Ti-Aug	Ti-Aug, Ti-Mgt, Ilm	Ti-Mgt, Ilm	Hem, Ulv, Ant, Gth

Mineral abbreviations: Ab—albite, Anl—analime, Ant—anatase, Afs—Alkali feldspar, Ap—apatite, Bdy—baddeleyite, Bt—biotite, Cb—carbonates, Cpy—chalcopyrite, Chl—chlorite, Czo—clinozoisite, Di—diopside, Ep—epidote, Fl—fluorite, Gth—goethite, Hem—hematite, Hst—hastingsite, Ilm—ilmenite, Krs—kaersutite, Mlnt—melantherite, Ms—muscovite, Nph—nepheline, Ol—olivine, Pl—plagioclase, Po—pyrrhotite, Prg—pargasite, Prh—prehnite, Py—pyrite, Rmb—rhomboclase, Sdl—sodalite, Sp—sphalerite, sulf—sulfides, Ti-Aug—Ti-augite, Ti-Mgt—Ti-magnetite, Ttn—titanite, Ulv—ulvöspinel, Zrc—zirconolite.

The MTT facies is particularly characterized by the predominance of equigranular Ti-magnetite (about 80–85 vol.%) defining a cumulatic texture (Figure 3a,b). Ti-magnetite crystals are homogeneous, euhedral and strongly fractured, with well-defined contacts and fine oxi-exsolutions (Figure 3c,d). Overlaying the oxi-exsolutions, submillimetric ilmenite lamellae are arranged orthogonally to each other (Figure 3c,e). Substitution textures, as indicated by the formation of ulvöspinel in Ti-magnetite rims, are common (Figure 3d). Clinopyroxene is subordinate, disseminated through the matrix or present as euhedral to subhedral micro and macrocrystals. Clinopyroxene grains are also often zoned (diopside cores and Ti-augite rims; Figure 3f) and occasionally host Ti-magnetite inclusions (Figure 3f). Although less abundant, ilmenite occurs interstitially to Ti-magnetite and clinopyroxene crystals (Figure 3e,g,h).

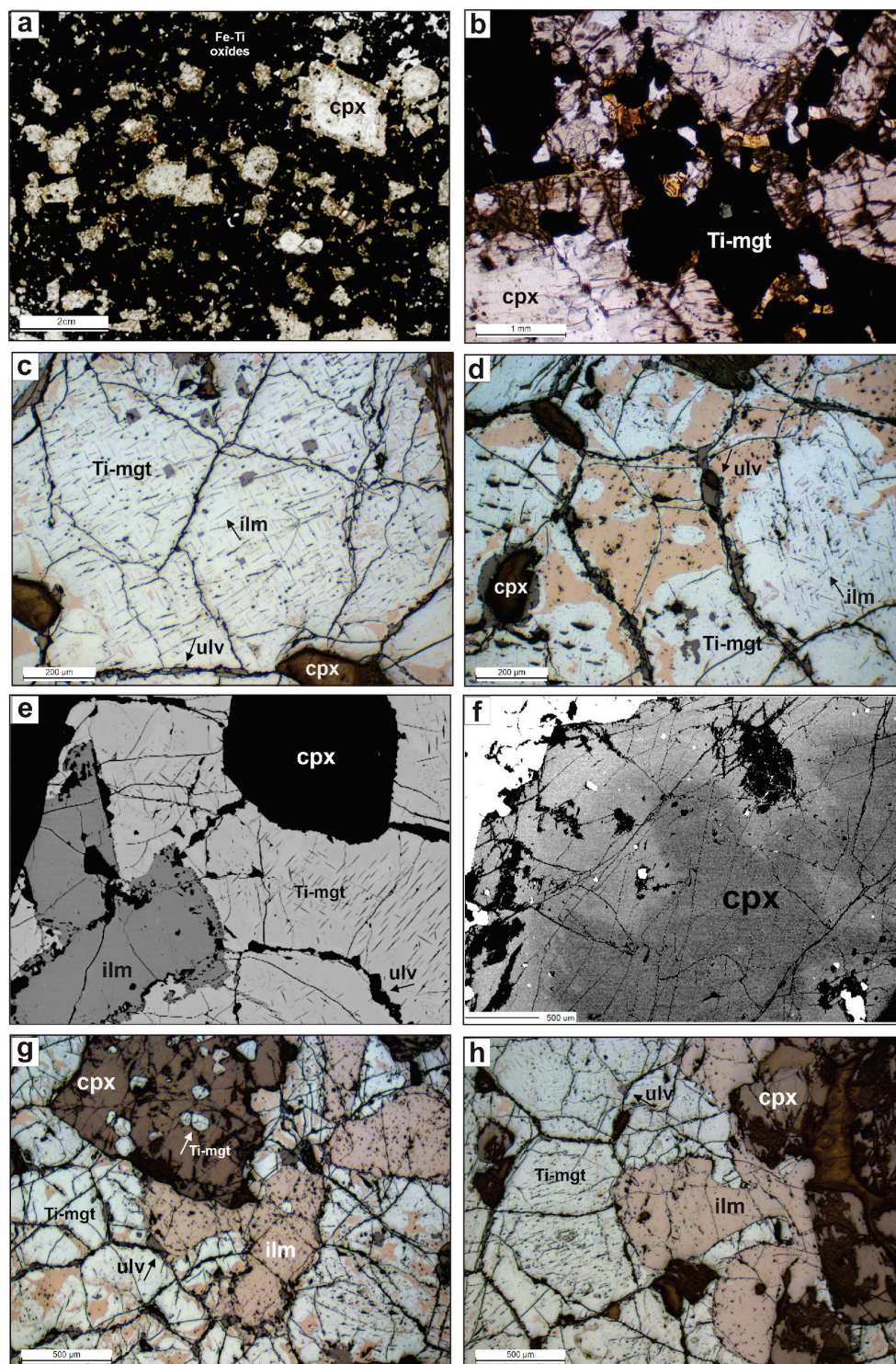


Figure 3. Petrographic aspects of the MTT facies. (a) MTT scanned thin section. Transmitted light: (b) Photomicrograph of MTT cumulatic texture. Reflected and plane-polarized light: (c) Euhedral magnetite crystals with submillimetric ilmenite lamellae and fine oxi-exsolutions. (d) Substitution textures to spinel predominantly at crystal rims. Backscattered electron image (BSE): (e) Cumulus Ti-magnetite, clinopyroxene and ilmenite. (f) Zoned clinopyroxene macrocrystal. Reflected and plane-polarized light: (g) Clinopyroxene grains with magnetite inclusions, cumulus magnetite and ilmenite (reflected and plane-polarized light). (h) Intercumulus ilmenite, cumulus magnetite and clinopyroxene (reflected and plane-polarized light). Abbreviations: cpx—clinopyroxene, ilm—ilmenite, Ti-mgt—Ti-magnetite, ulv—ulvöspinel.

4.2. Major Elements

4.2.1. Clinopyroxene

Clinopyroxene cores from both OCP and MTT (Figure 4) present two distinct $Mg\#_{cpx}$ [$Mg/(Mg + Fe_T)$, molecular proportions] populations that are divided into relict and cognate cores. Relict cores have a higher $Mg\#_{cpx}$ (0.84–0.88) and higher Cr_2O_3 contents (0.22–0.82 wt%) but lower TiO_2 (0.88–1.20 wt%), Na_2O (0.38–0.48 wt%) and Al_2O_3 (3.24–4.20 wt%) contents compared to intermediates and rims. The second core population has lower $Mg\#_{cpx}$ (0.76–0.83) and Cr_2O_3 contents (0–0.04 wt%) but higher TiO_2 (1.55–3.15 wt%), Na_2O (0.4–0.6 wt%) and Al_2O_3 (4.32–7.35 wt%) contents. Intermediate and rim domains have lower $Mg\#_{cpx}$ (0.76–0.83) and are equivalent to the second core population. Clinopyroxene crystals are positively correlated with Cr_2O_3 and negatively correlated with TiO_2 , Al_2O_3 and Na_2O .

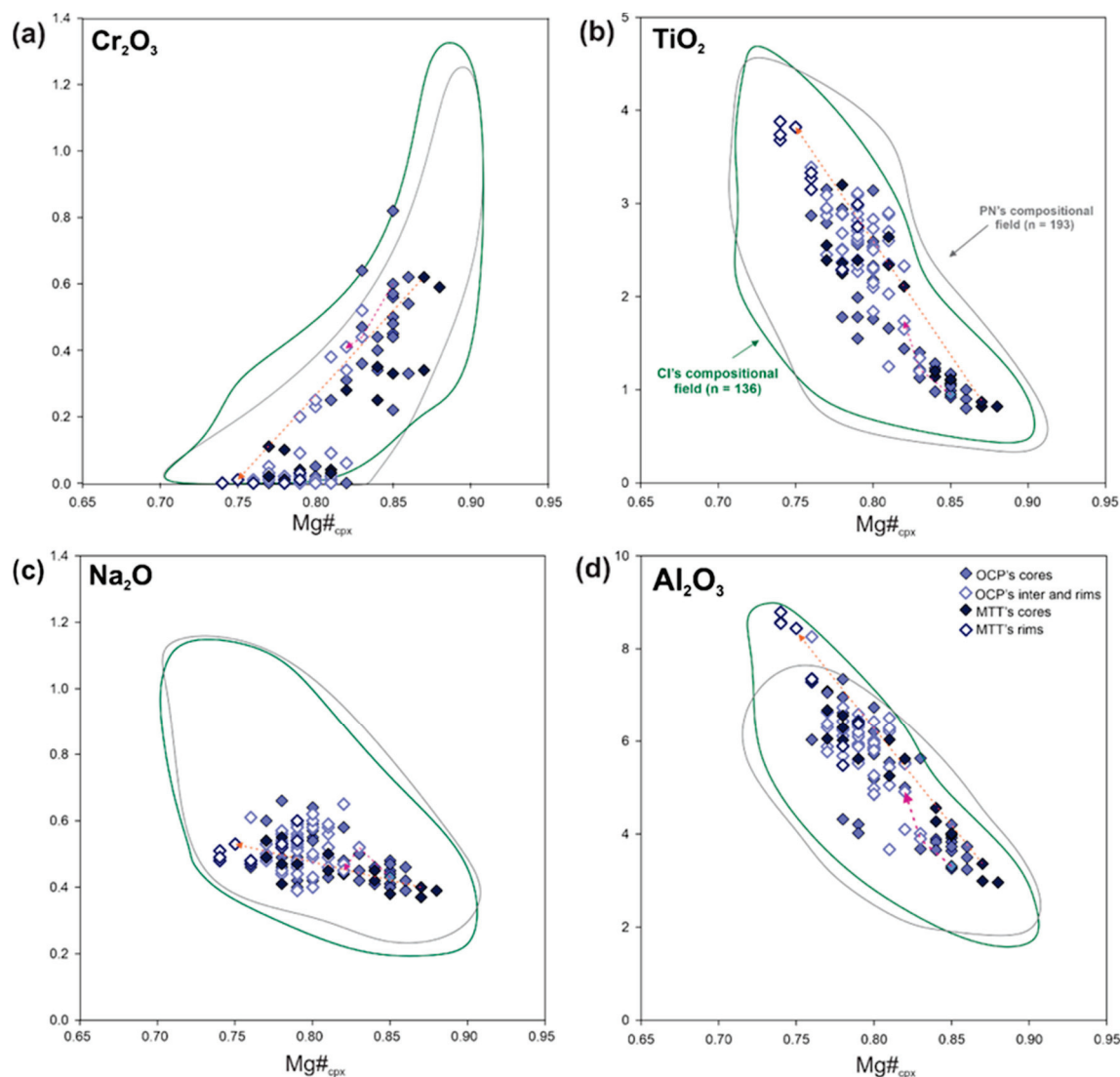


Figure 4. OCP and MTT clinopyroxene compositions compared to compiled clinopyroxene data (after [38]) of CI (green line) and other PN intrusions (gray line). (a) $Mg\#_{cpx}$ vs. Cr_2O_3 (b) $Mg\#_{cpx}$ vs. TiO_2 (c) $Mg\#_{cpx}$ vs. Na_2O (d) $Mg\#_{cpx}$ vs. Al_2O_3 . Pink dotted lines refer to core–intermediate–rim composition of one selected crystal from OCP facies. Orange dotted lines refer to core–rim composition of one selected crystal from MTT facies.

4.2.2. Fe-Ti Oxides

Fe-Ti oxides from OCP and MTT analyses, as with all PN intrusions, are consistent with the respective ulvöspinel–magnetite and ilmenite–hematite solid solution lines (Figure 5). Magnetite forms continuous solid solutions with ulvöspinel, originating Ti-magnetite. Ilmenites from MTT are close to the pure FeTiO_3 end-member while other populations from PN, including the OCP ilmenites, are more enriched in the R^{3+} component (Fe^{3+} , Cr, V, Al), mainly due to its Fe^{3+} content.

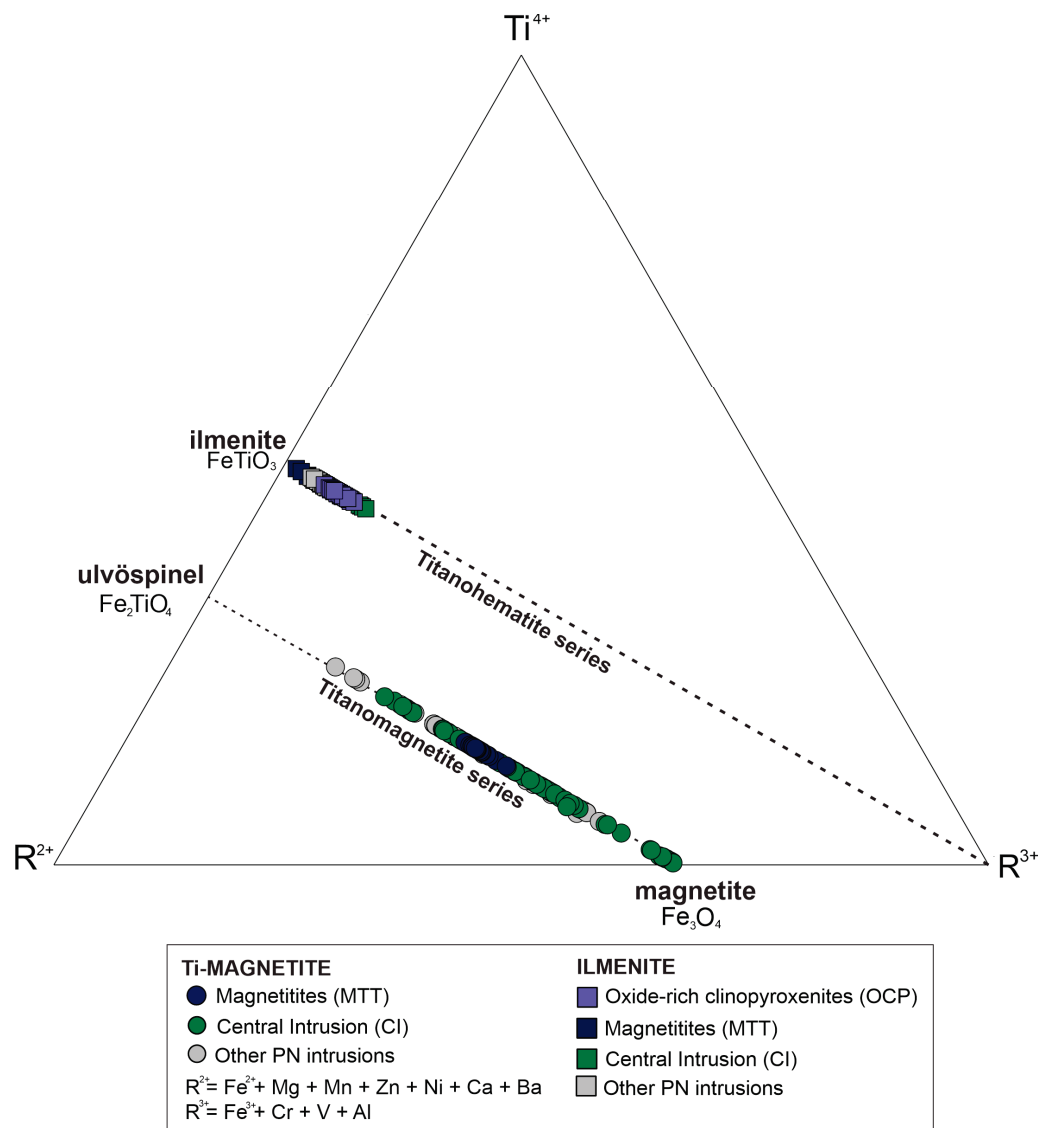


Figure 5. Ti- R_2 - R_3 ternary diagram of Fe-Ti oxides of PN with the magnetite–ulvöspinel and ilmenite–hematite solid solution lines, in atoms per formula unit (apfu).

Ilmenite and Ti-magnetite $\text{Mg\#}$ [$\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$, molecular proportions] compositions in violin-type diagrams (Figure 6) allow a better understanding of the OCP and MTT data distribution when compared to other PN intrusions. It is notable that Fe-Ti oxide crystals from OCP and MTT stand out from the other rocks of the massif due to their higher $\text{Mg\#}$ (crystals from both are Mg-rich). Ti-magnetite contents vary between $\text{Mg\#}_{\text{ti-mgt}} = 0.01\text{--}0.16$ and $\text{Mg\#}_{\text{ti-mgt}} = 0.02\text{--}0.1$ in CI and other intrusions, respectively. In the magnetitites, the range is $\text{Mg\#}_{\text{ti-mgt}} = 0.18\text{--}0.23$. Although some data have equivalent values to those observed in the rest of PN, most of the compositions have higher values. Ilmenite values vary between $\text{Mg\#}_{\text{ilm}} = 0.10\text{--}0.26$ and $\text{Mg\#}_{\text{ilm}} = 0.03\text{--}0.26$ in CI and other

intrusions, respectively. As noted for Ti-magnetite, some of the data are consistent with PN, but most of them are higher ($Mg\#_{ilm} = 0.37$).

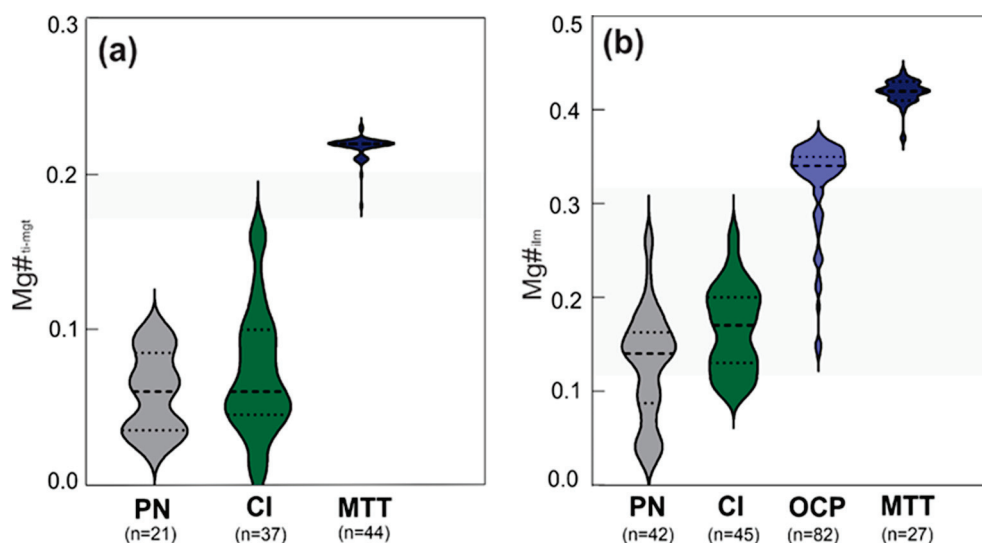


Figure 6. Mg# index of Ti-magnetite and ilmenite from OCP, MTT, CI and other PN intrusions. The grey field represents analyses with equivalent Mg# to other PN intrusions. (a) Mg# in Ti-magnetite. (b) Mg# in ilmenite. Abbreviations: OCP—oxide-rich clinopyroxenites, MTT—magnetitites, CI—Central Intrusion.

Ti-Magnetite

MTT's Ti-magnetites have TiO_2 (Figure 7a) and Cr_2O_3 (Figure 7c) contents within the observed range for the other lithologies of PN. Most of the results for Ti-magnetite indicate a substitution of Fe^{3+} by Si. The data show a positive correlation for FeO (Figure 8a) and a negative correlation for Fe_2O_3 (Figure 8b) in both EPMA and LA-ICP-MS analyses. They present particularly high contents of V (2523–3542 ppm), Mn (2267–3610 ppm) and Mg (11,581–40,590 ppm) when compared to Ti-magnetites from Fe-Ti-V deposits (Figure 9). Ni (36–65 ppm), Co (106–208 ppm), Cu (4–125 ppm), Cr (89–179 ppm), Nb (3–7 ppm) and Zr (24–46 ppm) contents are low, even though Zr and Nb contents are higher than most of the compiled data (Figure 9b).

Ilmenite

MTT ilmenites have higher TiO_2 contents (Figure 7b) than those observed in PN, while OCP ilmenites exhibit chemically coherent behavior with that observed in PN. OCP ilmenites (Figure 7d) have higher Cr_2O_3 contents than those observed in both MTT and the rest of the massif but, in general, all PN ilmenites are Cr-poor and close to lower detection limits. OCP ilmenites with lower $Mg\#_{ilm}$ and compositionally closer to PN are associated with a few rims or small crystals. Most of the OCP ilmenite presents higher contents of Mn (7534–9549 ppm), V (3575–4995 ppm), Zn (141–306 ppm) and Cr (339–794 ppm), while the MTT ilmenite presents higher Co (7–15 ppm), although in low concentration. Both facies have equivalent contents of Cu (14–32 ppm) and Zr (90–584 ppm) (Figure 10). Despite being derived from different textural features (i.e., enclaves, apatite-rich domain, matrix and inclusions in clinopyroxene), OCP ilmenites are within the same compositional range.

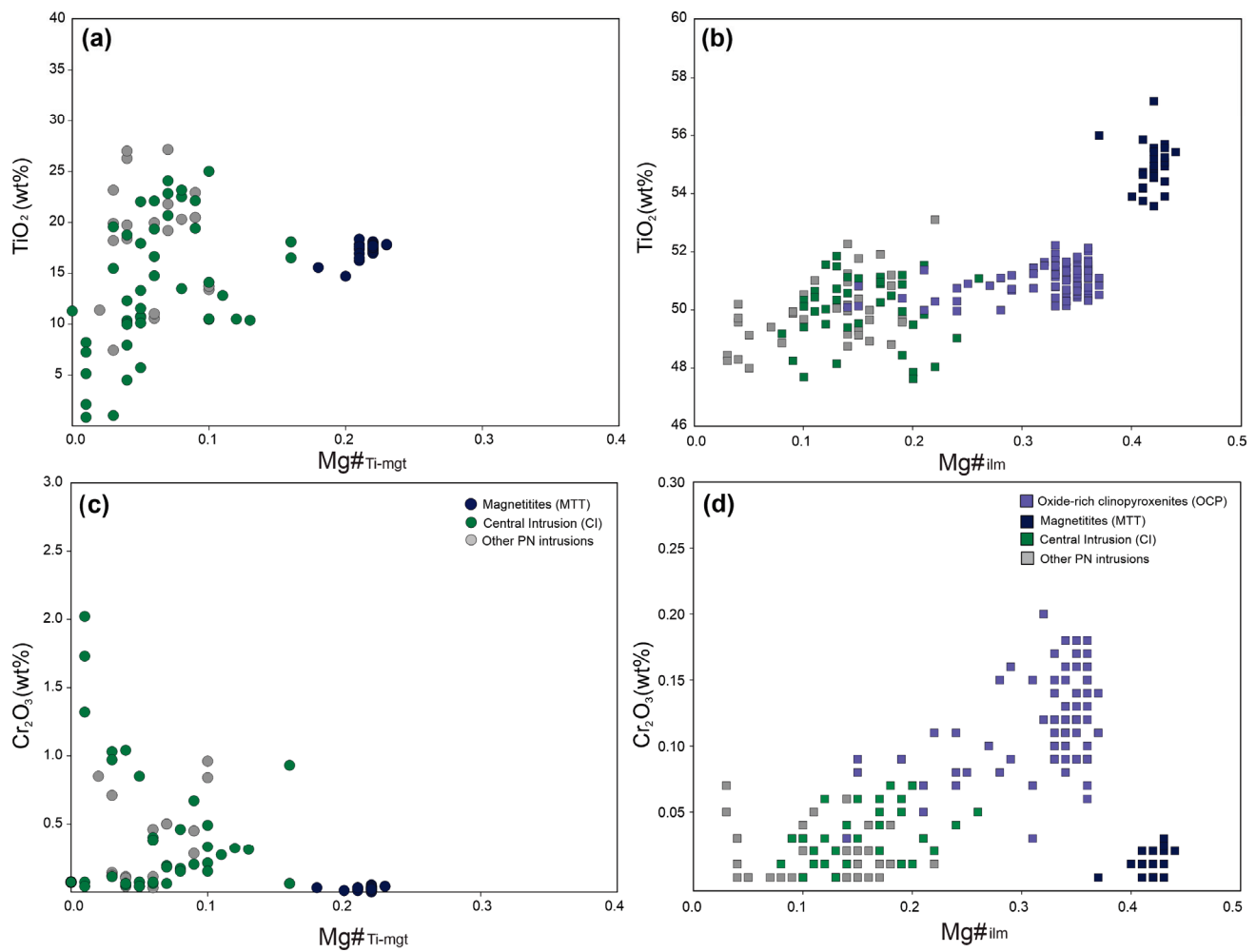


Figure 7. Mg# Fe-Ti oxides compositions vs. TiO_2 and Cr_2O_3 from OCP, MTT, CI and other PN intrusions. (a) Mg# vs. TiO_2 for Ti-magnetite populations. (b) Mg# vs. TiO_2 for ilmenite populations. (c) Mg# vs. Cr_2O_3 for Ti-magnetite populations. (d) Mg# vs. Cr_2O_3 for ilmenite populations.

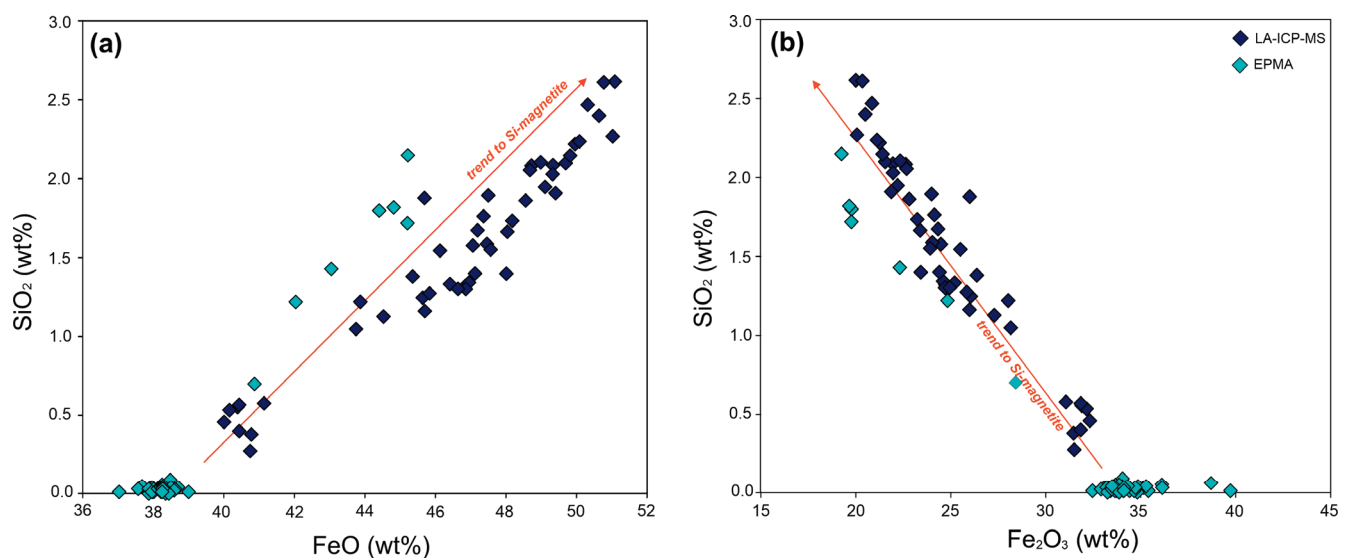


Figure 8. (a) SiO_2 vs. FeO (wt%) analyses of Ti-magnetite populations from MTT facies. (b) SiO_2 vs. Fe_2O_3 (wt%) analyses of Ti-magnetite populations from MTT facies. Results obtained in this study via laser ablation ICP-MS and electron microprobe (EPMA).

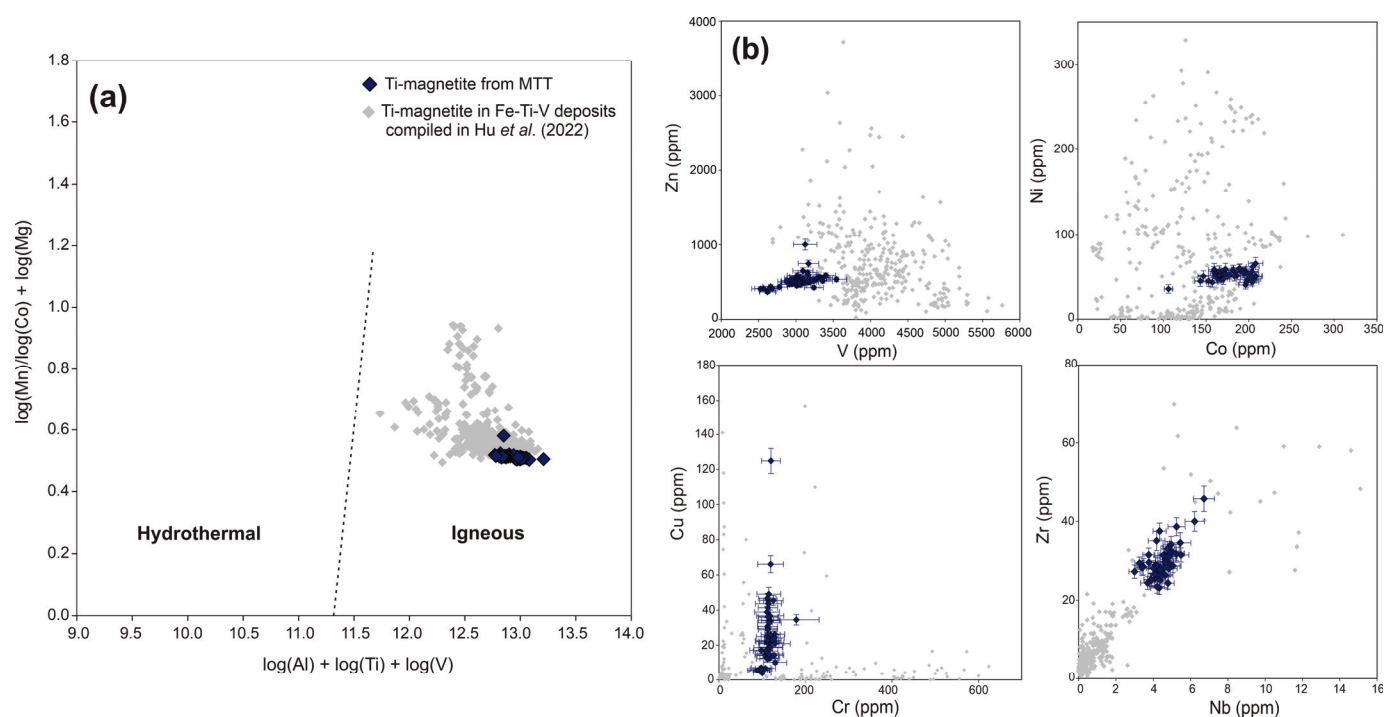


Figure 9. (a) Discriminant diagram of $\log(\text{Al}) + \log(\text{Ti}) + \log(\text{V})$ vs. $\log(\text{Mn})/[\log(\text{Co}) + \log(\text{Mg})]$ for Ti-magnetite from MTT facies and compiled data of Fe-Ti-V deposits, adapted from [51]. (b) Trace elements (ppm) diagrams for Ti-magnetite from MTT facies. Ti-magnetite compiled data from worldwide Fe-Ti-V deposits are presented for comparison [51].

4.2.3. Temperature and Oxygen Fugacity Conditions

Temperature (*solidus*, equilibrium) and oxygen fugacity conditions were estimated using magnetite-ilmenite pairs through the WinMlgob program [52] with calculations according to [53] and [54], respectively. Obtained pairs are considered to be in chemical equilibrium conditions as they passed a Mg/Mn partitioning test between magnetite and ilmenite (Figure 11a; [55]). The test assesses the quality of analytical data and determines whether Fe-Ti oxide pairs had their composition altered in post-magmatic processes. A total of 22 pairs from MTT, 13 pairs from CI and 10 pairs from other PN intrusions were obtained. The results show that temperatures from MTT pairs are between 769 and 886 °C and, therefore, equivalent to the CI distribution peak and range distribution within other PN intrusions (Figure 11b). Oxygen fugacity conditions ($f\text{O}_2$), plotted in a buffer generator [56], range from $f\text{O}_2 = -16$ to -13 , indicating a formation ambient controlled by the FMQ (fayalite–quartz–magnetite) buffer for magnetitites as well as most of the magnetite–ilmenite pairs from PN (Figure 11c). The results show a linear tendency for the MTT facies ($\Delta\text{FMQ} = -0.4$ to 0.5) within PN's range (Figure 11d).

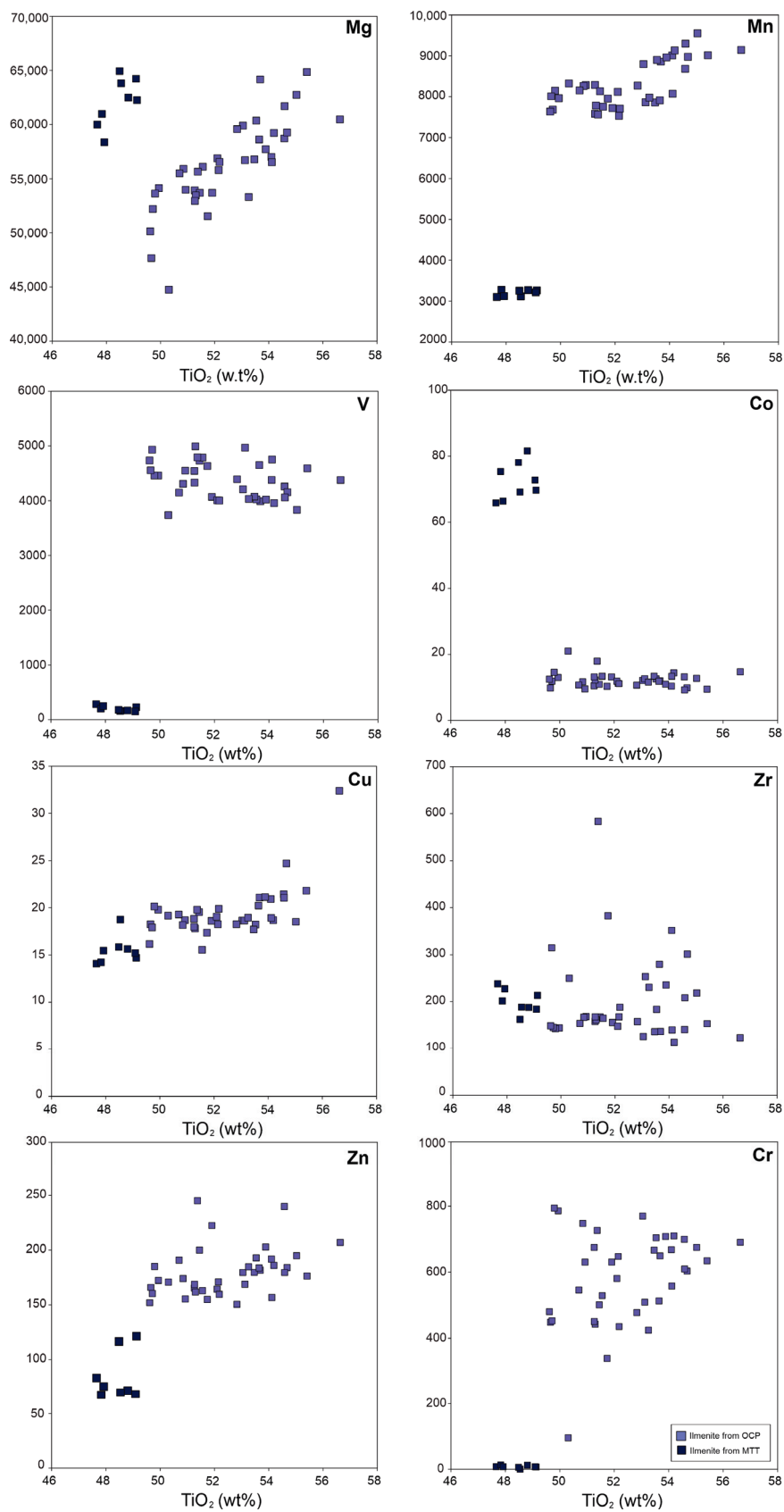


Figure 10. TiO_2 (wt%) vs. Mg, Mn, V, Co, Cu, Zr, Zn and Cr (ppm) contents of ilmenites from the OCP and MTT facies.

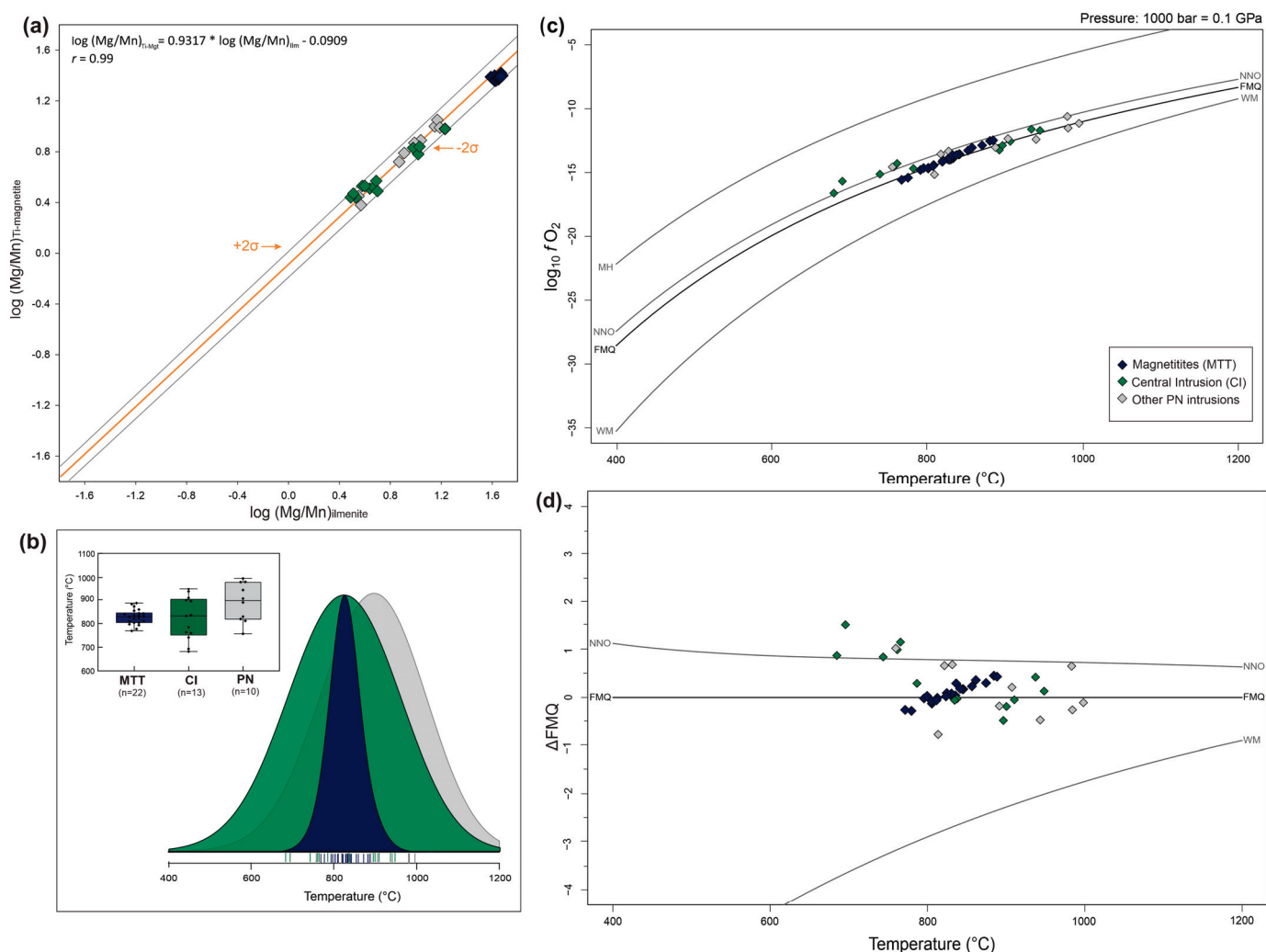


Figure 11. (a) Mg/Mn equilibrium test after [55] in magnetite–ilmenite pairs from PN. 2σ represents the standard deviation of the equilibrium line (in orange). (b) Kernel density estimation (KDE) and box plot diagrams for the obtained temperatures. Temperature estimation after [53]. (c) Temperature vs. oxygen fugacity of magnetite–ilmenite pairs from PN massif. (d) Temperature vs. ΔFMQ of magnetite–ilmenite pairs from PN massif. Oxygen fugacity estimation after [54]. Buffers were obtained in [56]. Abbreviations: MH—magnetite–hematite, NNO—nickel–nickel–oxide; FMQ—fayalite–magnetite–quartz; WM—wüstite–magnetite.

4.3. Whole-Rock Composition

4.3.1. Elemental Geochemistry

The magmatic evolution trend of PN intrusions is established through R_1 – R_2 indices (Figure 12a; [57]) with the most primitive lithotypes at the top and the most evolved ones at the bottom of the line. OCP is aligned with the massif evolution trend but subtly displaced to the right and close to the SiO_2 –saturation line. MTT, on the other hand, deviates from the geochemical behavior of the massif. Whole-rock behavior for OCP also indicates intermediate compositions between the average of PN clinopyroxene and Fe–Ti oxides mineral chemistry analyses, within the PN magmatic evolution trend, while MTT again diverges from the trend (Figure 12b).

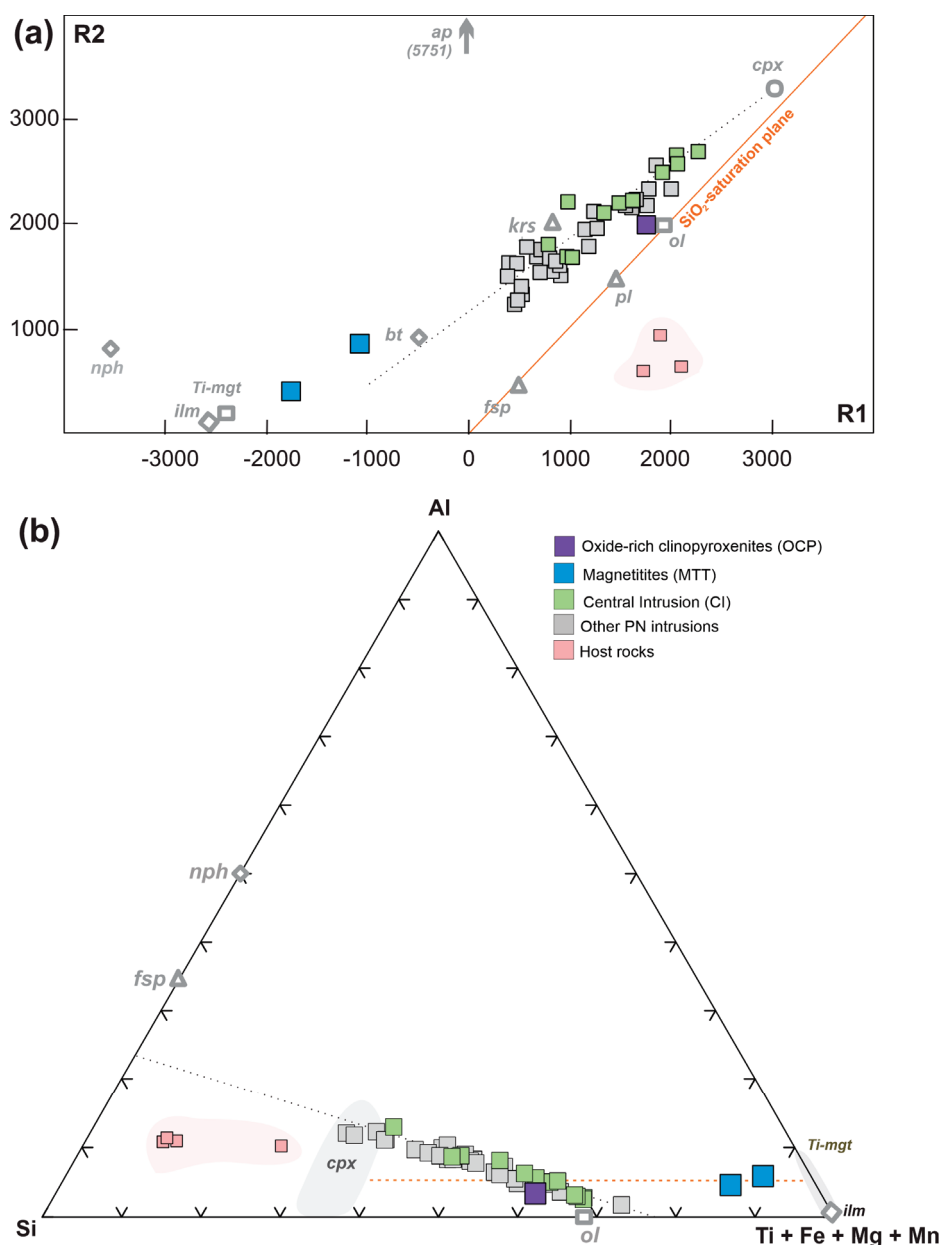


Figure 12. (a) R₁-R₂ diagram [57] for rocks from the PN massif and host rocks. Average mineral poles were compiled from [36] and are representative of the main assemblage found in PN (modified after [20]). (b) Al-Si-(Ti + Fe + Mg + Mn) ternary diagram for rocks from the PN massif and host rocks in molar proportions. Mineral chemistry data (in gray) for clinopyroxene and Fe-Ti oxides are from this work. Nepheline, feldspar and olivine compositions in the ternary are from their ideal formula. Abbreviations: cpx—clinopyroxene, Ti-mgt—Ti-magnetite, ol—olivine, ilm—ilmenite, nph—nepheline, fsp—alkali-feldspar, pl—plagioclase, ap—apatite, bt—biotite, krs—kaersutite.

Whole-rock results (Figure 13) highlight the TiO₂-rich nature of OCP (TiO₂: 7.81 wt%) and, especially, MTT (TiO₂: 15.36 and 17.87 wt%), as well as some CI hydrated lithotypes. Regarding trace element behavior, OCPs are enriched in transition elements, such as Co (220 ppm), Cu (391 ppm) and V (713 ppm), and they are depleted in Cr, Ni, Zr, Zn and Nb. MTT is enriched in Co (145–192 ppm), Cu (103–277 ppm) and Zn (398–492 ppm), besides presenting the highest values of V (1756–1834 ppm) in the massif. As OCPs, they are depleted in Zr (57.9–88.6 ppm) and Nb (5.36–7.16 ppm).

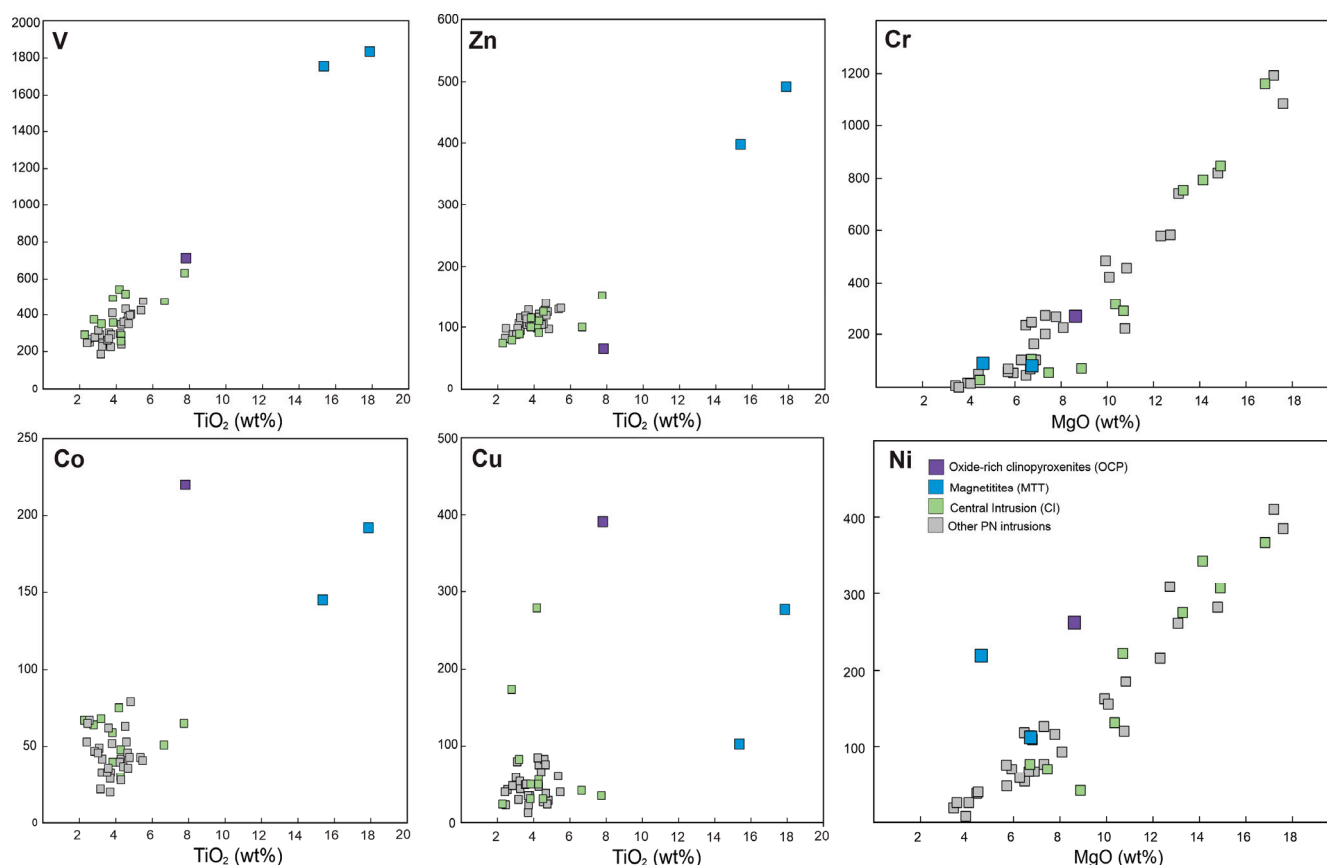


Figure 13. Bivariate diagrams of TiO_2 (wt%) vs. V, Zn, Co and Cu (ppm) from the PN massif rocks, and MgO (wt%) vs. Cr and Ni (ppm) from the PN massif rocks.

The MgO trend line (Figure 13) for these facies shows a compatible behavior for Cr and Ni. OCP exhibits higher MgO (8.62 wt%) compared to MTT (4.62 and 6.64, wt%) as well as a higher Cr value. Although the MgO contents differ in the two MTT samples, the Cr concentration remains relatively similar. For Ni, there is an enrichment in OCP and samples with lower MgO in MTT facies.

4.3.2. Sr Isotope Geochemistry

Geochemistry data of Sr isotopes were utilized to determine the $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratio from OCP and MTT (Figure 14). $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios in different lithotypes of PN massif show a variation predominantly between 0.7043 and 0.7064. The highest values correspond to monzonites ($^{87}\text{Sr}/^{86}\text{Sr}_i > 0.7060$; [36]) to the west-northwest and to south of the main exposure area. Lithotypes with the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values correspond to the Central Plug (CP) facies, one of the last magmatic activities of PN, while the lithotypes with highest $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios are more contaminated by the assimilation of crustal material from the host rocks ($^{87}\text{Sr}/^{86}\text{Sr}_i = 0.7150\text{--}0.7233$; [20]). OCP presents $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.7049$, similar to ratios found in CI's upper sequence or hydrated facies of the lower sequence of the same intrusion. MTT exhibits a $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratio (0.7047) between OCP and the CP facies.

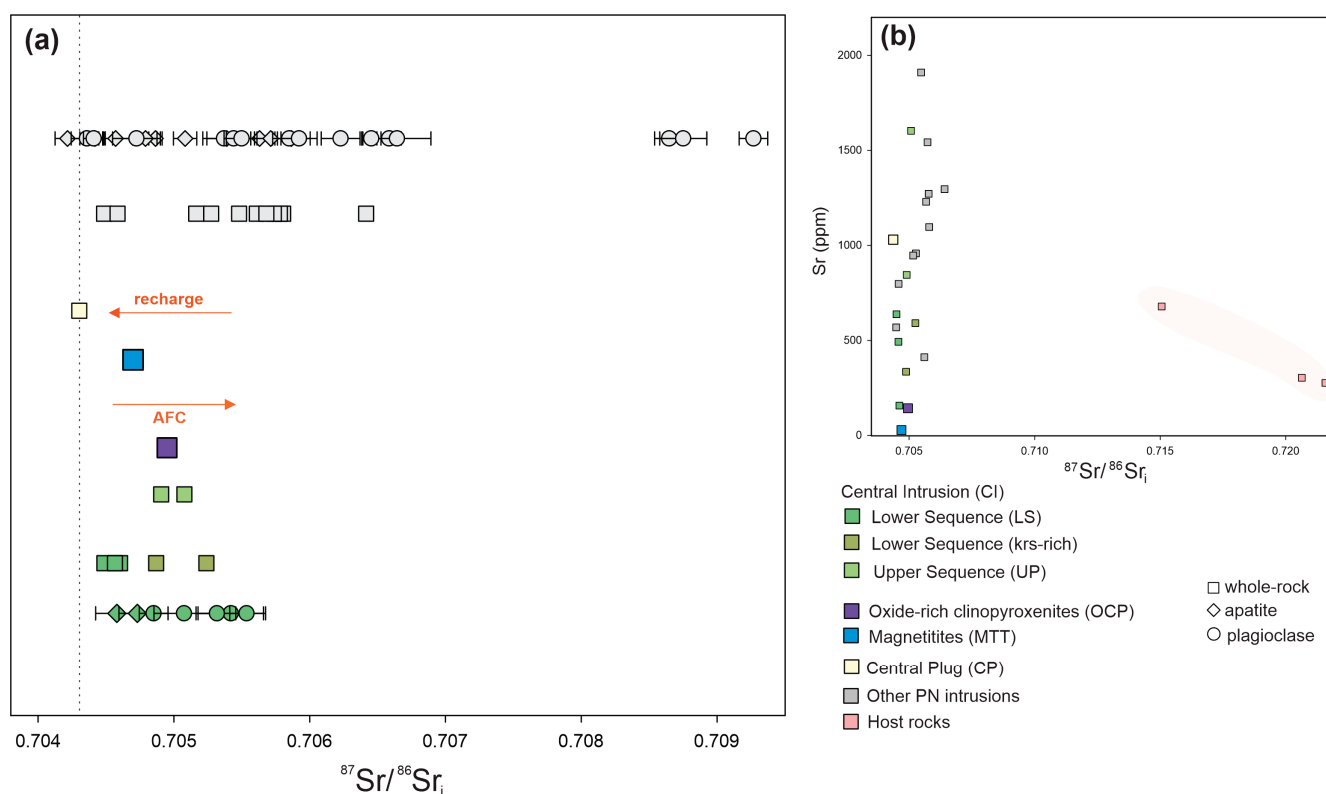


Figure 14. (a) $^{87}\text{Sr}/^{86}\text{Sr}_i$ of PN massif intrusions. Sr isotopes obtained in whole-rock, apatite and plagioclase analyses. (b) $^{87}\text{Sr}/^{86}\text{Sr}_i$ vs. Sr (ppm) from the PN massif rocks and host rocks. Compiled data from [20]. Abbreviations: AFC—assimilation + fractional crystallization.

4.4. X-ray Diffraction

X-ray data are consistent with chemical and petrographical results. In the MTT samples (Table 2), Ti-magnetite is the predominant phase, which is accompanied by minor quantities of ilmenite, spinel and varying amounts of Ti-bearing augite. In addition, anatase and goethite were also identified. The OCP (Figure 15) sample exhibits a more complex mineralogical composition, dominated by Ti-augite (67 wt%), alongside small proportions of diopside, ilmenite and pyrite. The presence of melantherite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in significant amounts and traces of rhomboclase ($(\text{H}_5\text{O}_2)\text{Fe}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$), both as alteration products of pyrite (Figure 2e–g), is noteworthy. Rietveld simulations used phases with chemical compositions similar to those observed in the samples. The refinement process accounted for sample height displacement, cell parameters, peak broadening, preferential orientation and thermal parameters. The substitution of Si in magnetite, up to 2.5 wt%, did not yield discernible shifts in its diffraction peaks.

Table 2. Mineralogical composition of magnetitite and oxide-rich clinopyroxenite samples determined by XRD_Rietveld method. GoF (Goodness of Fit) is a measure of the convergence of the calculated model toward the observed data (for details, see [58]).

	MTT		OCP
wt%	R118	SM82	R119
Ti-augite	2.0	25.7	68.7
Diopside			1.8
Ti-magnetite	84.2	63.6	

Table 2. Cont.

wt%	MTT		OCP
	R118	SM82	R119
Ilmenite	5.8	3.3	5.0
Anatase	0.9	0.5	
Spinel	5.1	4.3	
Goethite	1.9	2.6	
Pyrite			0.7
Melantherite			23.1
Rhomboclase			0.7
GoF	3.82	4.16	3.94

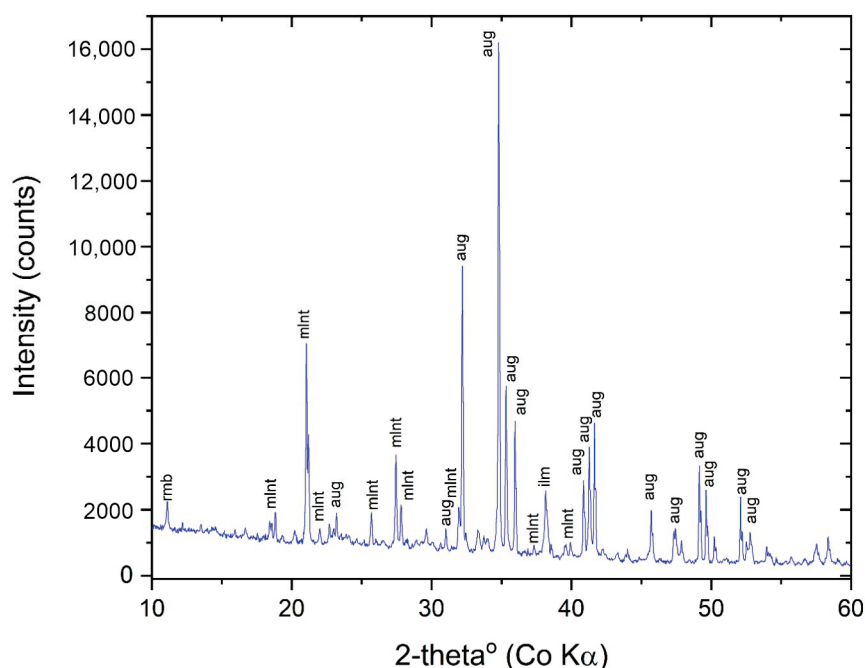


Figure 15. XRD diffractogram of the OCP facies. Abbreviations: rmb—rhomboclase, mlnt—melantherite, aug—augite, ilm—ilmenite.

5. Discussion

The processes responsible for the concentration of oxides in igneous rocks remain widely discussed in the literature (e.g., [8,59–63]) and involve a wide variety of geological, petrographic and compositional aspects. Several processes (both magmatic and hydrothermal) may be responsible for their formation and, although many mechanisms have been proposed, no single mechanism can explain all the different types of layering [14]. Some processes operate during the magma emplacement in the magma chamber, when the system is still predominantly liquid (e.g., [9,11,64]). Other processes act in response to magma convection patterns and/or to mechanical processes (e.g., [4]) or are responses of the magmatic system to intensive parameters (i.e., temperature, pressure, oxygen fugacity) variations (e.g., [62,63]). There are also processes occurring in the final stages of crystallization and during cooling (e.g., [65]). Recent studies indicate that high-temperature hydrothermal systems are able to precipitate high-Ti magnetite with ilmenite lamellae textures [51]. Many layers may have been formed from combinations of different processes (e.g., [66]).

Magnetite can be formed under diverse conditions, either crystallizing from silicate and sulfide melts at high temperatures or precipitating from hydrothermal fluids at lower temperatures [67]. Even though the Fe^{3+} -Si substitution observed in the MTT magnetite seems to be found in both magmatic and hydrothermal deposits (e.g., IOA deposits; [51]),

MTT chemical signatures are characteristically magmatic (Figure 9a) with trace elements contents coherent with Fe-Ti-V magmatic deposits data (Figure 9b). The observed enrichment in Zr and Nb, when compared to other Fe-Ti-V deposits, may be associated with the alkaline filiation of the PN complex, once magnetites from alkaline mafic-ultramafic intrusions are particularly enriched in these elements [68].

Petrographic and textural evidence indicate different magmatic crystallization stages for the Fe-Ti oxides of the studied PN lithotypes. The concentration of oxides in OCP occurs dispersedly between the clinopyroxene grains with the initial establishment of the cumulate fabric by clinopyroxene cores at an early stage, prior to the supersaturation, which is then followed by the continuous crystallization of clinopyroxene and ilmenite in the later stages. MTT facies do not display the same petrographic features recognized in OCP, besides the fact that the Fe-Ti oxides are evidently higher in volume. As magnetite corresponds to the main cumulus phase of MTT, the supersaturation in Fe-Ti oxides in this facies has occurred in a predominantly liquid context. Thus, it is suggested that the formation and accumulation of Ti-magnetite and ilmenite present in OCP and MTT rocks are associated with a particular process other than crystal-liquid fractionation and, yet, that both lithologies were not originated from the same process.

5.1. Crustal Contamination

Oxide supersaturation can occur in association with crustal assimilation processes, in which the interaction between the magmatic system and crustal felsic rocks forces the liquid out of its cotectic crystallization line toward the stability field of an oxide phase, consequently causing its unique crystallization [9,11]. PN host rocks are mainly metasyenogranites, metamonzogranites and biotite gneisses from the Serra da Água Limpá Batholith (645–630 Ma; [69]), with the latter being found especially in the northwestern contacts with PN [20]. The assimilation of crustal components, associated with the crystal-liquid fractionation of different magmatic pulses, has an important role in the evolution of the PN massif [20,22]. In this context, processes of crustal contamination could occur as a consequence of the interaction between the walls of the magma chamber and the adjacent host rock during magma ascent, as well as in the upper portions of the chamber, where the emplacement of magmatic material generates partial melting of the overlying supracrustal materials [20,22]. Direct evidence of such processes are registered in the various crustal xenoliths found in the most contaminated facies from PN.

Petrographic features such as the orientation and compaction of clinopyroxene grains (Figure 2a–c) and the presence of enclaves, as well as the stratigraphic level of OCP (Figure 1d), at the top of CI, suggest that the formation of this lithotype took place in the upper mush zones, near the upper magma chamber walls, where the assimilation of crustal contaminants from the partial melting of the crust would be favored. Evidence of crustal contamination are mainly found in the OCP facies, whose Sr isotopic ratio is equivalent to those found in considerably contaminated rocks from the upper sequence of CI and kaersutite-rich facies from PN (Figure 14). Sr isotopic signatures could also be affected by processes such as hydrothermal activity and mantle heterogeneities [70]. However, typically magmatic signatures observed in Ti-magnetite (Figure 9) suggest that the first scenario would not be plausible. Also, there are several limitations to discuss mantle source when dealing with a fossil magmatic chamber that present strong geological, petrographic and geochemical evidence of assimilation processes (e.g., [20,22]) OCP is also close to the SiO₂-saturation plane in the R₁-R₂ diagram, with whole-rock compositions close to highly contaminated rocks (Figure 12a). Additionally, the presence of acicular apatite is commonly related to assimilation events [71].

5.2. Magma Recharge

Mixing between partially differentiated and primitive liquids during episodes of magma chamber replenishment [9] is a viable model that explains Ti-magnetite supersaturation in MTT. Successive magmatic pulses of crystal-laden basanites characterize the

geometry and evolution of PN intrusions (e.g., [21,36,38]). The first studies on the OCP and MTT facies [36] proposed that both lithotypes could be associated with a new magmatic influx mixed with residual fractionated magma from a PN chamber. The magma recharge hypothesis is suggested by the geometry of these facies in the PN geological map (Figure 1c) where the rounded shape and arrangement of the body suggest a new pulse intruding the Central Intrusion. MTT has significantly less radiogenic Sr isotopic ratios than those from OCP and associated CI rocks, with values closer to those from the Central Plug facies (CP; Figure 14), which is located near the studied rocks and one of the last records of magmatic recharge of the massif. In this sense, the MTT presents MgO content slightly higher than that from CP, but lower from those from most PN rocks (Figure 13), which may be a further suggestion of hybridization of a new pulse when interacting with more evolved liquids. The arrival of a new pulse in a residual and evolved environment also explains the lower amount of silicate phases in MTT rocks. Similarly to the effect of crustal contamination on a primitive liquid, the interaction between the evolved magmatic system and new primitive batch of magma forces the liquid out of its cotectic crystallization line toward the stability field of an oxide phase (mainly Ti-magnetite), consequently causing its unique crystallization [9,11]. The authors of [22] also indicate a process of magmatic recharge, after the contamination process in the PN massif, through microanalytical isotopic approaches based on in situ analyses of alkali-feldspar crystals and contrasting compositions of crystal cores, intermediates and rims. Thus, for MTT facies, the interaction of a more evolved liquid resident in the magma chamber with a new, more primitive pulse could generate the expected Ti-magnetite supersaturation (e.g., [65]).

5.3. OCP and MTT Petrological Model

Previous works proposed a complex petrological model for the PN massif, highlighting the significant role of open-system processes [20,21,38]. Repeated influxes of antecryst-laden basanite magmas, possibly derived from the same magmatic reservoir, deposited their suspended crystals on the floor of an upper-crust magma chamber. In the initial stages of crystallization, crustal contamination processes occur due to the assimilation of xenoliths and partial melts from the surrounding host rock. Each PN intrusion is thus representative of relatively primitive magmas that had assimilated different degrees of partial melts of heterogeneous host rocks. The results of this study suggest that the accumulation of Fe-Ti oxides in the OCP facies occurred in a mush region and, therefore, is associated with the main pulse (Central Intrusion) evolution.

Clinopyroxene compositions from OCP are coherent with the complex plumbing system model proposed for PN massif by [38]. Clinopyroxene cores with higher Mg# resemble those described as antecrysts by [38], which were interpreted as formed in a deeper reservoir that fed the Ponte Nova massif. The more evolved cores determined in OCP, as well as the intermediates and rims with equivalent Mg#, crystallized in equilibrium with the magmatic system in lower pressure crystallization conditions.

Clinopyroxene grains are completely associated with CI evolution as well as the ilmenite inclusions in clinopyroxene (Figure 10) and other ilmenite crystals with the same chemical composition as PN (Figures 6b and 7b). The origin of a compositionally distinct Fe-Ti oxide population would be enabled by the assimilation of crustal contaminants in the mush region, generating a local disequilibrium and, thus, promoting the supersaturation. From the results obtained for the MTT facies, in turn, we propose that the Fe-Ti oxides (i.e., Ti-magnetite and ilmenite) from the MTT facies have its origin associated with the interaction of PN residual liquids and a more primitive one, characterizing a new pulse in PN magmatic evolution.

The proposed unified model (Figure 16), therefore, consists of the following stages: (1) establishment of the cumulate framework in the mush zone of PN's upper walls, with consequent heat loss to its host rocks and eventual assimilation of partially melted crustal components; (2) Fe-Ti oxide supersaturation triggered by crustal assimilation, forming OCP; (3) subsequent to OCP, in the final stages of crystallization, a new episode of magma

recharge forming MTT; (4) the eventual erosion of the uppermost sequences of PN, exposing the lithologies approached in this study.

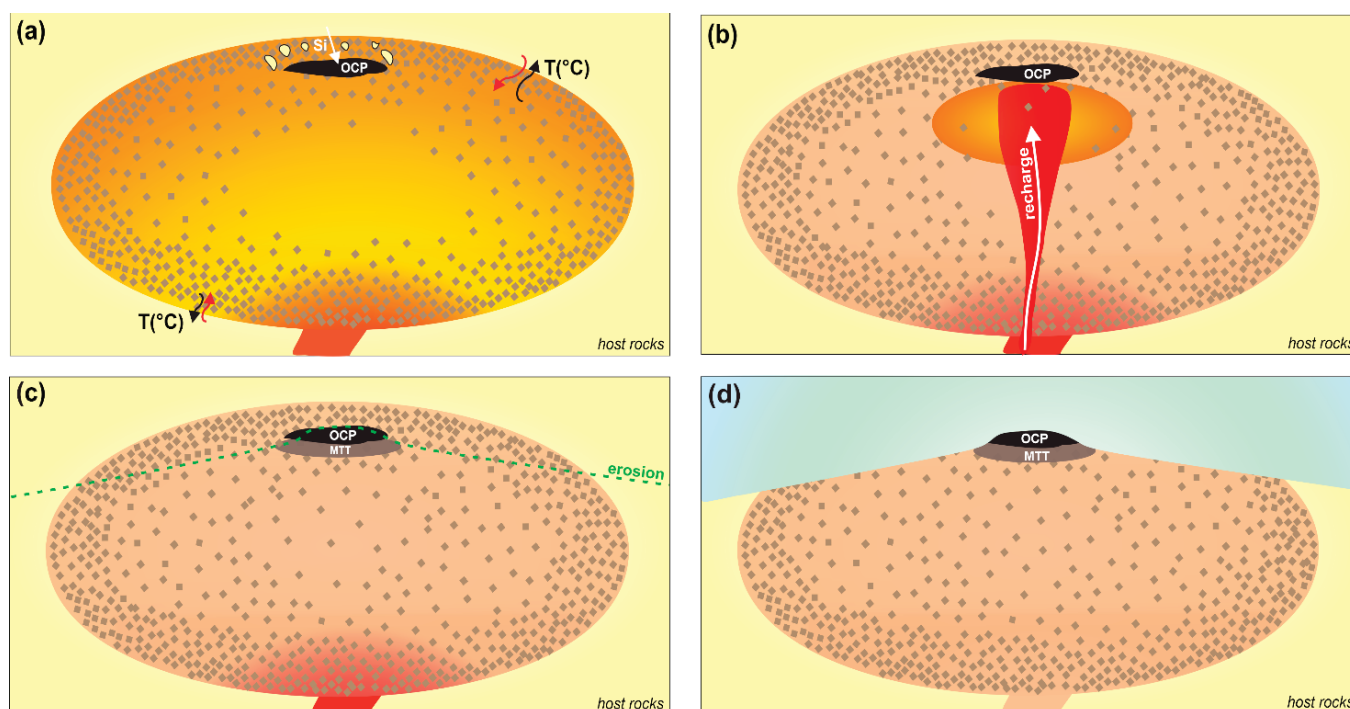


Figure 16. Schematic model for the proposed origin to OCP and MTT facies. (a) Assimilation of partially melted crustal components into the Central Intrusion upper walls, leading to the displacement of the crystallization cotectic into the oxide phase and formation of OCP facies. (b) In the final stages of crystallization, and after the formation of OCP facies, a new episode of magma recharge in the PN massif. (c) Displacement of crystallization cotectic into the oxide phase due to the interaction of primitive and evolved liquids during a magma recharge episode, forming the MTT facies. (d) Eventual erosion of the uppermost sequences of PN, exposing the lithologies approached in this study.

Regarding imprints of post-magmatic processes on the studied rocks, the absolute absence of magnetite in OCP is unusual (e.g., [8,60–63,66]). The minerals composing the interstitial assembly consist exclusively of the ilmenite–sulfide pair or just ilmenite. Ilmenite crystals, in turn, exhibit various degrees of corrosion (Figure 3e–h), suggesting that post-magmatic reactions may have affected the rock. Ti-magnetite is unstable in the presence of sulfur-rich fluids and reducing conditions of oxygen fugacity [72,73]. Equilibrium processes within the oxide structure tend to remove Ti contents from magnetite to ilmenite according to the following equilibrium:



From the reaction, typical ilmenite trellis lamellae would be formed. With continued cooling (approximately 300 °C; [74]), the interaction with hydrothermal S-rich fluids would cause the ilmenite to be incipiently corroded and unstable magnetite to be completely replaced by sulfides (mainly pyrite and chalcopyrite). The elongated ilmenite crystals, often acicular as oriented orthogonally, would therefore represent relict features. The greater presence of sulfides evidently associated with veins and fractured domains in the cumulate framework, i.e., regions with the possibility of fluid percolation, supports this hypothesis. The absence of magnetite hampers to estimate temperature and $f\text{O}_2$ conditions for the OCP facies. However, studies estimate that the conditions in which oxi-exsolution would occur start at 700 °C and QFM ~ 0.5 [73], which are values consistent with those obtained for MTT and within the estimated variation range of PN massif (Figure 11).

6. Conclusions

Based on petrography, mineral chemistry, whole-rock geochemistry and radiogenic isotopic ratios, we conclude that the Fe-Ti-oxide-rich facies of the PN massif are formed in an open-system environment. However, OCP and MTT originated in different stages of the chamber evolution, and they are representative of distinct open-system processes. OCPs are formed as a consequence of the assimilation of crustal contaminants in the upper levels of the PN chamber, which is a process also registered in marginal facies of the massif. For MTT, we propose that magma recharge would be a more appropriate model to justify the observed Ti-magnetite and ilmenite supersaturation. This mechanism is consistent with our preferred model for the entire massif, which considers repeated influxes of antecryst-laden basanite magmas in a shallow magma chamber.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14070724/s1>. Supplementary Materials S1—Major element compositions of clinopyroxene and Fe-Ti oxides from the Ponte Nova massif. Table S1. Analytical parameters and calibration standards used for WDS analyses of clinopyroxene, Ti-magnetite and ilmenite. Table S2. Major element compositions in mass% of clinopyroxene from the OCP and MTT facies. Structural formula calculated on the basis of 6 oxygens. Table S3. Major element compositions in mass% of Ti-magnetite from the Ponte Nova massif. Structural formula calculated on the basis of 32 oxygens. Table S4. Major element compositions in mass% of ilmenite from the Ponte Nova massif. Structural formula calculated on the basis of 6 oxygens. Table S5. Temperature and oxygen fugacity estimations obtained in magnetite-ilmenite pairs utilizing the WINMIGob software (version 1.0.7) [52]. Supplementary Materials S2—LA-ICP-MS analyses of Fe-Ti oxides from OCP and MTT facies. Table S6. Trace element compositions for BCR-2G (USGS) calibration (primary) standard used for routines of trace elements analyses. Recommended values are from [75]. Table S7. Trace element compositions for BIR-1G quality-control monitor (reference materials) used for routines of trace element analyses. Recommended values are from [75]. Table S8. Trace element compositions of Ti-magnetite from the MTT facies. Table S9. Trace element composition compositions of ilmenite from OCP and MTT facies. Supplementary Materials S3—Table S10. Elemental geochemical analyses (whole-rock and Sr isotopes) from the OCP and MTT facies.

Author Contributions: Conceptualization, R.G.A. and L.C.; investigation, A.A.d.S., R.G.A., L.C. and L.M.C.T.; data curation, A.A.d.S., R.G.A., L.C., L.M.C.T., F.R.D.d.A., J.V.M., E.R. and C.d.B.G.; writing—original draft preparation, A.A.d.S., R.G.A., L.C., L.M.C.T. and F.R.D.d.A.; writing—review and editing, A.A.d.S., R.G.A., L.C., L.M.C.T., F.R.D.d.A., J.V.M., E.R. and C.d.B.G.; visualization, A.A.d.S. and R.G.A.; project administration, R.G.A.; funding acquisition, R.G.A. and E.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by grants from Brazilian Agencies: FAPESP (Procs. 2019/22084-8; 2023/11675-0) and Brazilian National Research Council CNPq for research and productivity grants (404020/2021-6, 310055/2021-0).

Data Availability Statement: All data are included within the article.

Acknowledgments: CAPES is acknowledged for the post-graduate scholarship for A.A.S. and L.M.C.T. L.C. Thanks FAPESP for the postdoctoral fellowship (process 23/12323-0). We thank the analytical support of the technicians of the laboratories of GeoAnalítica-USP and LCT-USP facilities.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Cawthorn, R.G. *Layered Intrusions, Developments in Petrology*; Elsevier: Amsterdam, The Netherlands, 1996.
2. Latypov, R.M.; Namur, O.; Bai, Y.; Barnes, S.J.; Chistyakova, S.Y.; Holness, M.B.; Iacono-Marziano, G.; Kruger, W.A.J.; O'Driscoll, B.; Smith, W.D.; et al. Layered intrusions: Fundamentals, novel observations and concepts, and controversial issues. *Earth-Sci. Rev.* **2024**, *249*, 104653. [CrossRef]
3. Lee, C.A. A review of mineralization in the Bushveld Complex and some other layered intrusions. In *Layered Intrusions*; Cawthorn, R.G., Ed.; Elsevier Science B.V.: Amsterdam, The Netherlands, 1996; pp. 103–145. [CrossRef]
4. Yao, Z.; Mungall, J.E. Magnetite layer formation in the Bushveld complex of South Africa. *Nat. Commun.* **2022**, *13*, 146. [CrossRef] [PubMed]

5. Namur, O.; Higgins, M.D.; Vander Auwera, J. The Sept Iles intrusive suite, Quebec, Canada. In *Layered Intrusions*; Charlier, B., Namur, O., Latypov, R., Tegner, C., Eds.; Springer: Dordrecht, The Netherlands, 2015; pp. 465–515. [CrossRef]
6. Duchesne, J.-C.; Charlier, B. Geochemistry of cumulates from the Bjerkreim–Sokndal layered intrusion (S. Norway). Part I: Constraints from major elements on the mechanism of cumulate formation and on the jotunite liquid line of descent. *Lithos* **2005**, *83*, 229–254. [CrossRef]
7. Zhou, M.F.; Robinson, P.T.; Lesher, C.M.; Keays, R.R.; Zhang, C.J.; Malpas, J. Geochemistry, petrogenesis and metallogenesis of the Panzhihua gabbroic layered intrusion and associated Fe–Ti–V oxide deposits, Sichuan Province, SW China. *J. Petrol.* **2005**, *46*, 2253–2280. [CrossRef]
8. Chen, X.D.; Li, Y.G.; Luo, Z.H.; Fei, G.C.; Luo, W.; Zhang, T.J.; Peng, X.C.; Zou, Y.S. Formation of Fe–Ti oxide and Ni–Co sulfide ores by concentric tube flow and hydrous melt-rich recharge into the cooling crystal mush: Example from the Hongge intrusion in Panxi region, SW China. *Ore Geol. Rev.* **2023**, *160*, 105594. [CrossRef]
9. Irvine, T.N. Origin of chromitite layers in the Muskox intrusion and other stratiform intrusions: A new interpretation. *Geology* **1977**, *5*, 273–277. [CrossRef]
10. Ganino, C.; Arndt, N.T.; Zhou, M.-F.; Gaillard, F.; Chauvel, C. Interaction of magma with sedimentary wall rock and magnetite ore genesis in Panzhihua mafic intrusion, SW China. *Mineral. Depos.* **2008**, *43*, 677–694. [CrossRef]
11. Irvine, T.N. Crystallization sequences in the Muskox intrusions and other layered intrusions: II Origin of chromitite layers and similar deposits of other magmatic ores. *Geochim. Cosmochim. Acta* **1975**, *39*, 991–1008. [CrossRef]
12. Charlier, B.; Namur, O.; Toplis, M.J.; Schiano, P.; Cluzel, N.; Higgins, M.D.; Vander Auwera, J. Large-scale silicate liquid immiscibility during differentiation of tholeiitic basalt to granite and the origin of the Daly gap. *Geology* **2011**, *39*, 907–910. [CrossRef]
13. Namur, O.; Charlier, B.; Holness, M.B. Dual origin of Fe–Ti–P gabbros by immiscibility and fractional crystallisation of evolved tholeiitic basalts in the Sept Iles layered intrusion. *Lithos* **2012**, *154*, 100–114. [CrossRef]
14. Naslund, H.R.; McBirney, A.R. Mechanisms of formation of Igneous Layering. In *Layered Intrusions*; Cawthorn, R.G., Ed.; Elsevier Science B.V: Amsterdam, The Netherlands, 1996; pp. 1–43. [CrossRef]
15. Derby, O.A. On the magnetite ore districts of Jacupiranga and Ipanema, São Paulo, Brazil. *Am. J. Sci.* **1891**, *41*, 311–321. [CrossRef]
16. Krasnova, N.I.; Petrov, T.G.; Balaganskaya, E.G.; Garcia, D.; Moutte, J.; Zaitsev, A.N.; Wall, F. Introduction to phoscorites: Occurrence, composition, nomenclature and petrogenesis. In *Phoscorites and Carbonatites from Mantle to Mine: The Key Example of the Kola Alkaline Province*; Wall, F., Zaitsev, A.N., Eds.; Mineralogical Society Series; Mineralogical Society of Great Britain & Ireland: Middlesex, UK, 2004; pp. 45–79.
17. Mikhailova, J.A.; Kalashnikov, A.O.; Sokharev, V.A.; Pakhomovsky, Y.A.; Konopleva, N.G.; Yakovenchuk, V.N.; Bazai, A.V.; Gor’yanov, P.; Ivanyuk, G.Y. 3D mineralogical mapping of the Kovdor phoscorite–carbonatite complex (Russia). *Miner. Depos.* **2016**, *51*, 131–149. [CrossRef]
18. Azzone, R.G.; Ruberti, E.; Enrich, G.E.R.; Gomes, C.B. Geologia e geocronologia do maciço alcalino máfico-ultramáfico Ponte Nova (SP-MG). *Geol. USP—Série Científica* **2009**, *9*, 26–46. [CrossRef]
19. Riccomini, C.; Velásquez, V.F.; Gomes, C.B. Tectonic controls of the Mesozoic and Cenozoic alkaline magmatism in the central-southeastern Brazilian Platform. In *Mesozoic to Cenozoic Alkaline Magmatism in the Brazilian Platform*; Comin-Chiaramonti, P., Gomes, C.B., Eds.; Edusp/Fapesp: São Paulo, Brazil, 2005; pp. 31–56.
20. Azzone, R.G.; Munoz, P.M.; Enrich, G.E.R.; Alves, A.; Ruberti, E.; Gomes, C.B. Petrographic, geochemical and isotopic evidence of crustal assimilation processes in the Ponte Nova alkaline mafic-ultramafic massif, SE Brazil. *Lithos* **2016**, *260*, 58–75. [CrossRef]
21. Azzone, R.G.; Chmyz, L.; Guarino, V.; Alves, A.; Gomes, C.B.; Ruberti, E. Isotopic clues tracking the open-system evolution of the Ponte Nova mafic-ultramafic alkaline massif, SE Brazil: The contribution of Pb isotopes. *Geochemistry* **2020**, *80*, 125648. [CrossRef]
22. Ambrosio, M.R. The Crustal Assimilation in Alkaline Basic Magmas: The Ponte Nova Mafic-Ultramafic Massif and Dikes/Plugs of the Mantiqueira Range (SP-MG). Doctoral Thesis, University of São Paulo, Institute of Geosciences, São Paulo, Brazil, 2022. [CrossRef]
23. Vaz, O.R.S.; Salomão, M.; Pedroso, E.; Pereira, R.; Neumann, R.; Garcia, P.; Tupinambá, M. Magnetita vanadifera do Maciço Ponte Nova: Uma Abordagem Exploratória. *Anu. Inst. Geociênc.—UFRJ* **2017**, *40*, 75–81. [CrossRef]
24. de Almeida, F.F.M. Relações tectônicas das rochas alcalinas mesozóicas da região meridional da plataforma sul-americana. *Rev. Bras. Geociênc.* **1983**, *13*, 139–158. [CrossRef]
25. de Almeida, F.F.M. Distribuição regional e relações tectônicas do magmatismo pós-paleozoico no Brasil. *Rev. Bras. Geociênc.* **1986**, *16*, 325–349. [CrossRef]
26. Morbidelli, L.; Gomes, C.B.; Beccaluva, L.; Brotzu, P.; Conte, A.M.; Ruberti, E.; Traversa, G. Mineralogical, petrological and geochemical aspects of alkaline and alkaline-carbonatite associations from Brazil. *Earth Sci. Rev.* **1995**, *39*, 135–168. [CrossRef]
27. Beccaluva, L.; Barbieri, M.; Born, H.; Brotzu, P.; Coltorti, M.; Conte, A.; Garbarino, C.; Gomes, C.B.; Macciotta, G.; Morbidelli, L.; et al. Fractional crystallization and liquid immiscibility processes in the alkaline-carbonatite complex of Juquiá, São Paulo, Brazil. *J. Petrol.* **1992**, *33*, 1371–1404. [CrossRef]
28. Ruberti, E.; Gomes, C.B.; Comin-Chiaramonti, P. The alkaline magmatism from the Ponta Grossa arch. In *Mesozoic to Cenozoic Alkaline Magmatism in the Brazilian Platform*; Comin-Chiaramonti, P., Gomes, C.B., Eds.; Edusp/Fapesp: São Paulo, Brazil, 2005; pp. 473–521.

29. Herz, N. Timing of spreading in the South Atlantic: Information from Brazilian alkalic rocks. *Geol. Soc. Am. Bull.* **1977**, *88*, 101–112. [CrossRef]
30. Ulbrich, H.H.G.J.; Gomes, C.B. Alkaline rocks from continental Brazil. *Earth-Sci. Rev.* **1981**, *17*, 135–154. [CrossRef]
31. Brotzu, P.; Barbieri, M.; Beccaluva, L.; Garbarino, C.; Gomes, C.B.; Macciotta, G.; Melluso, L.; Morbidelli, L.; Ruberti, E.; Sígolo, J.B.; et al. Petrology and geochemistry of the Passa Quatro alkaline complex (MG-SP-RJ), Brazil. *J. S. Am. Earth Sci.* **1992**, *4*, 237–252. [CrossRef]
32. Brotzu, P.; Gomes, C.; Melluso, L.; Morbidelli, L.; Morra, V.; Ruberti, E. Petrogenesis of coexisting SiO₂-undersaturated to SiO₂-oversaturated felsic igneous rocks: The alkaline complex of Itatiaia, southeastern Brazil. *Lithos* **1997**, *40*, 133–156. [CrossRef]
33. Ulbrich, H.H.G.J.; Vlach, S.R.F.; Demaiffe, D.; Ulbrich, M.N.C. Structure and origin of the Poços de Caldas Alkaline Massif, SE Brazil. In *Mesozoic to Cenozoic Alkaline Magmatism in the Brazilian Platform*; Comin-Chiaramonti, P., Gomes, C.B., Eds.; Edusp/Fapesp: São Paulo, Brazil, 2005; pp. 367–418.
34. Bellieni, G.; Montes Lauer, C.R.; De Min, A.; Piccirillo, E.M.; Cavazzini, G.; Melfi, A.J.; Pacca, I.G. Early and Late Cretaceous magmatism from São Sebastião Island (SE-Brazil): Geochemistry and petrology. *Geochim. Bras.* **1990**, *4*, 59–83.
35. Enrich, G.E.R.; Ruberti, E.; Gomes, C.B. Geology and geochronology of Monte de Trigo island alkaline suite, southeastern Brazil. *Rev. Bras. Geociênc.* **2009**, *39*, 67–80. [CrossRef]
36. Azzone, R.G. Petrogênese do Maciço Alcalino Máfico-Ultramáfico Ponte Nova (SP-MG). Doctoral Thesis, University of São Paulo, Institute of Geosciences, São Paulo, Brazil, 2008. [CrossRef]
37. Azzone, R.G.; Ruberti, E.; Enrich, G.E.R.; Gomes, C.B. Zr- and Ba-rich minerals from the Ponte Nova alkaline mafic-ultramafic massif, southeastern Brazil: Indication of an enriched mantle source. *Can. Mineral.* **2009**, *47*, 1087–1103. [CrossRef]
38. Azzone, R.G.; Tarazona, L.M.C.; Ambrosio, M.R.; Guarino, V.; Chmyz, L.; Lima, N.M.; Ruberti, E. The Hidden Magmatic Chamber from the Ponte Nova Mafic-Ultramafic Alkaline Massif, SE. Brazil: Clues from Clinopyroxene and Olivine Antecrysts. *Minerals* **2022**, *12*, 775. [CrossRef]
39. Bastin, G.F.; Van Loo, F.J.J.; Heijligers, H.J.M. Evaluation and use of gaussian $\phi(\rho z)$ curves in quantitative electron probe microanalysis: A new optimization. *X-ray Spectrom.* **1984**, *13*, 91–97. [CrossRef]
40. Deer, W.A.; Howie, R.A.; Zussman, J. *An Introduction to the Rock-Forming Minerals*, 2nd ed.; Longman Scientific & Technical: London, UK, 1992.
41. Morimoto, N. Nomenclature of pyroxenes. *Mineral. Petrol.* **1988**, *39*, 55–76. [CrossRef]
42. Droop, G.T.R. A general equation for estimating Fe³⁺ concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. *Mineral. Mag.* **1987**, *51*, 431–435. [CrossRef]
43. Carmichael, I.S.E. The iron-titanium oxides of salic volcanic rocks and their associated ferromagnesian silicates. *Contrib. Mineral. Petrol.* **1967**, *14*, 36–64. [CrossRef]
44. Griffin, W.L. GLITTER: Data reduction software for laser ablation ICP-MS. In *Laser Ablation ICP-MS in the Earth Sciences*; Sylvester, P., Ed.; Short Course Series; Mineralogical Association of Canada: Ottawa, ON, Canada, 2008; pp. 308–311.
45. Mori, P.E.; Reeves, S.; Correia, C.T.; Haukka, M. Development of a fused glass disc XRF facility and comparison with the pressed powder pellet technique at Instituto de Geociências, São Paulo University. *Rev. Bras. Geociênc.* **1999**, *29*, 441–446. [CrossRef]
46. Navarro, M.S.; Andrade, S.; Ulbrich, H.H.G.J.; Girardi, V.A.V. The analysis of rare earth elements with ICP-MS in basaltic and related rocks: Testing the efficiency of sample decomposition procedures. *Geostand. Geoanal. Res.* **2008**, *32*, 167–180. [CrossRef]
47. Torquato, J.R.; Kawashita, K. Geologia nuclear—O método Rb/Sr. *Rev. Geol.* **1994**, *7*, 91–123.
48. Sato, K.; Tassinari, C.C.G.; Kawashita, K.; Petronilho, L. O método geocronológico Sm-Nd no IG/USP e suas aplicações. *An. Acad. Bras. Ciênc.* **1995**, *67*, 313–336.
49. Doebelin, N.; Kleeberg, R. Profex: A graphical user interface for the Rietveld refinement program BGMN. *J. Appl. Crystallogr.* **2015**, *48*, 1573–1580. [CrossRef] [PubMed]
50. Gražulis, S.; Chateigner, D.; Downs, R.T.; Yokochi, A.F.T.; Quirós, M.; Lutterotti, L.; Le Bail, A. Crystallography Open Database—an open-access collection of crystal structures. *J. Appl. Crystallogr.* **2009**, *42*, 726–729. [CrossRef] [PubMed]
51. Hu, B.; Zeng, L.-P.; Liao, W.; Wen, G.; Hu, H.; Li, M.Y.H.; Zhao, X.-F. The Origin and Discrimination of High-Ti Magnetite in Magmatic-Hydrothermal Systems: Insight from Machine Learning Analysis. *Econ. Geol.* **2022**, *117*, 1613–1627. [CrossRef]
52. Yavuz, F. WinMlgob: A Windows program for magnetite-ilmenite geothermometer and oxygen barometer. *J. Geosci.* **2021**, *66*, 51–69. [CrossRef]
53. Ghiorso, M.S.; Evans, B.W. Thermodynamics of rhombohedral oxide solid solutions and a revision of the Fe-Ti two-oxide geothermometer and oxygen-barometer. *Am. J. Sci.* **2008**, *308*, 957–1039. [CrossRef]
54. Sauerzapf, U.; Lattard, D.; Buchard, M.; Engelmann, R. The Titanomagnetite-Ilmenite equilibrium: New Experimental Data and Thermo-oxybarometric Application to the Crystallization of Basic to Intermediate Rocks. *J. Petrol.* **2008**, *49*, 1161–1185. [CrossRef]
55. Bacon, C.R.; Hirschmann, M.M. Mg/Mn partitioning as a test for equilibrium between Fe-Ti oxides. *Am. Mineral.* **1988**, *73*, 57–61.
56. Anenburg, M. Oxygen Fugacity Buffer Calculator. 2021. Available online: <https://fo2.rses.anu.edu.au/fo2app/> (accessed on 25 July 2023).
57. De la Roche, H.; Leterrier, J.; Grandclaude, P.; Marchal, M. A classification of volcanic and plutonic rocks using R1-R2 diagram and major-element analyses—Its relationships with current nomenclature. *Chem. Geol.* **1980**, *29*, 183–210. [CrossRef]
58. Toby, B.H. R factors in Rietveld analysis: How good is good enough? *Powder Diffr.* **2006**, *21*, 67–70. [CrossRef]

59. Wang, K.; Wang, C.Y.; Ren, Z.Y. Apatite-hosted melt inclusions from the Panzhihua gabbroic-layered intrusion associated with a giant Fe-Ti oxide deposit in SW China: Insights for magma unmixing within a crystal mush. *Contrib. Mineral. Petrol.* **2018**, *173*, 59. [CrossRef]
60. Khedr, M.Z.; Takazawa, E.; Arai, S.; Stern, R.J.; Morishita, T.; El-Awady, A. Styles of Fe-Ti-V ore deposits in the Neoproterozoic layered mafic-ultramafic intrusions, south Eastern Desert of Egypt: Evidence for fractional crystallization of V-rich melts. *J. Afr. Earth Sci.* **2022**, *194*, 104620. [CrossRef]
61. Mokchah, N.; Mathieu, L. Origin and evolution of the iron-rich upper unit and Fe-Ti-V mineralization of the Neoarchean Lac Doré Layered Intrusion, Chibougamau, Québec. *J. Petrol.* **2022**, *63*, egac006. [CrossRef]
62. Shu, X.J.; Wang, X.L.; Chen, L.; Wang, D.; Dai, Z.Y. Open-system differentiation of mafic magmas before the formation of layered Fe-Ti(V) deposits in Southeast China. *Ore Geol. Rev.* **2023**, *158*, 105527. [CrossRef]
63. Wang, M.; Zhang, Q.; Li, Z.; Wang, J.; Wang, J. In situ crystallization of Fe-Ti oxides in the Bijigou layered intrusion: Insights from crystal size distributions and compositions of magnetite and ilmenite. *J. Asian Earth Sci.* **2023**, *255*, 105773. [CrossRef]
64. Spandler, C.; Mavrogenes, J.; Arculus, R. Origin of chromitites in layered intrusions: Evidence from chromite-hosted melt inclusions from the Stillwater complex. *Geology* **2005**, *33*, 893–896. [CrossRef]
65. Boudreau, A.E. The Stillwater Complex—Overview and the significance of volatiles. *Mineral. Mag.* **2016**, *80*, 585–637. [CrossRef]
66. Tornos, F.; Hanchar, J.M.; Steele-Macinnis, M.; Crespo, E.; Kamenetsky, V.S.; Casquet, C. Formation of magnetite-(apatite) systems by crystallizing ultrabasic iron-rich melts and slag separation. *Miner. Depos.* **2023**, *59*, 189–225. [CrossRef]
67. Dare, S.A.S.; Barnes, S.J.; Beaudoin, G.; Méric, J.; Boutroy, E.; Potvin-Doucet, C. Trace elements in magnetite as petrogenetic indicators. *Miner. Depos.* **2014**, *49*, 785–796. [CrossRef]
68. Wang, Z.C.; Huang, X.W.; Liu, P.P.; Zhou, M.F. Trace element systematics of magnetite from alkaline mafic-ultramafic intrusions of the Permian Emeishan large igneous province, SW China. *Contrib. Mineral. Petrol.* **2024**, *179*, 8. [CrossRef]
69. Vinagre, R.; Trouw, R.A.J.; Mendes, J.C.; Duffles, P.; Peternel, R.; Matos, G. New evidence of a Magmatic Arc in the Southern Brasília Belt, Brazil: The Serra da Água Limpa Batholith (Socorro-Guaxupé Nappe). *J. S. Am. Earth. Sci.* **2014**, *54*, 120–139. [CrossRef]
70. White, W.M. Radiogenic Isotope Geochemistry. In *Geochemistry*; White, W.M., Ed.; John Wiley & Sons: Hoboken, NJ, USA, 2023; pp. 312–360.
71. Hibbard, M.J. *Petrography to Petrogenesis*; Prentice Hall: Hoboken, NJ, USA, 1995.
72. Svetlitskaya, T.V.; Nevolko, P.A.; Fominykh, P.A. Fe-Ti Oxide Assemblages from the Contact-Metamorphosed Mafic-Ultramafic Rocks of the Sedova Zaimka Intrusion (Western Siberia, Russia): The Tracking of Metamorphic Transformations. *Minerals* **2020**, *10*, 253. [CrossRef]
73. Pang, K.N.; Zhou, M.F.; Lindsley, D.H.; Zhao, D.; Malpas, J. Origin of Fe-Ti Oxide Ores in Mafic Intrusions: Evidence from the Panzhihua Intrusion, SW China. *J. Petrol.* **2008**, *49*, 295–313. [CrossRef]
74. Qian, G.; Brugger, J.; Skinner, W.; Guorong, C.; Pring, A. An experimental study of the mechanisms of the replacement of magnetite by pyrite up to 300 °C. *Geochim. Cosmochim. Acta* **2010**, *74*, 5610–5630. [CrossRef]
75. Jochum, K.P.; Nohl, U.; Herwig, K.; Lammel, E.; Stoll, B.; Hofmann, A.W. GeoRem: A New Geochemical Database for Reference Materials and Isotopic Standards. *Geostand. Geoanalytical Res.* **2005**, *29*, 333–338. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Mineralogy and Geochemistry of Early Triassic Granite in South China: Insights into Source Region Characteristics and REE Mineralization

Liya Yang ¹, Yongfeng Cai ^{1,2,*}, Jieting Ouyang ¹, Fang Xu ¹, Yankun Chen ¹ and Yun Zhou ¹

¹ Guangxi Key Laboratory of Hidden Metallic Ore Deposits Exploration, Guilin University of Technology, Guilin 541004, China; yangliya0701@163.com (L.Y.); ouyangjt2000@163.com (J.O.); 17713657451@163.com (F.X.); 15673653873@163.com (Y.C.); zhouyun@glut.edu.cn (Y.Z.)

² Collaborative Innovation Center for Exploration of Nonferrous Metal Deposits and Efficient Utilization of Resources, Guilin University of Technology, Guilin 541006, China

* Correspondence: caiyongfeng@glut.edu.cn

Abstract: Regolith-hosted rare-earth element (REE) deposits are some of the most important types of REE deposits. The relationship between Late Paleozoic and Early Mesozoic granite and regolith-hosted REE deposits is still poorly studied. Detailed geochronology, geochemistry, and rare-earth mineralogy analyses of Early Triassic granite in the South China Block were conducted. The geochronological results showed that four representative granite samples yielded formation ages of 245 ± 1 Ma, 244 ± 1 Ma, 244 ± 1 Ma, and 244 ± 2 Ma, respectively. The granites show geochemical affinity to A-type granite. They are characterized by enrichment in Rb, Th, and U, are depleted in Ba, Sr, P, and Ti, and show obvious negative Nb and Ta anomalies. They have high light rare-earth element (LREE) and low heavy rare-earth element (HREE) contents, with obvious negative Eu anomalies. They were derived from the partial melting of a sediment source and underwent intense fractional crystallization during the magma evolution process. They contain a certain number of rare-earth-element-bearing minerals, such as monazite, xenotime, apatite, and zircon. Their REE compositions and mineral associations are similar to those of the parent rocks from typical regolith-hosted REE deposits in South China. The highly weathered horizon at the ridge of the granite weathering crust profile has the highest REE content. A comprehensive analysis indicated that the degree of magma evolution, geomorphology, and weathering are important factors controlling the formation of regolith-hosted REE deposits in the area.

Keywords: regolith-hosted REE deposits; granite; REE mineralogy; zircon U-Pb dating; Early Triassic; Darongshan–Shiwandashan

1. Introduction

The Tethys Ocean, which was named by Suess (1893) [1], was a trans-equatorial ocean between Eurasia, Africa, and India. Many studies have shown that the Tethys Ocean existed at different geological times and had different evolutionary processes [2]. Metcalfe (2021) divides the Tethys Ocean into the Late Silurian Prototethys, Devonian–Late Triassic Paleotethys, Middle Permian–Late Cretaceous Mesotethys, and Jurassic–Cretaceous Neotethys [3]. The Paleotethys was a Paleozoic ocean between the continents of Gondwana and Laurasia [4–7]. This has been well documented in Southeast Asia [8–14]. Previous studies have shown that the framework of the Eastern Paleotethys is complex. The main ocean basin is represented by the Changning–Menglian suture zone, which extends to

Thailand [15,16]. The branches of the ocean basin are represented by a series of suture zones, such as the Jinshajiang, Ailaoshan, Songma, and Hainan suture zones [17,18]. In addition, the Tethyan metallogenic domain is a world-famous metallogenic domain that includes different types of deposits, such as skarn Fe deposits, porphyry Cu–Mo–Au, sediment-hosted Pb–Zn deposits, granite-related Sn–W deposits, and so on [19]. In South China, there are numerous granite outcrops along the Tethyan tectonic domain. However, the relationship between the Late Paleozoic and Early Mesozoic granite and regolith-hosted REE deposits in South China is poorly studied.

The Darongshan–Shiwandashan granite belt, an important Late Paleozoic to Early Mesozoic granite belt in South China, is located at the intersection of the Paleo-Pacific and Paleotethys tectonic domains. A thick granitoid weathering crust that is preserved in the Darongshan–Shiwandashan area and some regolith-hosted REE deposits have been discovered [20–24]. The Darongshan–Shiwandashan granite belt provides an ideal location for revealing the Late Paleozoic to Early Mesozoic tectonic evolution of South China and discussing the relationship between granite and regolith-hosted REE deposits. In this study, petrography, zircon U–Pb geochronology, geochemistry, and REE mineralogical data of granites from the Darongshan–Shiwandashan granite belt are presented. Our aims are to (1) discuss the petrogenesis, source characteristics, and tectonic environment of the granite and (2) reveal the ore-controlling conditions of the regolith-hosted REE deposit.

2. Geological Background

The South China Block is composed of the Yangtze Block in the northwest and the Cathaysia Block in the southeast (Figure 1a). The Darongshan–Shiwandashan granite belt is located at the junction of the South China Block, Indochina Block, and Pacific Plate (Figure 1a). The granite belt has an NE trend and extends from Wuzhou in the northeast to the Beibu Gulf in the southwest, with a length of approximately 400 km and a width of approximately 20–75 km [25]. It is mainly controlled by the Bobai–Cenxi and Lingshan–Tengxian faults and is composed of Darongshan, Pubei, Taima, and Jiuzhou plutons (Figure 1b) [26,27]. Previous studies showed that the Taima pluton formed at 249–236 Ma [28–30]. The formation age of the Darongshan pluton is 251–243 Ma [31,32]. The Pubei pluton formed at 252–244 Ma [33,34]. Granites from the Jiuzhou pluton have LA-ICP-MS zircon U–Pb ages of 248–245 Ma [26]. Granites from the above plutons generally display obvious negative Nb–Ta anomalies, high Rb, Th, and U contents, low Ba and Sr contents, high Zr/Nb and Ba/Nb ratios, and low Th/Nb and Ta/La ratios [26,28,31,33]. In addition, a few volcanic rocks, such as 247–245 Ma dacite porphyry and ~246 Ma basalt, were reported in the Banba and Hengxian areas [35–37].

The wall rocks of the Darongshan–Shiwandashan granite are mainly Silurian, Devonian, Permian, Triassic, and Jurassic sedimentary and volcanic rocks (Figure 1c). The Silurian rocks are mainly composed of a set of shales. The Devonian rocks are composed of mudstone, sandstone, and siltstone and are in interdigitated or gradational contact with the Silurian. The Upper Permian is mainly composed of limestone and clastic limestone with a small amount of siliceous limestone. The Lower Permian strata are composed of carbonate, volcanic breccia, and mafic lava. The Lower Triassic rocks are mainly a set of sedimentary shallow marine carbonates and clastic rocks. The Middle Triassic rocks mainly consist of terrigenous clastic turbidite, and the Upper Triassic rocks are a suite of lithologic clastic rocks and terrigenous red beds. The Jurassic strata are mainly composed of argillaceous siltstone, breccia, and medium- to coarse-grained feldspar quartz sandstone [26].

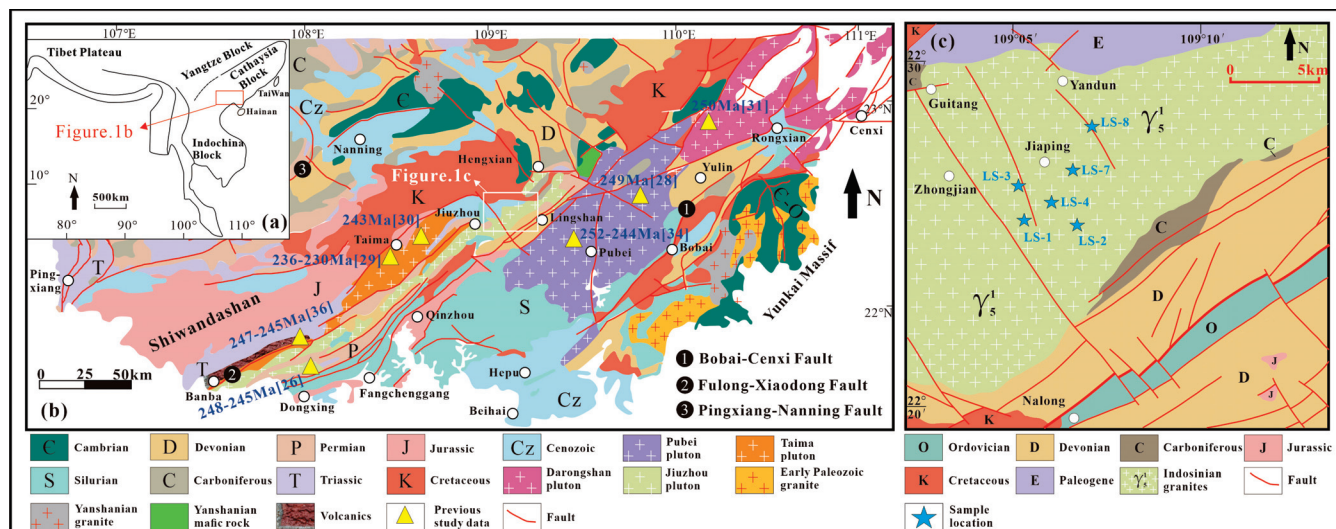


Figure 1. (a) Simplified tectonic map showing major tectonic units in Southeast Asia (modified after [38]). (b) Simplified geological map showing major plutons of Darongshan–Shiwandashan granite belt (modified after [26]). (c) Sketch of a geological map showing sampling locations.

3. Petrological Characteristics

Four granite samples (LS-3, LS-4, LS-7, and LS-8) from the Darongshan–Shiwandashan granite belt were selected for geochronological analysis (Figure 2). The sampling locations are shown in Figure 1c.



Figure 2. Field photographs showing the granite weathering crust from Darongshan–Shiwandashan, southeast Guangxi.

Sample LS-3 was biotite granite and was grayish-black with a medium-to coarse-grained texture and massive texture (Figure 3a). The main minerals were quartz, plagioclase, K-feldspar, and biotite (Figure 3b). The quartz (25–35 vol%) was euhedral to anhedral, with sharp contacts. The plagioclase (20–30 vol%) exhibited twinning lamellae. The biotite (10–15 vol%) was a dark-brown, flaky, and had semi-idiomorphic sheets. The K-feldspar (10–15 vol%) was idiomorphic with a grain size of 400–1000 μm .

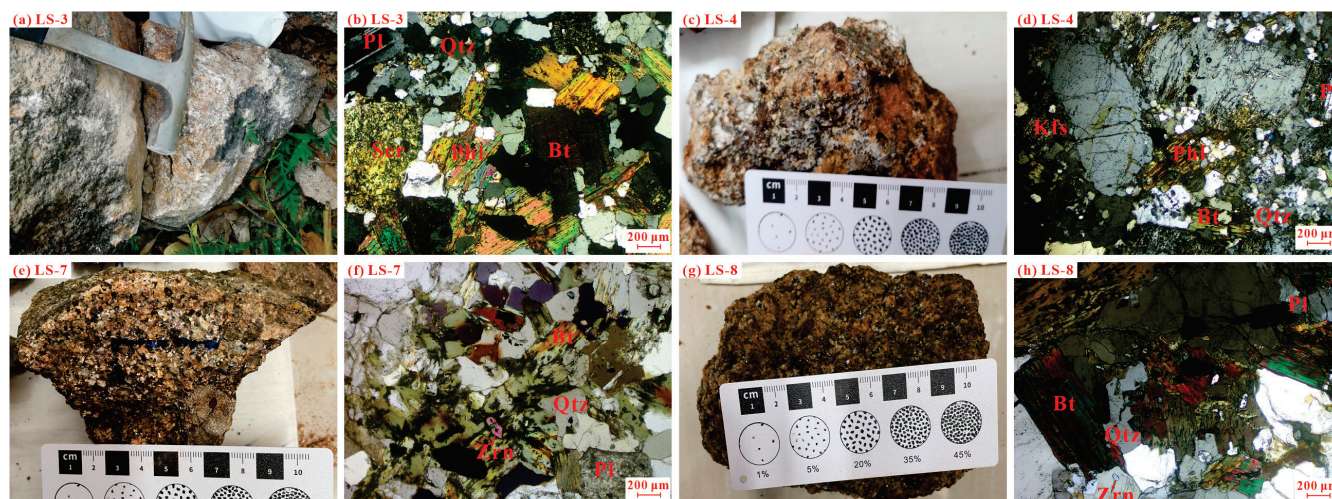


Figure 3. Field photographs (a,c,e,g) and photomicrographs (b,d,f,h) of granite from Darongshan–Shiwandashan, southeast Guangxi. Bt—biotite; Qtz—quartz; Pl—plagioclase; Kfs—K-feldspar; Phl—phlogopite; Ser—sericite; Zrn—zircon.

Sample LS-4 was biotite granite and was coarse-grained with a massive texture (Figure 3c). The main minerals were quartz, plagioclase, biotite, and K-feldspar (Figure 3d). The biotite (20–30 vol%) was dark brown with a 200–800 µm grain size. The K-feldspar (25–35 vol%) was euhedral to subhedral with a size of 300–1000 µm.

Sample LS-7 was biotite granite and was coarse-grained with a massive texture (Figure 3e). The main minerals were quartz, biotite, and plagioclase. The quartz (30–35 vol%) was irregular with a clean surface. The biotite (10–15 vol%) was dark brown with a size of 200–600 µm. The plagioclase (5–10 vol%) was dark gray with a grain size of 200–500 µm (Figure 3f).

Sample LS-8 was alkaline feldspar granite and was obtained from a spheroidal granite mass. It was grayish-black, and it had a coarse-grained and massive texture (Figure 3g). The main minerals were quartz (25–35 vol%), plagioclase (20–25 vol%), K-feldspar (10–15 vol%), and biotite (10–15 vol%) (Figure 3h).

4. Results

4.1. Zircon U-Pb Dating Results

The LA-ICP-MS zircon U-Pb analysis results are shown in Table 1. CL images show that most of the zircons were brown and idiomorphic, with lengths of 100–350 µm and widths of 90–150 µm (Figure 4). They were characterized by clear oscillating zones, indicating a magmatic source for the texture.

Twenty zircon grains from sample LS-3 were selected for U-Pb isotope testing, and the results showed that the U content was 223–2117 ppm, the Th content was 164–1385 ppm, and the Th/U ratio varied from 0.21 to 1.19 (Table 1). Among them, 16 zircons were located at or near the U-Pb age concordance and gave a weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 245 ± 1 Ma (MSWD = 0.02, 1σ) (Figure 4a,b), representing the crystallization age.

The results of the analysis of 20 zircon grains from sample LS-4 showed that the U content ranged from 216–1583 ppm and the Th content ranged from 86–954 ppm, with the Th/U ratio ranging from 0.07 to 0.77 (Table 1). Fifteen grains yielded a weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 244 ± 1 Ma (MSWD = 0.11, 1σ) (Figure 4c,d), representing the crystallization age.

Table 1. LA-ICP-MS zircon U-Pb isotope results of granite from Darongshan–Shiwandashan, south-east Guangxi.

Spot	Isotope Ratio						Age (Ma)			
	$^{207}\text{Pb}/^{206}\text{Pb}$	1 σ	$^{207}\text{Pb}/^{235}\text{U}$	1 σ	$^{206}\text{Pb}/^{238}\text{U}$	1 σ	$^{207}\text{Pb}/^{235}\text{U}$	1 σ	$^{206}\text{Pb}/^{238}\text{U}$	1 σ
Sample LS-3										
1	0.0999	0.0020	3.5422	0.0734	0.2572	0.0026	1537	16	1476	13
2	0.0816	0.0022	1.7865	0.0831	0.1593	0.0071	1041	30	953	39
3	0.0675	0.0011	1.1543	0.0213	0.1237	0.0009	779	10	752	5
4	0.0566	0.0028	0.2983	0.0147	0.0386	0.0007	265	11	244	5
5	0.0551	0.0027	0.2930	0.0147	0.0387	0.0007	261	12	245	5
6	0.0540	0.0030	0.2956	0.0317	0.0385	0.0023	263	25	244	14
7	0.0508	0.0011	0.2702	0.0060	0.0386	0.0003	243	5	244	2
8	0.0500	0.0008	0.2665	0.0043	0.0387	0.0003	240	3	245	2
9	0.0492	0.0044	0.2613	0.0226	0.0387	0.0008	236	18	245	5
10	0.0539	0.0089	0.2733	0.0401	0.0388	0.0010	245	32	246	6
11	0.0523	0.0025	0.2788	0.0131	0.0388	0.0006	250	10	245	4
12	0.0689	0.0011	1.4063	0.0639	0.1456	0.0058	892	27	876	33
13	0.0480	0.0026	0.2552	0.0133	0.0387	0.0007	231	11	245	4
14	0.0503	0.0025	0.2676	0.0125	0.0387	0.0005	241	10	245	3
15	0.0529	0.0020	0.2819	0.0109	0.0387	0.0004	252	9	245	3
16	0.0516	0.0015	0.2771	0.0089	0.0388	0.0004	248	7	245	3
17	0.0498	0.0022	0.2647	0.0115	0.0387	0.0004	238	9	245	2
18	0.0493	0.0010	0.2633	0.0052	0.0388	0.0004	237	4	245	2
19	0.0513	0.0016	0.2736	0.0086	0.0387	0.0004	246	7	245	3
20	0.0512	0.0011	0.2745	0.0067	0.0388	0.0004	246	5	245	2
Sample LS-4										
1	0.0541	0.0041	0.2866	0.0239	0.0382	0.0004	256	19	242	2
2	0.0530	0.0013	0.2829	0.0078	0.0387	0.0004	253	6	245	2
3	0.0485	0.0015	0.2578	0.0077	0.0386	0.0004	233	6	244	2
4	0.0501	0.0017	0.2658	0.0093	0.0386	0.0005	239	7	244	3
5	0.0502	0.0019	0.2672	0.0108	0.0386	0.0004	240	9	244	3
6	0.0543	0.0019	0.2891	0.0102	0.0386	0.0004	258	8	244	3
7	0.0694	0.0021	1.1172	0.0393	0.1172	0.0024	762	19	714	14
8	0.0517	0.0018	0.2771	0.0114	0.0387	0.0005	248	9	245	3
9	0.0669	0.0009	1.2181	0.0192	0.1320	0.0013	809	9	799	7
10	0.0487	0.0014	0.2590	0.0072	0.0386	0.0004	234	6	244	2
11	0.0568	0.0026	0.3013	0.0135	0.0387	0.0005	267	11	245	3
12	0.0484	0.0027	0.2583	0.0145	0.0388	0.0005	233	12	245	3
13	0.0758	0.0012	1.9556	0.0366	0.1875	0.0029	1100	13	1108	16
14	0.0719	0.0013	1.4987	0.0414	0.1507	0.0031	930	17	905	17
15	0.0500	0.0028	0.2654	0.0149	0.0386	0.0005	239	12	244	3
16	0.0485	0.0025	0.2588	0.0140	0.0387	0.0005	234	11	244	3
17	0.0709	0.0010	1.3233	0.0226	0.1355	0.0016	856	10	819	9
18	0.0509	0.0023	0.2708	0.0122	0.0386	0.0005	243	10	244	3
19	0.0497	0.0024	0.2655	0.0135	0.0387	0.0005	239	11	245	3
20	0.0485	0.0028	0.2599	0.0169	0.0386	0.0007	235	14	244	4
Sample LS-7										
1	0.0506	0.0011	0.2685	0.0060	0.0386	0.0006	242	5	244	4
2	0.0688	0.0008	1.3364	0.0163	0.1410	0.0011	862	7	850	6
3	0.0513	0.0009	0.2734	0.0051	0.0386	0.0002	245	4	244	1
4	0.0811	0.0009	1.3047	0.0227	0.1165	0.0012	848	10	710	7
5	0.0531	0.0022	0.2883	0.0116	0.0394	0.0003	257	9	249	2
6	0.0517	0.0013	0.2750	0.0084	0.0385	0.0004	247	7	243	3
7	0.0547	0.0011	0.2913	0.0064	0.0386	0.0003	260	5	244	2
8	0.0563	0.0010	0.5063	0.0101	0.0652	0.0006	416	7	407	4

Table 1. Cont.

Spot	Isotope Ratio						Age (Ma)			
	$^{207}\text{Pb}/^{206}\text{Pb}$	1σ	$^{207}\text{Pb}/^{235}\text{U}$	1σ	$^{206}\text{Pb}/^{238}\text{U}$	1σ	$^{207}\text{Pb}/^{235}\text{U}$	1σ	$^{206}\text{Pb}/^{238}\text{U}$	1σ
9	0.0552	0.0013	0.3486	0.0117	0.0460	0.0014	304	9	290	9
10	0.0504	0.0013	0.2676	0.0079	0.0386	0.0007	241	6	244	4
11	0.0548	0.0013	0.2923	0.0079	0.0386	0.0004	260	6	244	2
12	0.0910	0.0010	3.1411	0.1258	0.2457	0.0082	1443	31	1416	43
13	0.0542	0.0018	0.2880	0.0103	0.0386	0.0006	257	8	244	4
14	0.0533	0.0010	0.2840	0.0057	0.0386	0.0003	254	5	244	2
15	0.0510	0.0016	0.2692	0.0079	0.0384	0.0007	242	6	243	4
16	0.0533	0.0014	0.2824	0.0074	0.0386	0.0007	253	6	244	4
17	0.0611	0.0016	0.7590	0.0244	0.0899	0.0015	573	14	555	9
18	0.0499	0.0014	0.2662	0.0088	0.0387	0.0007	240	7	245	4
19	0.0566	0.0021	0.2955	0.0106	0.0379	0.0005	263	8	240	3
20	0.0509	0.0013	0.2716	0.0076	0.0386	0.0003	244	6	244	2
Sample LS-8										
1	0.0487	0.0027	0.2569	0.0139	0.0385	0.0006	232	11	243	4
2	0.0480	0.0018	0.2540	0.0087	0.0386	0.0004	230	7	244	2
3	0.0564	0.0033	0.3033	0.0206	0.0387	0.0005	269	16	245	3
4	0.0493	0.0014	0.2634	0.0084	0.0386	0.0004	237	7	244	2
5	0.0494	0.0015	0.2643	0.0091	0.0386	0.0004	238	7	244	2
6	0.0691	0.0017	1.5486	0.0379	0.1625	0.0016	950	15	971	9
7	0.0702	0.0014	1.5980	0.0318	0.1656	0.0018	969	12	988	10
8	0.0689	0.0014	1.2455	0.0259	0.1312	0.0013	821	12	795	7
9	0.0604	0.0015	0.7899	0.0208	0.0947	0.0009	591	12	583	5
10	0.0593	0.0011	0.8226	0.0172	0.1005	0.0009	610	10	617	5
11	0.0543	0.0012	0.4771	0.0129	0.0639	0.0014	396	9	399	8
12	0.0553	0.0015	0.5245	0.0138	0.0689	0.0006	428	9	430	4
13	0.0563	0.0045	0.2992	0.0222	0.0394	0.0007	266	17	249	5
14	0.0602	0.0030	0.3264	0.0166	0.0397	0.0007	287	13	251	5
15	0.0508	0.0038	0.2716	0.0215	0.0387	0.0008	244	17	245	5
16	0.1595	0.0019	8.2178	0.1121	0.3735	0.0028	2255	12	2046	13
17	0.1615	0.0009	8.7021	0.1713	0.3902	0.0071	2307	18	2124	33
18	0.0514	0.0014	0.2732	0.0076	0.0386	0.0004	245	6	244	2
19	0.0532	0.0021	0.2817	0.0109	0.0385	0.0004	252	9	244	2
20	0.0529	0.0014	0.2802	0.0071	0.0385	0.0003	251	6	243	2

Twenty zircons from sample LS-7 were selected for U-Pb isotope analysis. The results showed that the U content ranged from 330–1437 ppm, and the Th content ranged from 161–618 ppm, with a Th/U ratio of 0.19 to 1.59 (Table 1). Thirteen zircons yielded a weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 244 ± 1 Ma (MSWD = 0.20, 1σ) (Figure 4e,f), representing the crystallization age.

The results showed that twenty zircon grains from sample LS-8 had a U content of 314–1929 ppm and a Th content of 101–939 ppm, with a Th/U ratio of 0.17–1.31 (Table 1). Nine of the grains yielded a weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 244 ± 2 Ma (MSWD = 0.05, 1σ) (Figure 4g,h), representing the crystallization age.

The trace element composition of zircons in granite showed that they were enriched in Th, U, Ta, Pr, and Hf and relatively depleted in Nb, La, Sr, Nd, and Ti. Additionally, they had high contents of heavy rare-earth elements (HREEs) and low contents of light rare-earth elements (LREEs), accompanied by notable negative Eu anomalies (Figure 5, Tables 2 and 3).

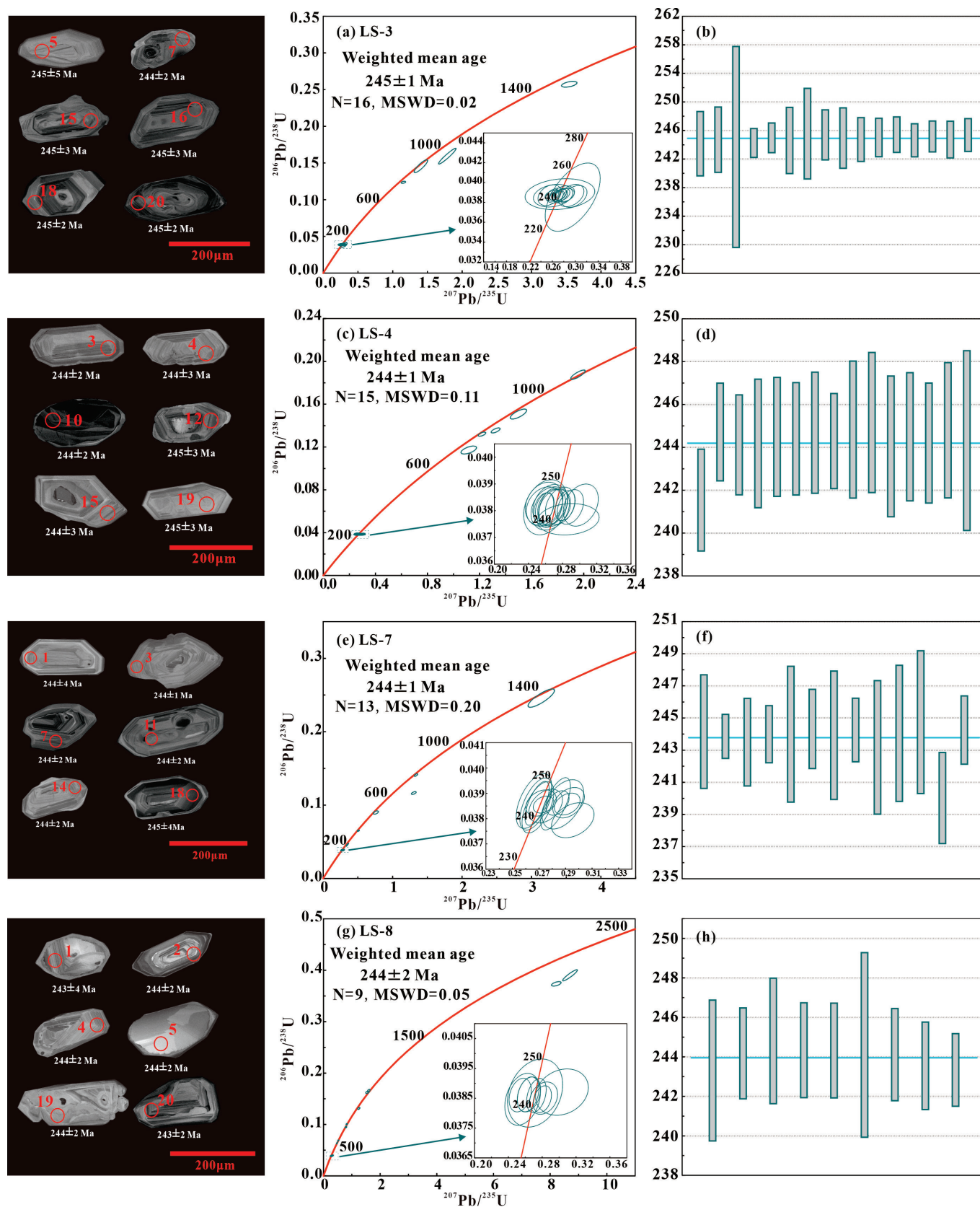


Figure 4. Cathodoluminescence images of representative zircons and plots of zircon U-Pb concordia and weighted mean age of sample (a,b) LS-3, (c,d) LS-4, (e,f) LS-7, and (g,h) LS-8 from Darongshan–Shiwandashan, southeast Guangxi.

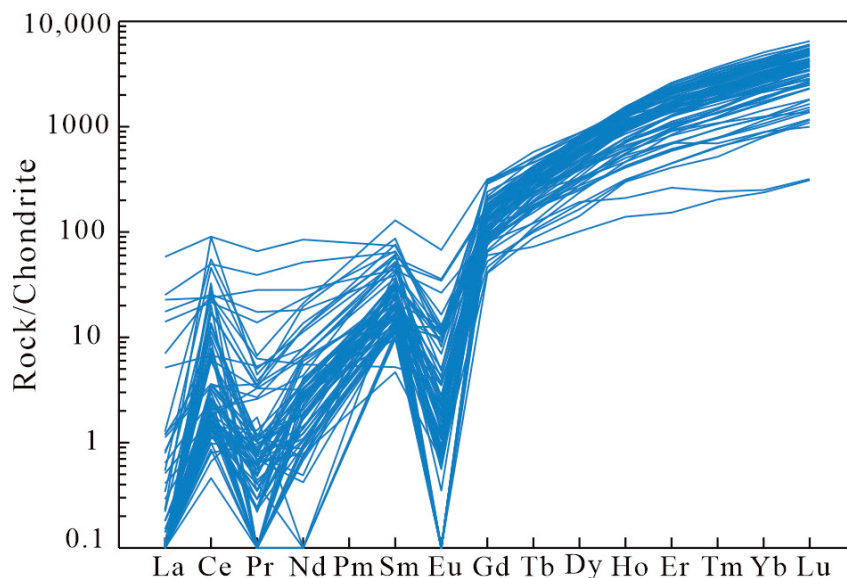


Figure 5. Chondrite-normalized REE distribution patterns of zircon from granite from Darongshan–Shiwandashan, southeast Guangxi.

Table 2. Trace element contents ($\times 10^{-6}$) of zircon from granite from Darongshan–Shiwandashan, southeast Guangxi.

Spot	Ti	Sr	Y	Nb	Hf	Ta	Th	U
Sample LS-3								
1	16.02	0.66	3415.07	5.94	36,285.96	2.77	403.50	248.48
2	18.04	0.45	2332.22	11.48	35,828.97	3.84	397.29	584.45
3	40.69	1.41	5938.22	7.76	34,708.51	3.90	1385.38	1168.20
4	29.42	2.91	7102.70	1.62	43,330.55	1.98	357.46	1227.92
5	23.48	3.07	6894.76	3.19	41,350.27	2.19	359.55	1310.39
6	32.70	0.73	7397.21	2.57	42,316.71	2.61	408.41	1163.66
7	20.28	0.76	7463.15	3.34	40,832.45	2.21	391.78	1845.89
8	21.86	1.02	7601.99	3.72	40,717.43	3.29	660.39	2116.91
9	17.09	0.49	2696.17	1.53	42,067.54	1.85	204.14	560.96
10	66.50	0.59	3104.57	1.84	33,066.26	1.07	164.29	222.63
11	39.22	0.75	7072.69	2.05	36,539.11	1.76	298.39	803.35
12	20.68	0.91	4711.55	5.17	38,742.47	3.64	372.86	1494.86
13	29.24	0.50	7276.29	2.34	39,248.61	2.11	256.58	1042.07
14	31.62	0.40	5309.05	1.57	41,428.61	0.94	273.81	689.79
15	28.51	1.58	6744.18	2.14	40,321.48	1.68	221.83	823.42
16	37.64	1.68	5107.88	2.13	39,232.64	1.63	291.85	755.58
17	33.29	0.35	4894.95	1.13	40,495.21	1.30	203.91	736.91
18	24.17	1.92	5273.35	6.15	40,866.41	4.47	899.62	2084.07
19	25.06	1.15	5225.81	2.03	41,904.34	1.87	247.49	913.45
20	21.95	1.06	3802.24	2.78	41,388.61	1.64	336.02	1167.46
Sample LS-4								
1	39.97	0.61	4687.48	2.38	39,629.59	0.37	200.12	732.85
2	22.38	1.93	6942.60	2.73	31,328.26	1.37	953.59	1238.51
3	18.75	0.79	3541.54	2.97	42,396.93	2.21	95.19	1277.53
4	25.21	0.47	7400.36	1.84	41,277.83	1.90	229.64	938.68
5	29.64	1.68	6262.68	1.05	39,574.41	2.34	254.68	865.42
6	27.90	1.21	6774.17	2.03	41,611.76	1.91	226.05	822.46
7	26.41	0.24	1357.71	5.77	32,359.66	2.16	85.91	215.93
8	24.31	0.82	4970.46	2.06	42,783.45	2.52	141.68	826.28

Table 2. Cont.

Spot	Ti	Sr	Y	Nb	Hf	Ta	Th	U
9	33.87	0.72	4430.67	10.39	34,581.06	6.01	915.99	1407.85
10	29.71	0.82	6532.83	2.03	41,360.48	2.03	213.49	857.87
11	29.08	1.02	5264.50	1.33	41,585.70	3.98	302.37	1085.31
12	27.97	0.64	5798.94	3.02	41,939.55	1.21	205.53	772.91
13	105.84	4.75	1394.44	7.65	32,826.19	3.68	433.78	778.27
14	20.10	0.00	1303.25	4.24	35,068.66	2.33	391.92	869.35
15	23.43	0.00	4575.70	1.90	42,350.65	2.12	207.21	866.00
16	21.31	0.32	2507.66	0.76	44,955.25	1.37	145.37	961.98
17	12.72	0.00	1145.92	4.35	41,097.37	4.47	480.62	1583.29
18	26.47	2.23	6566.34	2.25	41,409.00	0.90	220.21	765.22
19	30.26	1.23	5265.15	0.48	41,318.78	1.31	164.77	650.77
20	22.32	1.00	5431.69	1.16	41,714.42	0.79	174.98	715.41
Sample LS-7								
1	20.79	0.51	3994.29	2.00	33,533.17	1.74	219.82	946.90
2	19.92	0.51	668.06	2.83	33,995.09	1.77	250.05	633.27
3	27.24	0.97	6765.46	2.78	30,267.72	1.10	264.78	1026.42
4	37.89	0.82	3229.58	5.82	29,977.52	3.59	298.79	1437.43
5	70.02	0.73	4862.95	3.59	26,456.08	1.94	352.10	746.63
6	39.28	1.41	4051.94	1.99	22,866.98	1.10	291.29	708.98
7	39.66	1.21	5188.40	2.68	29,694.96	1.24	294.88	1010.19
8	13.01	0.64	2767.50	7.19	27,245.60	3.74	219.37	630.17
9	22.53	1.31	1985.15	4.30	30,895.28	3.47	173.98	878.37
10	24.42	0.83	6350.86	0.98	30,052.86	1.36	209.50	919.63
11	33.07	1.06	6029.14	4.43	28,357.20	1.60	618.05	829.02
12	22.65	6.31	2058.59	5.08	26,244.50	2.86	246.70	828.92
13	24.53	0.77	5169.57	1.01	31,728.21	1.65	234.49	961.33
14	28.74	0.71	5544.11	1.34	30,957.39	1.12	225.62	873.43
15	34.85	1.30	5494.83	1.54	33,091.26	0.94	188.21	699.83
16	28.26	0.74	5088.30	1.02	31,265.06	0.94	202.46	818.62
17	63.18	0.69	2880.95	7.71	24,914.42	3.01	522.39	329.55
18	19.44	0.99	7658.93	2.92	31,934.58	2.24	181.05	933.34
19	44.71	1.76	3375.30	3.19	20,453.63	0.97	253.36	431.27
20	25.77	0.29	4416.07	2.55	30,965.82	0.94	161.17	721.35
Sample LS-8								
1	23.32	0.55	4436.48	2.60	39,653.81	1.04	124.63	566.57
2	26.15	1.07	5105.89	1.32	42,187.94	1.52	182.04	665.70
3	37.16	2.13	8031.18	2.50	38,470.86	1.17	681.93	1380.40
4	27.34	1.22	7123.14	2.75	42,310.64	1.40	258.73	913.74
5	27.66	1.24	6220.90	1.40	39,460.02	1.55	291.34	916.66
6	10.58	0.41	2828.18	6.04	38,449.72	2.69	136.60	313.70
7	6.96	8.06	3183.31	9.07	39,689.68	3.75	165.83	424.42
8	9.63	0.62	2226.73	5.09	43,613.01	3.72	100.94	529.59
9	20.34	0.00	1887.85	5.26	33,511.00	2.91	195.72	698.73
10	35.21	1.13	4908.82	4.32	32,224.63	2.61	418.01	1049.32
11	3.05	1.28	2814.82	7.36	46,308.98	5.39	332.82	1928.85
12	10.98	0.30	4263.76	13.06	38,180.98	7.08	431.56	1342.76
13	40.48	0.43	3555.07	1.69	41,098.63	1.78	166.23	444.97
14	129.58	2.08	6184.30	2.57	34,772.64	1.77	320.47	652.75
15	40.13	1.75	5414.94	2.06	36,488.57	1.80	217.60	443.60
16	28.91	1.45	5215.68	7.93	24,440.27	5.69	939.27	717.12
17	24.78	0.72	3129.20	4.82	31,753.77	4.15	759.94	898.61
18	19.76	1.09	4679.96	1.17	42,457.75	1.29	167.06	955.20
19	24.74	0.60	6014.60	1.57	39,091.75	1.71	307.34	984.66
20	25.47	0.54	6965.97	1.46	38,094.75	1.12	338.48	1130.12

Table 3. REE element contents ($\times 10^{-6}$) of zircon from granite from Darongshan–Shiwandashan, southeast Guangxi.

Spot	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Sample LS-3														
1	0.00	51.02	0.18	2.95	12.96	1.86	63.53	25.51	305.01	117.46	487.09	100.50	859.15	170.94
2	0.00	57.82	0.00	1.26	5.60	2.10	50.96	16.52	222.31	82.75	336.71	70.14	603.47	133.19
3	0.23	41.58	1.06	16.19	33.82	1.80	178.67	54.77	600.35	223.43	869.48	166.55	1418.67	274.03
4	0.00	4.14	0.28	1.17	15.51	1.17	103.53	40.33	600.21	243.49	1097.89	226.94	2125.31	403.12
5	0.00	3.30	0.25	4.33	10.39	0.00	110.36	40.08	560.93	216.45	1032.34	226.74	2020.33	395.24
6	0.00	4.73	0.00	3.11	13.61	0.00	108.68	41.93	610.81	242.74	1082.91	234.42	1912.91	377.89
7	0.08	3.40	0.12	1.43	8.50	0.12	86.74	39.15	574.16	251.07	1135.57	255.93	2191.19	448.05
8	0.00	5.80	0.14	3.64	15.19	0.00	100.50	43.91	600.26	251.89	1165.67	244.68	2156.60	434.22
9	0.00	3.45	0.00	5.57	8.25	0.00	54.22	26.20	237.17	88.18	336.87	51.37	438.64	73.79
10	0.00	6.21	0.28	3.35	13.85	1.55	77.11	20.67	243.96	121.61	515.37	107.23	1080.12	210.48
11	0.00	3.18	0.91	4.29	15.09	0.69	117.71	41.86	579.96	216.08	978.88	213.28	1859.90	382.57
12	0.00	16.47	0.00	1.30	9.16	0.00	67.41	28.17	395.96	155.97	781.72	163.58	1469.90	303.18
13	0.00	1.17	0.48	0.00	11.69	0.46	120.69	44.86	580.83	234.36	1131.84	242.35	2043.00	413.70
14	0.09	4.62	0.22	5.31	10.32	0.85	89.87	34.25	461.64	183.80	813.00	162.32	1520.89	285.23
15	0.00	2.78	0.14	3.71	12.94	0.26	80.08	38.62	524.75	216.00	988.15	206.70	1820.98	361.77
16	0.00	5.32	0.06	4.47	8.61	0.59	75.55	35.17	429.40	176.05	798.08	163.60	1404.07	287.31
17	0.00	1.74	0.25	2.51	6.96	0.16	77.96	30.66	386.54	163.61	749.96	150.66	1371.57	276.03
18	12.04	45.40	4.81	24.58	17.35	0.12	78.19	33.21	454.46	182.16	814.80	165.25	1531.38	282.11
19	0.35	2.96	0.00	3.74	8.12	0.13	59.55	27.43	417.24	174.01	809.34	166.69	1530.95	297.06
20	0.00	3.54	0.00	1.02	5.48	0.32	44.73	23.23	298.16	128.30	596.62	130.76	1141.04	224.91
Sample LS-4														
1	0.12	2.61	0.10	4.09	6.65	0.73	62.19	27.10	380.45	152.26	721.19	142.68	1326.39	255.69
2	9.65	38.11	3.82	31.63	29.19	2.00	171.39	55.19	642.43	234.19	997.05	210.53	1776.23	322.64
3	0.12	4.67	0.19	0.57	5.88	0.18	39.93	17.73	266.47	120.24	615.46	145.37	1455.68	312.91
4	0.00	2.32	0.15	1.82	13.99	0.14	99.07	38.36	555.93	238.32	1090.57	223.32	2110.91	404.35
5	0.10	3.55	0.08	4.36	7.18	0.00	86.80	38.58	487.75	204.22	972.27	195.88	1818.87	350.68
6	0.00	2.59	0.07	3.94	8.95	0.00	80.91	35.12	551.15	212.47	1033.83	217.07	1959.96	386.65
7	0.07	11.55	0.11	0.00	4.26	0.32	27.65	11.22	136.17	51.62	214.68	46.85	434.81	87.02
8	0.00	2.12	0.08	1.41	6.45	0.15	73.63	28.49	397.20	165.81	794.43	170.56	1603.12	316.70
9	0.00	30.82	0.93	16.25	27.09	0.22	124.67	40.29	445.74	159.34	653.90	128.96	1117.04	209.42
10	0.00	3.17	0.17	3.37	7.26	0.11	88.51	39.33	524.51	212.16	971.12	206.23	1884.92	363.19
11	0.83	6.37	0.33	0.97	6.61	0.31	58.09	34.98	408.14	170.48	825.06	187.23	1668.24	329.93
12	0.00	3.20	0.16	1.84	7.30	0.00	82.65	31.16	447.07	199.85	908.13	177.21	1570.81	311.13
13	4.82	43.96	1.73	7.48	2.31	0.65	31.37	10.76	121.24	50.27	216.44	47.83	401.73	85.59
14	0.00	24.21	0.22	1.93	5.11	0.00	24.24	9.47	104.41	49.16	196.09	38.31	391.55	81.21
15	0.00	4.06	0.00	0.00	4.48	0.00	51.11	27.81	356.86	152.99	725.92	159.64	1344.01	296.01
16	0.00	1.52	0.00	0.92	5.22	0.59	52.99	19.34	237.10	76.10	328.91	70.97	600.20	121.62
17	0.57	10.85	0.90	8.56	8.95	0.42	47.94	13.07	142.02	34.47	126.47	17.97	123.31	23.58
18	0.20	2.81	0.16	7.27	11.32	0.29	94.01	36.91	512.95	211.31	996.85	205.72	1848.47	382.52
19	0.00	2.52	0.00	2.62	5.93	0.00	68.57	30.98	429.32	185.59	825.50	178.37	1630.12	318.84
20	0.00	1.77	0.00	3.81	4.32	0.00	67.75	28.31	450.58	175.36	805.83	180.65	1583.95	315.81
Sample LS-7														
1	0.00	2.04	0.11	1.66	6.29	0.20	48.47	21.50	322.13	128.66	616.92	132.47	1184.78	235.41
2	0.00	13.91	0.10	3.60	7.62	0.62	35.81	7.83	74.68	22.86	73.33	15.05	116.98	22.97
3	0.00	2.72	0.16	3.49	12.57	0.06	98.02	42.23	578.75	231.29	1010.09	213.53	1859.30	369.25
4	15.64	42.12	7.77	38.15	19.45	4.45	53.55	20.73	292.36	99.47	468.50	101.64	945.64	191.20
5	0.00	6.40	0.74	10.62	23.11	0.38	110.68	41.21	432.63	162.36	668.41	132.01	1215.00	235.19
6	3.54	11.96	1.47	10.54	20.95	0.21	90.83	33.99	390.03	140.23	605.31	121.00	1084.26	211.61
7	0.77	5.99	0.99	9.14	16.18	0.47	90.43	37.13	454.69	171.57	777.80	159.88	1459.41	279.07
8	0.54	17.88	0.21	1.64	7.62	1.55	45.76	18.71	231.40	91.60	436.56	90.65	831.48	169.74
9	0.00	10.63	0.19	1.48	5.84	1.67	57.37	19.70	203.41	67.31	288.63	57.60	567.05	112.96
10	0.00	2.53	0.36	4.82	11.60	0.36	92.64	37.13	511.62	206.98	975.75	210.62	1818.81	352.77
11	0.81	10.60	0.32	8.84	19.19	1.51	121.46	45.81	563.69	207.84	904.12	174.93	1523.82	274.95
12	17.32	88.13	10.77	69.73	28.47	2.76	67.72	18.08	182.49	69.82	295.08	58.38	527.11	107.17
13	0.00	2.85	0.13	5.05	10.17	0.24	64.26	31.81	428.85	169.76	794.66	170.80	1514.21	285.17
14	0.04	2.73	0.15	4.64	8.12	0.38	77.25	34.44	454.71	190.71	864.60	181.12	1540.52	313.49
15	0.00	1.96	0.31	3.63	9.10	0.33	74.23	33.63	465.53	177.81	874.28	179.43	1548.95	314.56
16	0.00	1.41	0.27	2.48	9.22	0.09	63.93	29.18	411.41	168.62	778.44	166.56	1462.03	281.36
17	0.15	159.99	1.22	18.41	25.28	6.00	104.89	28.22	290.54	96.91	395.28	78.83	707.29	134.43
18	0.00	3.31	0.00	0.98	13.55	0.15	95.05	41.43	592.98	253.61	1211.28	261.68	2342.72	441.33
19	0.00	5.73	0.29	4.82	14.13	1.75	79.22	27.16	313.43	117.69	504.25	98.88	953.19	184.23
20	0.28	2.15	0.06	1.25	5.17	0.11	64.54	24.95	346.00	146.97	670.86	140.84	1328.17	259.07
Sample LS-8														
1	0.00	0.81	0.00	2.35	7.14	0.12	48.71	24.08	328.74	149.84	694.53	153.97	1420.21	278.17
2	0.00	2.25	0.23	3.92	5.95	0.00	73.87	28.52	406.44	173.04	830.84	171.17	1607.92	313.12
3	0.44	4.38	0.17	8.06	9.19	0.32	130.31	52.64	606.73	252.06	1255.14	273.56	2503.92	480.67
4	0.00	2.14	0.07	2.30	11.82	0.12	103.58	44.36	569.28	227.00	1027.05	215.29	1901.18	365.74
5	0.00	2.66	0.07	5.45	11.58	0.00	100.46	37.73	527.05	218.49	989.81	199.40	1785.57	358.25
6	0.00	35.92	0.00	1.17	4.92	0.38	50.35	17.73	220.76	99.77	464.93	101.24	899.54	195.84
7	39.92	160.29	18.11	114.64	32.79	2.18	77.80	25.89	283.63	115.21	536.09	111.94	1059.02	226.33
8	0.15	23.80	0.18	1.06	2.07	0.11	24.70	12.00	174.21	76.08	402.88	92.11	930.34	203.35
9	0.00	20.15	0.33	2.53	10.95	0.61	46.85	18.12	191.30	67.06	282.27	57.35	499.28	101.48
10	0.08	30.25	0.97	26.54	38.47	1.37	170.81	49.68	515.12	177.76	721.84	136.83	1108.54	210.90
11	0.00	13.08	0.00	0.00	4.90	0.19	38.50	13.28	206.32	89.74	454.54	108.18	1175.25	281.02

Table 3. Cont.

Spot	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
12	0.00	22.83	0.29	2.54	9.36	2.18	58.57	28.40	356.74	148.52	699.75	155.62	1531.46	319.36
13	0.00	2.80	0.21	0.67	18.42	1.96	82.75	32.76	345.73	109.20	434.82	80.13	616.13	102.05
14	0.00	3.69	0.72	5.86	26.42	0.81	181.61	62.19	644.01	208.86	778.36	136.30	1048.55	190.46
15	0.00	4.13	0.21	8.62	21.60	0.40	143.70	43.21	513.93	187.71	822.46	151.58	1284.02	251.89
16	0.87	97.71	1.85	28.45	57.28	11.35	189.01	48.96	562.27	194.06	728.16	137.26	1271.49	258.31
17	0.37	81.00	1.39	15.25	22.31	5.78	98.69	28.49	307.54	104.98	445.11	88.89	816.01	171.13
18	0.00	2.34	0.07	1.91	5.41	0.00	68.95	28.52	379.34	159.17	715.41	152.28	1325.48	275.00
19	0.00	2.36	0.10	2.24	8.60	0.00	76.71	36.64	483.79	199.36	930.42	191.68	1736.57	349.66
20	0.00	2.79	0.24	2.79	9.47	0.22	97.84	44.14	573.81	225.67	1064.11	215.44	1902.84	369.54

4.2. Geochemical Characteristics

4.2.1. Major Elements

The SiO₂ content of the samples was 67.92 wt.%–69.76 wt.% (Table 4). The total alkali (Na₂O + K₂O) content ranged from 5.59 wt.% to 6.35 wt.%. They were rich in K₂O (K₂O/Na₂O = 0.39–0.63) and belonged to the high-K calc-alkaline series (Figure 6a; [39]). The Al₂O₃ content was 13.96 wt.%–15.62 wt.%, and the aluminum saturation index (A/CNK) was high (1.17–1.63), as it belonged to peraluminous rock (Figure 6b; [40]). The differentiation index (DI) ranged from 72.8 to 76.4, indicating a high degree of magma differentiation.

Table 4. Compositions of major (wt.%), trace, and REEs ($\times 10^{-6}$) in granite from Darongshan–Shiwandashan, southeast Guangxi.

Sample	LS-1	LS-2	LS-3	LS-4	LS-7	LS-8
SiO ₂	69.76	69.52	67.92	68.64	69.68	68.63
TiO ₂	0.72	0.79	0.80	0.85	0.76	0.73
Al ₂ O ₃	13.96	14.22	14.97	15.38	14.76	15.62
Fe ₂ O ₃ ^T	5.15	5.93	5.55	5.99	5.19	5.92
MgO	1.68	1.76	1.67	1.71	1.52	1.81
CaO	2.44	1.70	2.50	1.33	1.61	1.51
K ₂ O	3.72	3.93	3.91	4.27	4.23	3.68
Na ₂ O	2.34	1.94	2.43	1.66	2.05	1.91
MnO	0.07	0.08	0.07	0.07	0.06	0.06
P ₂ O ₅	0.16	0.13	0.17	0.10	0.13	0.12
LOI	1.17	1.80	1.32	2.83	2.05	2.21
Total	99.13	99.32	99.97	99.51	99.78	99.94
Mg [#]	43.16	40.89	41.27	39.96	40.63	41.63
FeO ^T /MgO	2.76	3.03	2.98	3.15	3.06	2.94
Na ₂ O + K ₂ O	6.06	5.87	6.35	5.93	6.28	5.59
K ₂ O/Na ₂ O	0.63	0.49	0.62	0.39	0.48	0.52
A/CNK	1.17	1.39	1.21	1.61	1.40	1.63
Sc	11.18	17.34	14.05	13.40	12.45	16.82
Rb	182.69	205.22	205.36	203.05	208.55	285.70
Sr	86.97	77.00	98.29	63.16	88.66	86.14
Y	36.99	43.82	38.32	38.94	44.45	54.72
Zr	294.16	280.56	309.39	313.05	276.48	388.40
Nb	12.44	14.75	14.91	14.56	14.49	15.89
Cs	6.51	7.71	8.76	7.98	9.17	13.12
Ba	579.33	585.95	702.74	687.83	843.72	1508.39
La	54.10	56.09	57.88	54.04	63.41	62.49
Ce	107.90	102.56	102.27	96.95	110.77	99.89
Pr	10.84	11.25	11.31	10.77	12.66	12.48
Nd	40.08	42.00	41.70	39.23	47.00	45.61
Sm	7.71	7.91	7.99	7.39	9.16	9.11
Eu	1.24	1.23	1.41	1.23	1.76	1.81

Table 4. Cont.

Sample	LS-1	LS-2	LS-3	LS-4	LS-7	LS-8
Gd	7.94	8.20	8.14	7.74	9.42	10.27
Tb	1.06	1.16	1.09	1.00	1.27	1.47
Dy	6.02	7.34	6.51	6.33	7.61	9.05
Ho	1.14	1.42	1.21	1.26	1.42	1.81
Er	3.12	3.81	3.20	3.58	3.84	4.89
Tm	0.44	0.55	0.38	0.49	0.53	0.66
Yb	2.84	3.55	2.92	3.47	3.65	4.65
Lu	0.41	0.48	0.40	0.50	0.50	0.66
Hf	7.06	6.82	7.56	7.66	6.78	9.94
Ta	0.79	0.97	0.93	0.95	0.93	1.10
Th	20.73	22.42	21.97	21.81	21.52	21.37
U	3.57	4.74	4.08	3.75	3.84	5.40
∑HREE	22.97	26.51	23.86	24.36	28.25	33.46
∑LREE	221.86	221.03	222.56	209.61	244.77	231.39
∑REE	244.83	247.54	246.41	233.98	273.02	264.85
Y/Nb	2.97	2.97	2.57	2.67	3.07	3.44
Nb/Ta	15.74	15.22	16.04	15.31	15.58	14.49
Zr/Hf	41.66	41.11	40.93	40.87	40.78	39.07
Zr + Nb + Ce + Y	451.49	441.69	464.89	463.49	446.19	558.89
Th + U	24.30	27.15	26.05	25.56	25.36	26.77
Rb/Sr	2.10	2.67	2.09	3.21	2.35	3.32
La/Nb	4.35	3.80	3.88	3.71	4.38	3.93
Th/La	0.38	0.40	0.38	0.40	0.34	0.34
Y/Ta	46.79	45.20	41.23	40.94	47.80	49.89
T(°C)	848	861	853	885	860	908

In the Harker diagrams (Figures 7 and 8), Al_2O_3 , K_2O , MgO , TiO_2 , CaO , Na_2O , MnO , P_2O_5 , Ba, Rb, and SiO_2 showed negative correlations, indicating that fractional crystallization played a role during magma evolution.

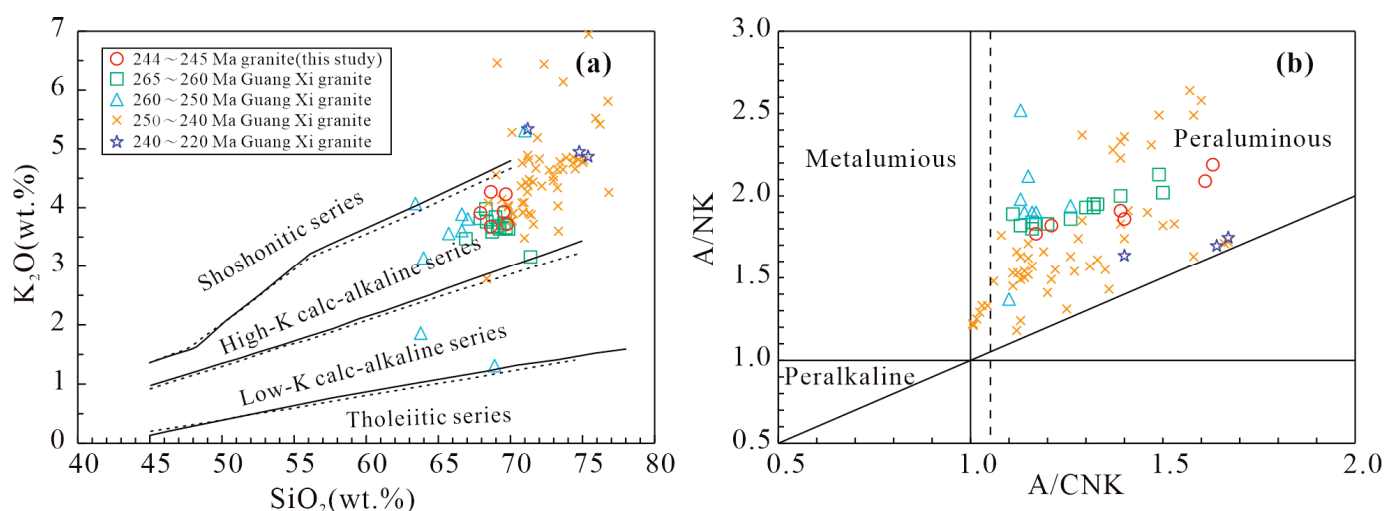


Figure 6. Plots of (a) K_2O versus SiO_2 and (b) A/NK versus A/CNK in granite from Darongshan–Shiwandashan, southeast Guangxi. Data source: 265–260 Ma granites: [41]; 260–250 Ma granites: [42]; 250–240 Ma granites: [26,43–45]; 240–220 Ma granites: [46].

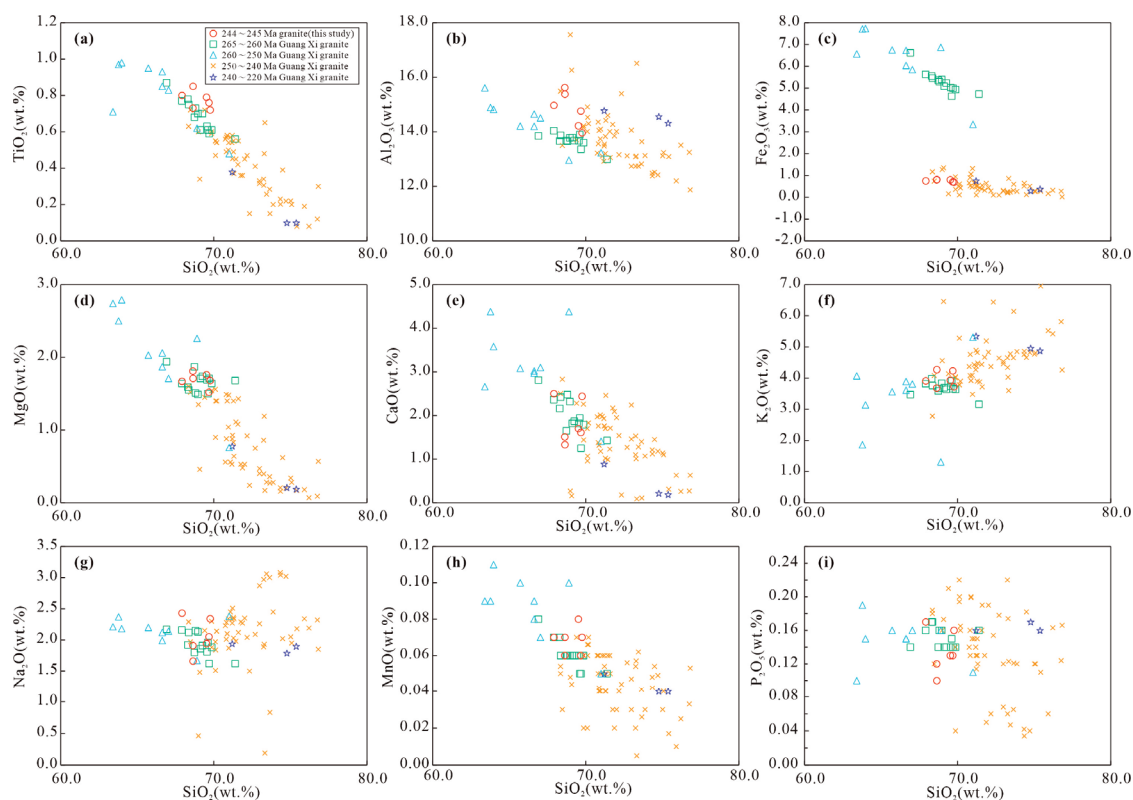


Figure 7. Plots of (a) TiO_2 , (b) Al_2O_3 , (c) Fe_2O_3 , (d) MgO , (e) CaO , (f) K_2O , (g) Na_2O , (h) MnO , and (i) P_2O_5 versus SiO_2 in granite from Darongshan–Shiwandashan, southeast Guangxi. Data sources are the same as in Figure 6.

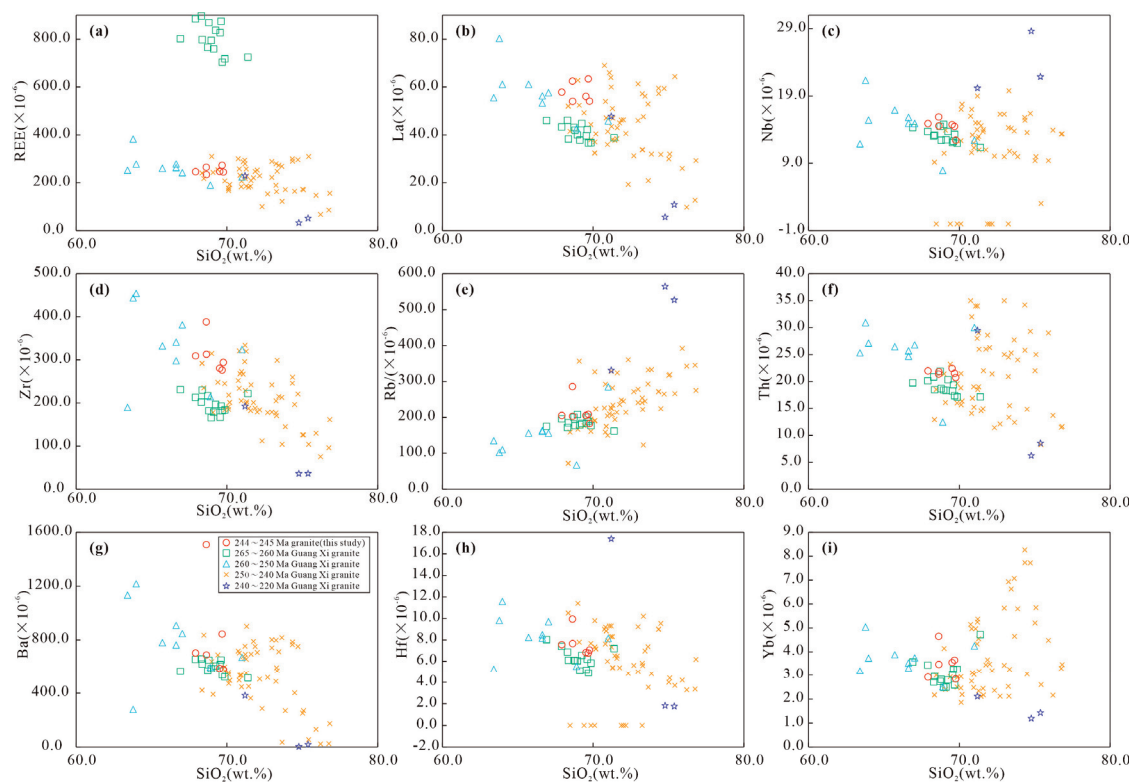


Figure 8. Plots of (a) REE, (b) La, (c) Nb, (d) Zr, (e) Rb, (f) Th, (g) Ba, (h) Hf, and (i) Yb versus SiO_2 in granite from Darongshan–Shiwandashan, southeast Guangxi. Data sources are the same as in Figure 6.

4.2.2. Trace and REE Elements

The granite samples were rich in Rb, Th, and U and depleted in Ba, Nb, Ta, Sr, P, and Ti (Figure 9a). The LREE and HREE contents of the samples were 210.0×10^{-6} – 245.0×10^{-6} and 23.0×10^{-6} – 33.0×10^{-6} , respectively, indicating that LREEs were relatively enriched. The REE contents were 234.0×10^{-6} – 273.0×10^{-6} , with an average of 252.0×10^{-6} , which was much higher than that in the original mantle (7.43×10^{-6}). The $(\text{La}/\text{Sm})_{\text{N}}$ and $(\text{Gd}/\text{Yb})_{\text{N}}$ ratios are 4.43–4.72 and 1.82–2.31, respectively, with obvious negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.15$ – 0.18) (Figure 9b).

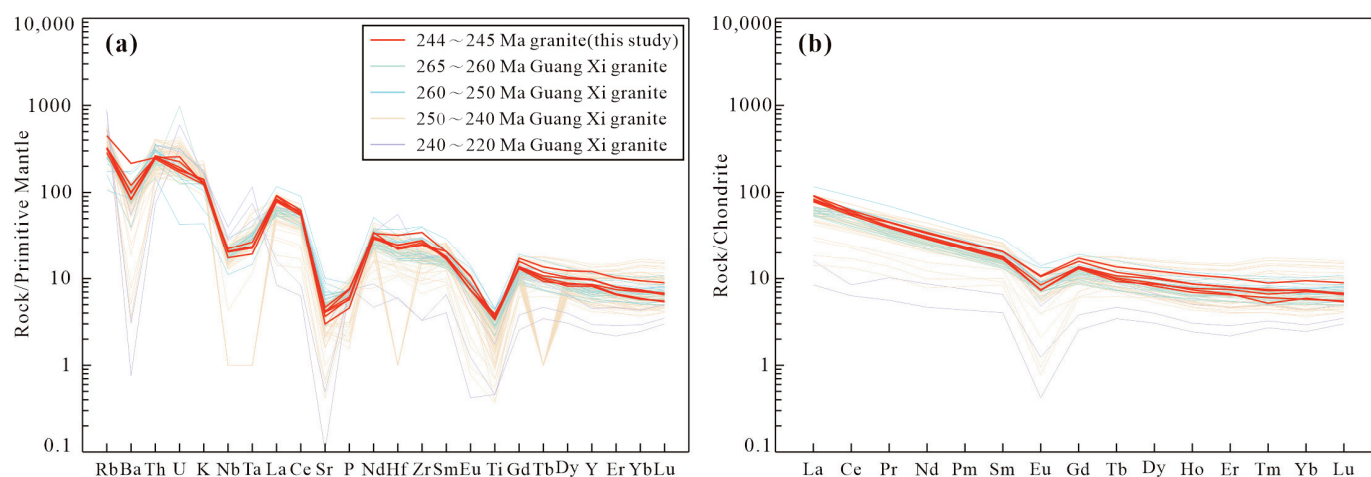


Figure 9. (a) Chondrite-normalized REE distribution patterns and (b) primitive-mantle-normalized multi-element diagrams of granite from Darongshan-Shiwandashan, southeast Guangxi. Data sources are the same as in Figure 6.

4.2.3. Characteristics of Rare-Earth Minerals

Previous studies have shown that rare-earth elements in granite occur primarily in two types: (1) primary REE-bearing minerals and (2) REE replacements in secondary minerals [47,48]. Scanning electron microscopy (SEM) analyses of the granite samples revealed that the samples primarily contained REE-bearing minerals, such as monazite, xenotime, zircon, and apatite. Zircon and apatite were primarily formed through magma crystallization and occurred in rock-forming minerals, such as biotite (Figure 10). Xenotime was distributed along the edges or fractures of apatite (Figure 10a), indicating that they were mainly formed through hydrothermal alteration. These REE-bearing minerals had relatively high rare-earth element contents and were the main carriers of rare-earth elements in the parent rock, as shown by energy-dispersive spectroscopy (EDS) in Figure 11 and Table 5.

Xenotime (YPO_4) is a phosphate mineral and one of the most important carriers of rare-earth elements. It mainly occurs as granular grains between plagioclase and quartz, with particle sizes ranging from 40 to 100 μm (Figure 10a). Its Y_2O_3 , Gd_2O_3 , and Dy_2O_3 contents are 47.40 wt.%, 2.53 wt.%, and 4.42 wt.%, respectively (Figure 11a, Table 5).

Zircon ($\text{Zr}[\text{SiO}_4]$) is a silicate mineral and a common accessory mineral in granite. It primarily occurs as euhedral grains that are interstitial or enclosed in minerals, such as feldspar, biotite, and quartz, with grain sizes ranging from 50 to 100 μm (Figure 10b). It is mainly composed of ZrO_2 (69.19 wt.%) and SiO_2 (30.81 wt.%) (Figure 11b, Table 5).

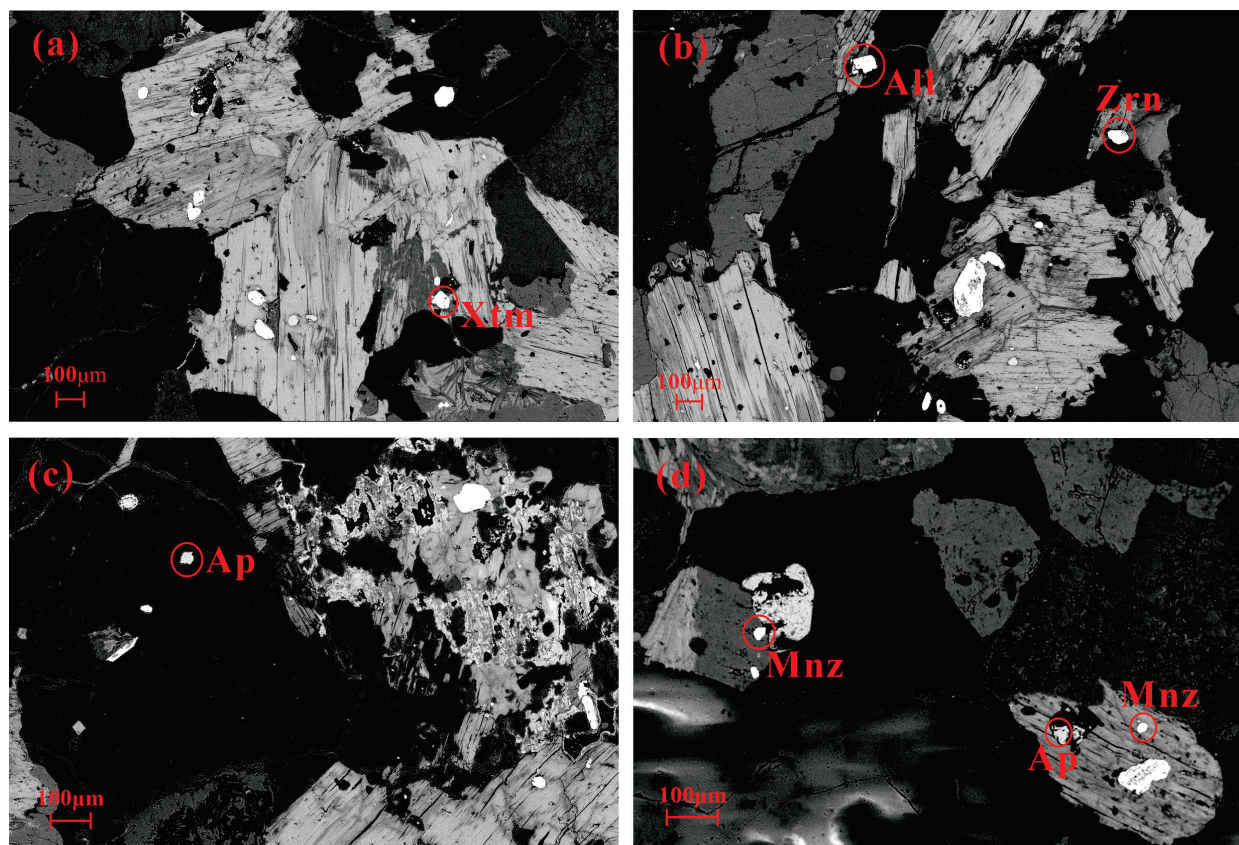


Figure 10. SEM images (a–d) of granite from Darongshan–Shiwandashan, southeast Guangxi. Xtm—Xenotime; Ap—Apatite; Mnz—Monazite; Zrn—Zircon; All—Allantite.

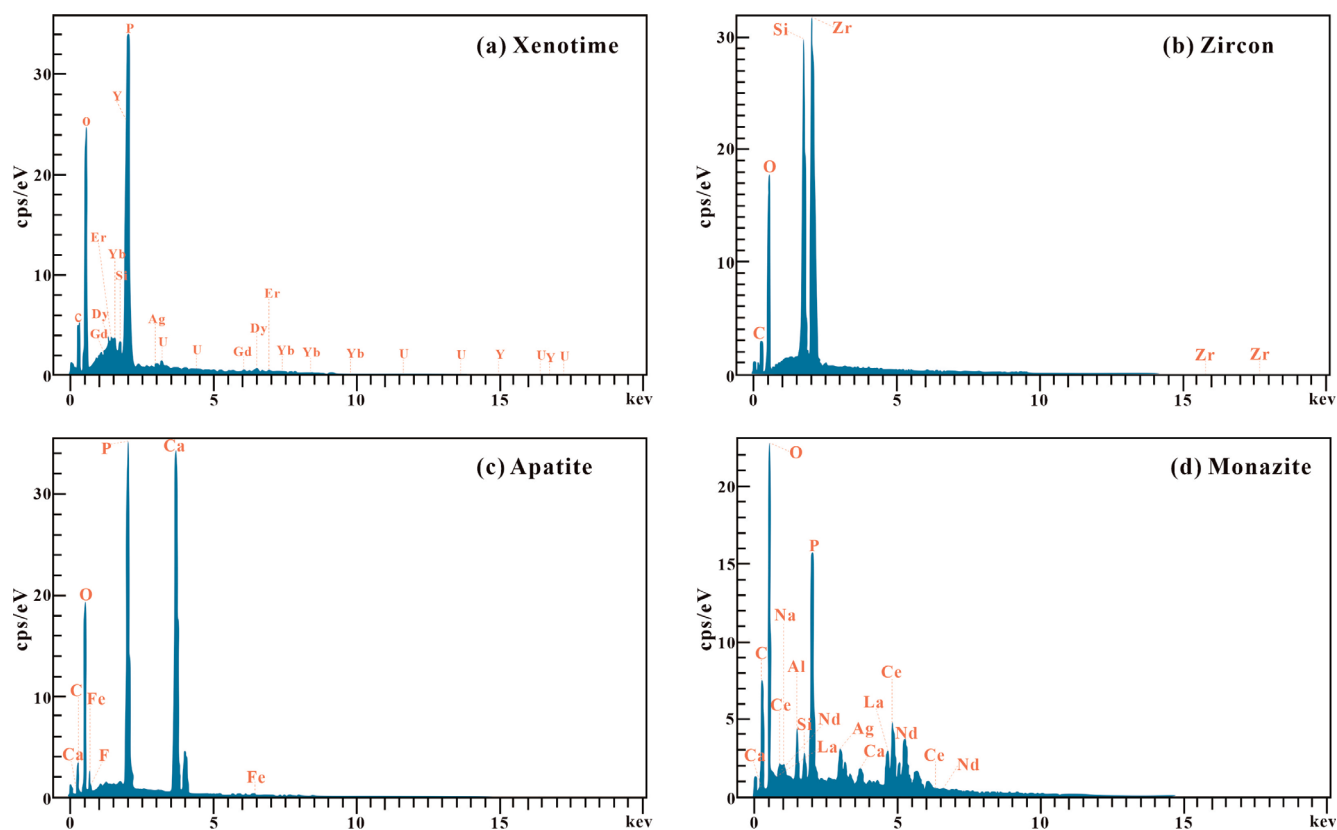


Figure 11. Spectrogram of energy analysis of (a) xenotime, (b) zircon, (c) apatite, and (d) monazite in granite from Darongshan–Shiwandashan, southeast Guangxi.

Table 5. Results of energy spectrum analysis of REE-bearing minerals in granite from Darongshan–Shiwandashan, southeast Guangxi.

REE Minerals	Oxide	Content (wt.%)
Monazite	P ₂ O ₅	27.18
	La ₂ O ₃	15.34
	Ce ₂ O ₃	30.25
	Nd ₂ O ₃	11.49
	SiO ₂	2.58
Xenotime	P ₂ O ₅	34.57
	Y ₂ O ₃	47.40
	Gd ₂ O ₃	2.53
	Dy ₂ O ₃	4.42
Zircon	SiO ₂	30.81
	ZrO ₂	69.19
Apatite	P ₂ O ₅	42.69
	CaO	52.51
	FeO	1.05

Apatite from the granite samples mainly occurred as euhedral or subhedral grains with sizes ranging from 20 to 110 μm (Figure 10c). It is always enclosed by minerals such as quartz and feldspar. Its P₂O₅, CaO, and FeO contents are 42.69 wt.%, 52.51 wt.%, and 1.05 wt.%, respectively (Figure 11c, Table 5).

In this study, monazite was mainly distributed within minerals such as feldspar and quartz (Figure 10d). It was rich in rare-earth elements, with La₂O₃ content of 15.34 wt.%, Ce₂O₃ content of 30.25 wt.%, and Nd₂O₃ content of 11.49 wt.% (Figure 11d, Table 5).

5. Discussion

5.1. Rock Type

The genetic type of igneous rock is closely related to geodynamic processes [49]. Research indicates that determining the genesis type of granite is of great significance for studying magma evolution processes and the characteristics of magma source regions. According to its genesis and properties, granite can be classified into the A-, S-, I-, and M-types [50–52]. I-, S-, and M-type granite classification mainly emphasizes the difference in the magma source region, while A-type granites mainly reflect the specific geodynamic background. Mineralogy is an important indicator for distinguishing A-, S-, and I-type granites. S-type granite contains peraluminous minerals (such as cordierite). I-type granite most commonly contains hornblende. A-type granite is characterized by alkaline ferromagnesian minerals [50,53]. M-type granite is produced through the differentiation of basic magma and is a mantle-derived granite [50]. In addition, the aluminum saturation index (A/CNK) of I-type granite is less than 1.1, and it is mainly produced by crust–mantle interactions. S-type granite is derived from crust-derived sediments, and its A/CNK ratio is greater than 1.1 [51,52]. A-type granite is formed through magma crystallization at relatively high temperatures and under alkaline, anhydrous, and anorogenic conditions (“3A”), and it is characterized by $\text{Zr} > 250 \times 10^{-6}$, $(\text{Zr} + \text{Ce} + \text{Nb} + \text{Y}) > 350 \times 10^{-6}$, $\text{FeO}^{\text{T}}/\text{MgO} > 16$, and $10,000 \times \text{Ga}/\text{Al} > 2.5$ [51,52].

Compared with I-type granite, the samples in this study showed high A/CNK ratios (>1.1 , Table 4), and there was no hornblende in the photomicrographs, indicating that they were not I-type granite. The P₂O₅ content was low (0.10–0.17 wt.%; Table 4), and SiO₂ was negatively correlated with P₂O₅ (Figure 7i), indicating that they were different from S-type granite. They showed obvious negative Eu anomalies (Figure 9b), high

$10,000 \times \text{Ga}/\text{Al}$ values (2.16–5.37, average = 3.42), and high $(\text{Zr} + \text{Nb} + \text{Ce} + \text{Y})$ contents (441.69×10^{-6} – 558.89×10^{-6} , average = 471.11×10^{-6}). These features are similar to those of A-type granites. In the discriminant diagrams proposed by Whalen (1987), all samples fell into the area of A-type granite [54] (Figure 12a,b). These data indicate that the samples in this study were A-type granite.

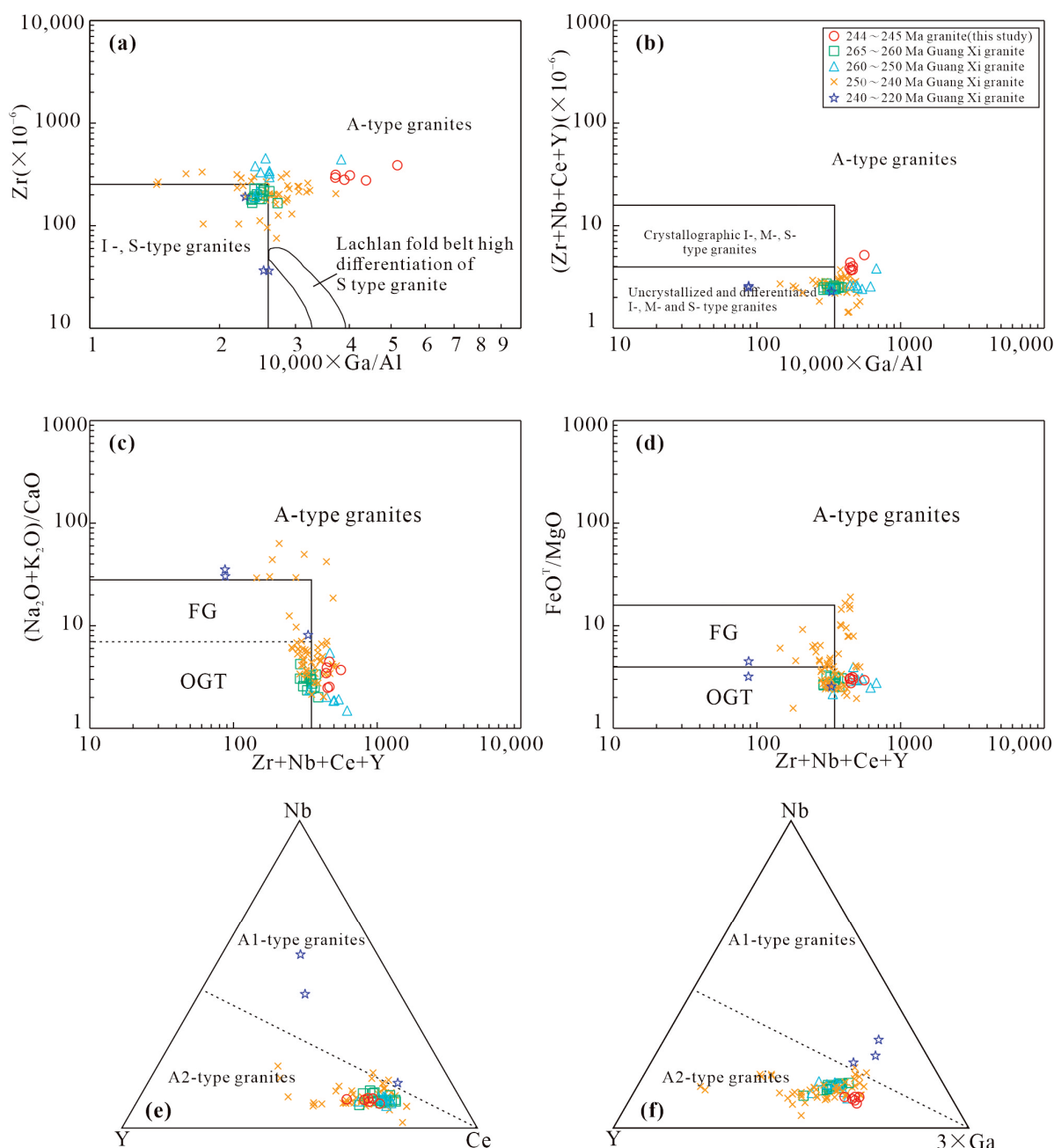


Figure 12. Plots of (a) $10,000 \times \text{Ga}/\text{Al}$ versus Zr , (b) $10,000 \times \text{Ga}/\text{Al}$ versus $(\text{Zr} + \text{Nb} + \text{Ce} + \text{Y})$, (c) $(\text{Zr} + \text{Nb} + \text{Ce} + \text{Y})$ versus $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{CaO}$, (d) $(\text{Zr} + \text{Nb} + \text{Ce} + \text{Y})$ versus $(\text{FeO}^T/\text{MgO})$, (e) Nb–Y–Ce, and (f) Nb–Y– $3 \times \text{Ga}$ for granite from Darongshan–Shiwandashan, southeast Guangxi. Data sources are the same as in Figure 6.

It is worth noting that highly differentiated I-type, S-type, and A-type granites have similar geochemical characteristic. The P_2O_5 content of S-type granite is commonly greater than 0.20%, and is positively correlated with the degree of crystallization differentiation [55]. Wang et al. (2000) proposed that FeO^T content and formation temperature can distinguish between highly differentiated I-type and A-type granite. The FeO^T content of highly

differentiated I-type granite is less than 1.00%, and the formation temperature is lower (764 °C) [56]. A-type granite has higher FeO^T content (>1.00%) and forms at higher temperatures (>800 °C). Whalen et al. (1987) and Eby (1992) proposed a series of diagrams to further distinguish highly differentiated I-type, S-type, and A-type granites [54,57] (Figure 12c,d).

The P_2O_5 content of the granite samples is low (0.10%–0.16%), and the FeO^T content ranges from 4.63% to 5.39%, which is significantly different from S-type granite ($\text{P}_2\text{O}_5 > 0.20\%$) and highly differentiated I-type granite ($\text{FeO}^T < 1.00\%$). The saturation temperature of zircon determines the formation temperature of granite to be 848–908 °C, with an average temperature of 869 °C (Table 4), which is greater than 764 °C. In the highly differentiated granite type discrimination diagrams (Figure 12c,d), all the samples also fall within the A-type granite area.

A-type granite can be further subdivided into A1- and A2-type granites [57]. The geochemical composition of A1-type granite is consistent with oceanic island basalt (OIB), and it is mainly formed in anorogenic environments, such as intraplate rifting, mantle plumes, or hotspot activities [57]. The geochemical composition of A2-type granite is similar to that of continental crust and island arc basalt, and it is mainly derived from back-arc basins, post-collision areas, or post-orogenic extension environments [57]. The samples in this study were characterized by low Nb and high Y contents that were similar to those of A2-type granite. In the Nb–Y–Ce discrimination diagram, all of the samples fell into the area of A2-type granite (Figure 12e,f). This evidence indicates that the granite samples were A2-type granite.

5.2. Characteristics of the Source Region

According to the geochemical characteristics, the granite samples had high Al_2O_3 (13.96 wt.%–15.62 wt.%) and alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O} = 5.59 \text{ wt.\%} - 6.35 \text{ wt.\%}$) contents. Their $\text{Mg}^\#$ values were 40–43, lower than that of mantle-derived magma ($\text{Mg}^\# > 45$). The Nb/Ta (14.49–16.04), Zr/Hf (39.07–41.66), and Rb/Sr (2.09–3.32) ratios were similar to those of continental crust (Nb/Ta = 12, Zr/Hf = 33, Rb/Sr > 0.5). In the δEu versus $(\text{La}/\text{Yb})_N$ and Ce/Nb versus Y/Nb diagrams, the samples fell within the area of the crust type or average crustal composition (Figure 13a,b). The isotopic data of contemporaneous granites in the study area showed that the granites had enriched Nd isotopic and zircon Hf isotopic compositions ($\epsilon_{\text{Nd}}(t)$ and $\epsilon_{\text{Hf}}(t)$ values of −13.6 to −11.9 and −21.9 to −8.8, respectively, [41]).

All of the above evidence suggests that the samples were mainly derived from crustal material. The geochemical compositions of the samples further indicated that their A/MF, C/MF, and $\text{CaO}/\text{Na}_2\text{O}$ ratios were similar to those of metasediment or sandy source rock (Figure 13e,f). This suggests that the granites originated from partial melting of sandy source rock.

In the Harker diagrams, the contents of Al_2O_3 , K_2O , MgO , TiO_2 , CaO , Na_2O , MnO , P_2O_5 , Ba, and Rb showed a negative correlation with SiO_2 (Figures 7 and 8). In the La–La/Sm diagram (Figure 14a), the samples showed an obvious trend of fractional crystallization. Additionally, they had a high differentiation index ($\text{DI} = 72.8\text{--}76.4$). This evidence indicates that fractional crystallization occurred during magma evolution. In the related diagrams, fractional crystallization of plagioclase and accessory minerals (such as monazite and allanite) can be observed (Figure 14b–d). The depletion of P and Ti (Figure 9a) indicates the crystallization of phosphorus- and titanium-bearing minerals. The negative anomalies of Eu and Sr (Figure 9b) are related to the crystallization of plagioclase (Figure 14b,c).

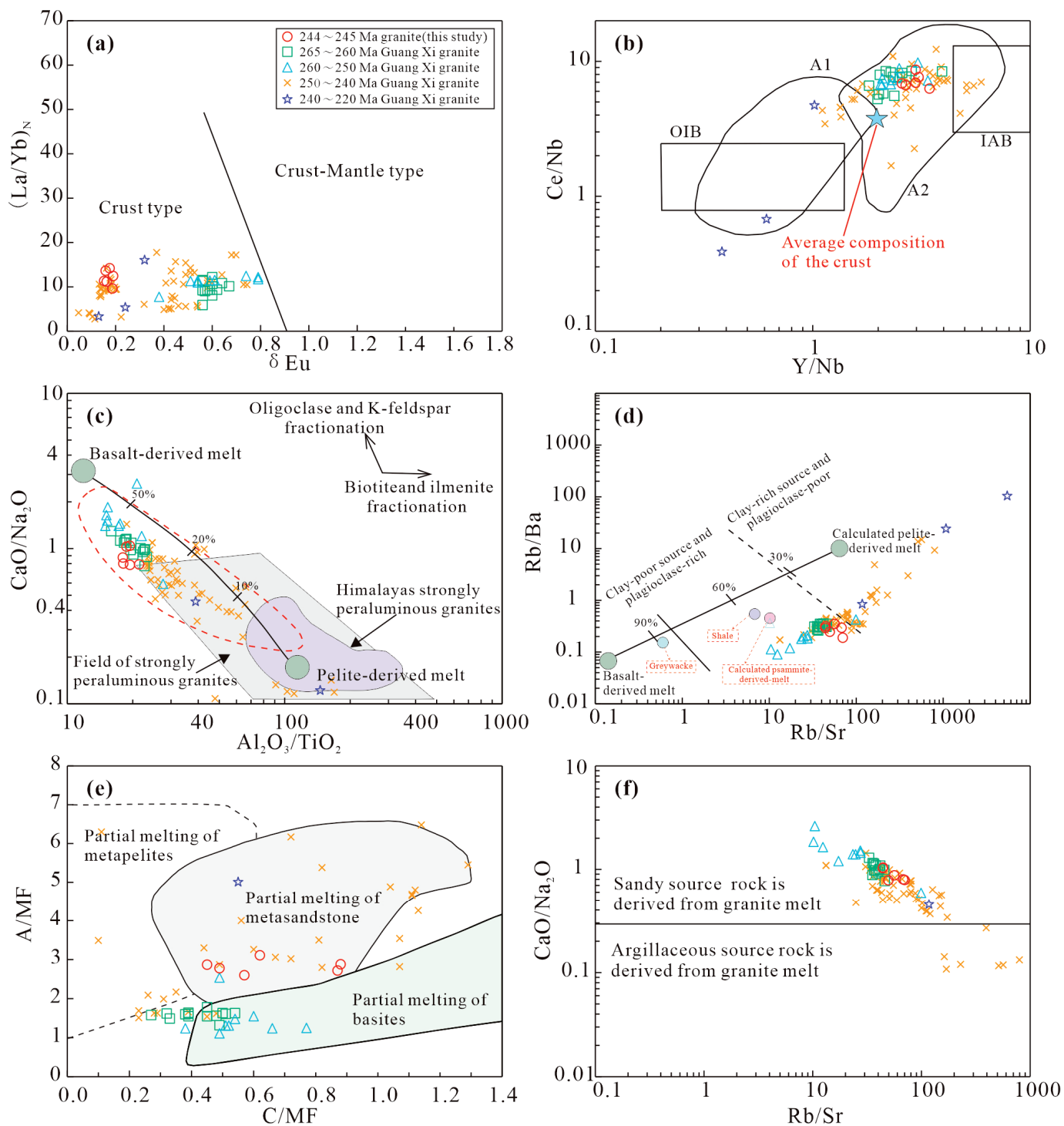


Figure 13. Plots of (a) δEu versus $(La/Yb)_N$, (b) Y/Nb versus Ce/Nb , (c) Al_2O_3/TiO_2 versus CaO/Na_2O , (d) Rb/Sr versus Rb/Ba , (e) C/MF versus A/MF , and (f) Rb/Sr versus CaO/Na_2O for granite from Darongshan–Shiwandashan, southeast Guangxi. Data sources are the same as in Figure 6.

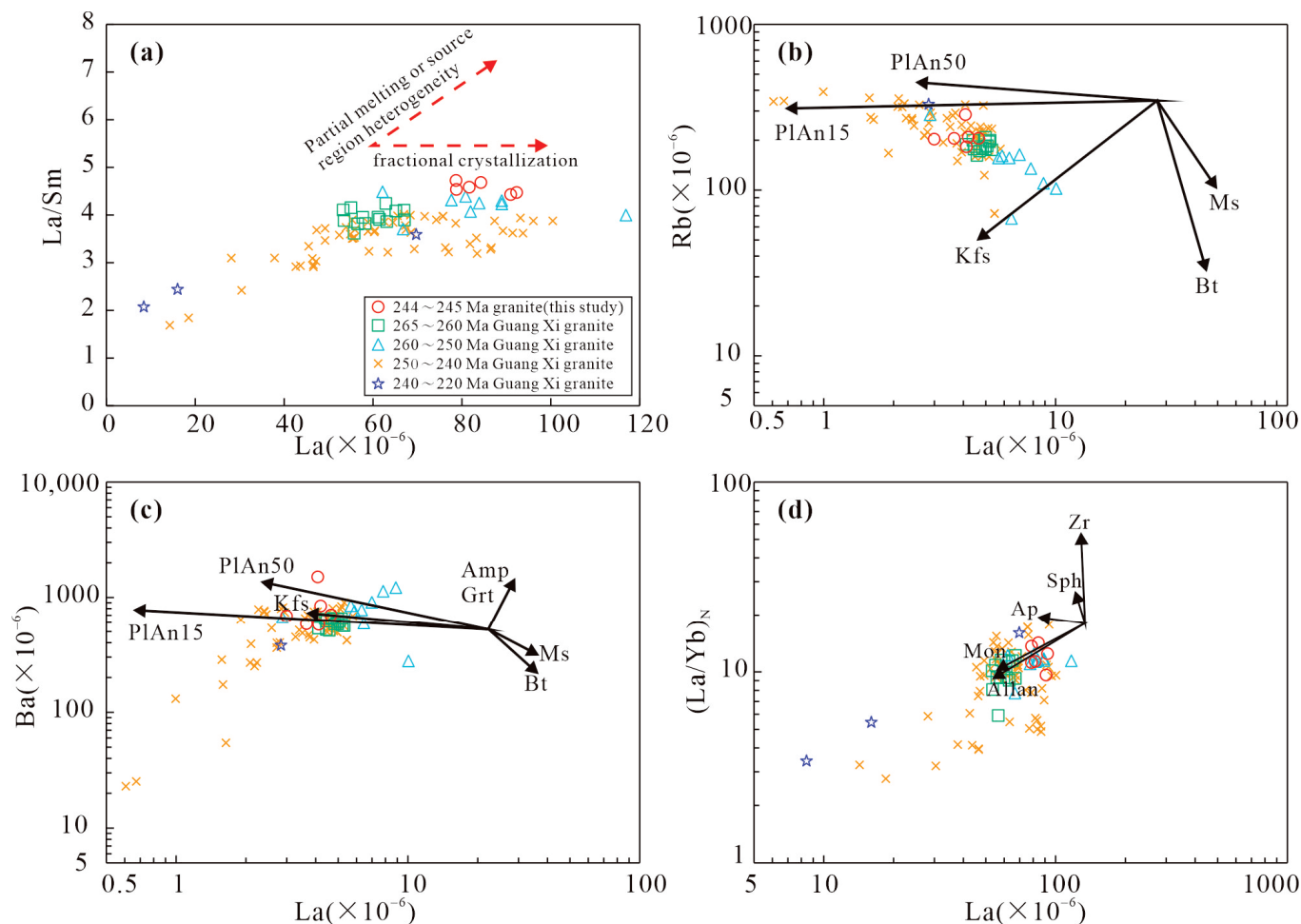


Figure 14. Plots of (a) La versus La/Sm, (b) La versus Rb, (c) La versus Ba, and (d) La versus $(La/Yb)_N$ for granite from Darongshan–Shiwandashan, southeast Guangxi. Data sources are the same as in Figure 6. Pl—plagioclase; Kfs—K-feldspar; Bt—biotite; Ms—muscovite; Amp—amphibolite; Grt—garnet; Zr—zircon; Sph—sphaerocobaltite; Ap—apatite; Allan—allanite; Mon—monazite.

5.3. Tectonic Environment

As discussed above, the formation age of the granite samples in this study was 244–245 Ma, and they were A2-type granite. Previous studies have shown that A-type granite forms in an extensional tectonic environment [57,58]. This indicates that the samples were formed in an extensional environment. In addition, they fell into the area of within-plate granite (WPG) (Figure 15a,b), further indicating that they formed in an extension setting.

Extensive magmatism occurred in the South China and Indochina blocks during the Late Paleozoic to Early Mesozoic periods. The Jinshajiang suture zone outcropped 247–246 Ma rhyolite that was formed by a collision event caused by the subduction of the Paleotethys oceanic crust [59]. In addition, 253–247 Ma granite and volcanic rocks were reported in the Ailaoshan suture zone, and their tectonic settings were syn-collision or arc-continent collision [60–62]. Roger et al. (2012) and Wang et al. (2014) proposed that the formation of Early Triassic (248 Ma) granite in northern Vietnam (Indochina block) was related to continental collision or arc-continent collision resulting from the subduction of the Paleotethys oceanic crust [63,64].

Granite from the Darongshan–Shiwandashan granite belt is considered to have been formed through the subduction of the Paleotethys oceanic crust [42]. Recent studies have revealed that contemporaneous basalt (250–248 Ma), diabase (247 Ma), and dacite porphyry

(247–245 Ma) were preserved in the Darongshan–Shiwandashan area [65,66], and their formation was related to the evolution of Paleotethys [38]. These data indicate that the Late Paleozoic to Early Mesozoic tectonic evolution of the Darongshan–Shiwandashan area was influenced by the evolution of Paleotethys.

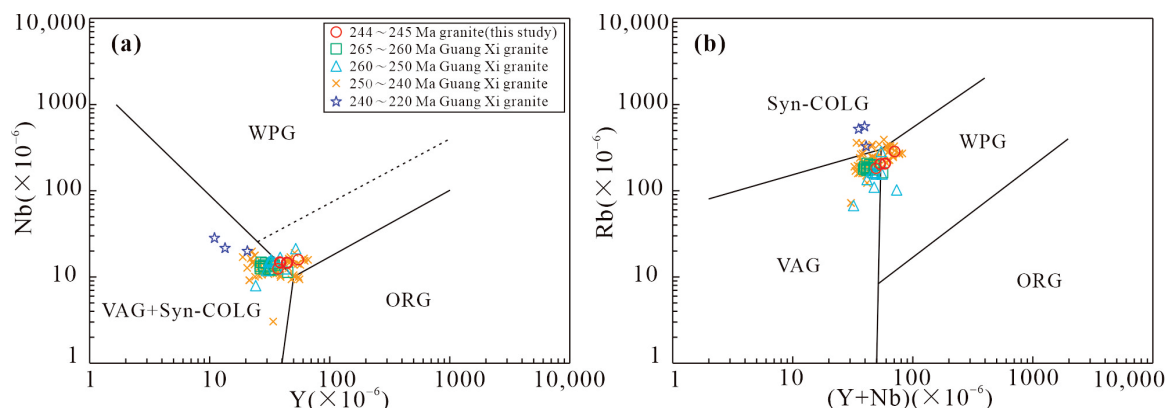


Figure 15. Plots of (a) Y versus Nb and (b) Y + Nb versus Rb of granite from Darongshan–Shiwandashan, southeast Guangxi. Data sources are the same as in Figure 6.

Considering the above, it is suggested that records of Paleotethys are well preserved in the South China and Indochina blocks (Figure 16), and the Early Triassic A-type granite in the Darongshan–Shiwandashan area was formed in an extensional tectonic background, which was related to the evolution of Paleotethys.

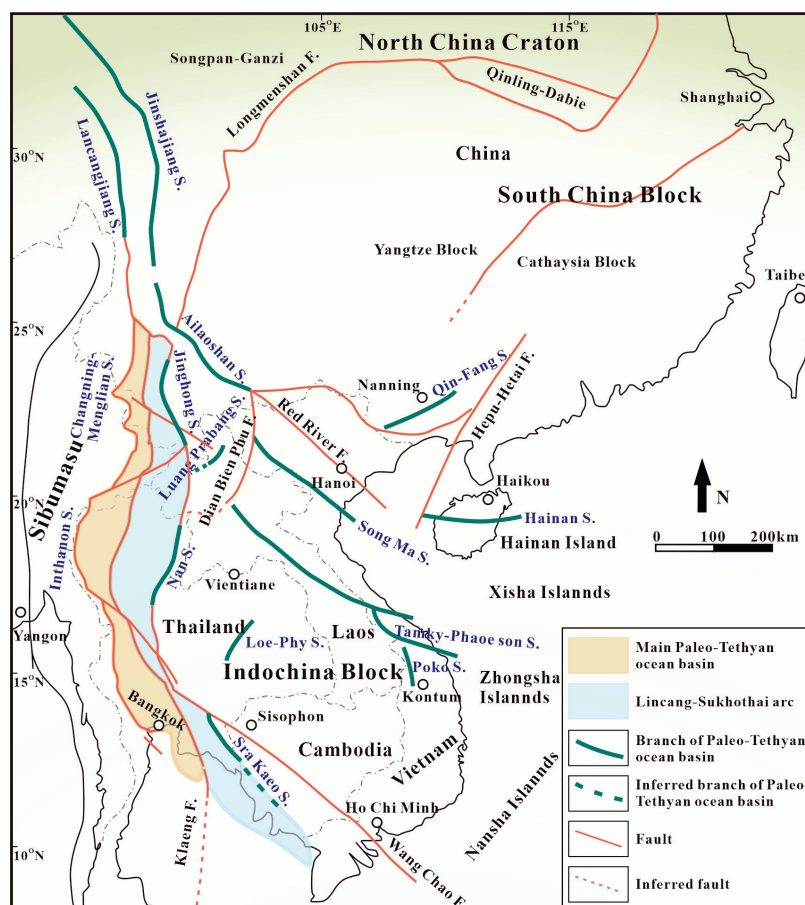


Figure 16. Spatiotemporal framework of main and branched Paleotethyan ocean basin in SE Asia. Modified from [26].

5.4. Ore-Controlling Factors of Regolith-Hosted REE Deposits

5.4.1. Parent Rock Properties

Previous studies have shown that the formation and scale of regolith-hosted REE deposits are directly related to the content of rare-earth elements in the parent rocks [67,68]. Weathering of parent rocks enriched in light rare-earth elements results in light rare-earth regolith-hosted REE deposits, whereas weathering of those enriched in heavy rare-earth elements forms heavy rare-earth regolith-hosted REE deposits [67,69]. The parent rocks of regolith-hosted light REE deposits are mainly biotite monzonite granite, muscovite granite, granite-porphyry, two mica granite, syenite, tuff, and rhyolite, which contain accessory minerals enriched in light rare-earth elements such as bastnaesite, monazite, apatite, titanite, and allanite. The parent rocks of regolith-hosted heavy REE deposits are mostly medium-fine-grained two-mica granite and muscovite granite, which contain accessory minerals enriched in heavy rare-earth elements such as fergusonite, gadolinite, xenotime, euxenite, polycrase, thorite, and zircon [67,70].

The granite samples in this study contain REE-bearing minerals such as xenotime, monazite, apatite, and zircon that are enriched in rare-earth elements. The energy spectrum results show that the content of rare-earth oxides in monazite and xenotime is relatively high (Table 4). The total amount of rare-earth elements (234.0×10^{-6} – 273.0×10^{-6}) in the granite samples was much higher than the lower limit values of the parent rock (132.0×10^{-6}) [71]. In addition, the ratios and contents of rare-earth elements, together with the rare-earth mineral associations of the samples, are similar to those in the ore-forming parent rocks in Jiangxi and Yunnan (Table 6; Figure 17). This evidence indicates that the granites in this area show a good material basis for forming regolith-hosted REE deposits.

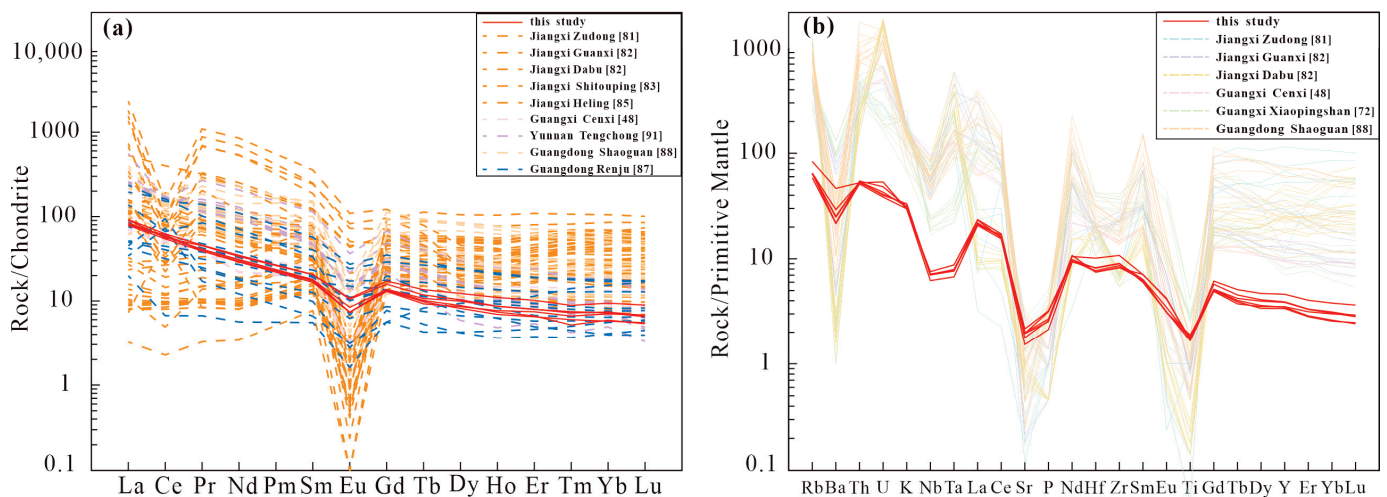


Figure 17. (a) Chondrite-normalized REE distribution patterns and (b) primitive-mantle-normalized multi-element diagrams of parent rocks of some typical regolith-hosted REE deposits in South China.

The distribution of regolith-hosted REE deposits/mineralization in the Darongshan–Shiwandashan area is closely related to the lithology. Outcrops of biotite granite, muscovite granite, and two-mica granite show higher total rare-earth element (REE) content (206×10^{-6} – 343×10^{-6} , this study; [71]), and regolith-hosted REE deposits/mineralization are also distributed in the above lithologic areas. In contrast, the Yong'an pluton, a part of the Darongshan–Shiwandashan granite belt, is mainly composed of granodiorite, and its REE content is 175×10^{-6} – 241×10^{-6} [45], which is obviously different from the above lithologic areas. At present, no regolith-hosted REE deposits have been found in

the Yong'an area. One of the main reasons for this is that the Yong'an pluton underwent relatively weak magma evolution.

Previous studies have shown that strong fractional crystallization favors the crystallization of REE-bearing minerals such as zircon, sphene, apatite, monazite, and xenotime, which are easily decomposed and adsorbed during later weathering processes, thus providing a material basis for the enrichment of rare-earth elements [72–74]. Studies have further pointed out that the fractionation and leaching of rare-earth elements in the parent rock must have a high degree of magma evolution [75–77]. The granite in this study underwent fractional crystallization (Figures 7, 8 and 14). Therefore, strong fractional crystallization of parent rocks may be favorable for the formation of regolith-hosted REE deposits.

Table 6. Comparison of parent rocks of typical regolith-hosted REE deposits in South China.

Name of Deposit	Parent Rock/Age	Rare-Earth Minerals	ΣREE ($\times 10^{-6}$)	ΣLREE ($\times 10^{-6}$)	ΣHREE ($\times 10^{-6}$)	ΣLREE / ΣHREE	Reference
Guangxi Qinfang	granite	Apatite, zircon, xenotime, monazite	252	225	27	8.58	this study
Jiangxi Dafuzu	granite (226 Ma)	Apatite, xenotime	328–414	199–242	82–107	1.2–2.4	[78]
Jiangxi Wulitin	Biotite monzonitic granite (238 Ma)	Apatite, allanite	354–453	305–407	46–48	6.3–8.9	[79]
Jiangxi Shangyou	Medium coarse-grained porphyritic biotite granite	Zircon, xenotime	148	61	87	0.63	[80]
Jiangxi Zudong	Biotite potassium feldspar granite	Xenotime, monazite	261	75	187	0.51	[81]
Jiangxi Guanxi	Alkaline feldspar granite (190 Ma)	Xenotime, monazite	469	419	50	8.38	[82]
Jiangxi Dabu	Muscovite granite (155 Ma)	Xenotime, monazite	125	55	70	0.79	[82]
Jiangxi Shitouping	granite	Xenotime, monazite, bastnaesite	685	351	334	1.2	[83]
Jiangxi Qingxi	Biotite granite (230 Ma)	Xenotime	398	356	42	8.5	[84]
Jiangxi Heling	Granite porphyry	Apatite, zircon, bastnaesite	808	724	84	8.6	[85]
Guangdong Renju	Granodiorite	Xenotime, zircon	338	287	51	5.61	[86]
Guangdong Renju	Quartz diorite	Apatite, zircon, sphene, bastnaesite	298	267	31	9.44	[87]
Guangdong Shaoguan	Biotite granite (162 Ma)	Xenotime	297	205	20	6.7	[88]
Guangxi Huashan	Biotite granite	Sphene	323	245	78	3.12	[89]
Guangxi Cenxi	Granite (155 Ma)	Apatite, zircon, monazite, bastnaesite	279	199	79	2.55	[48]
Guangxi Dazhou	Biotite granite	Allanite	299	217	82	2.65	[90]
Guangxi Xiaopingshan	Biotite monzonitic granite	Apatite, zircon, monazite	343	228	114	2	[72]
Yunnan Tengchong	granite	Xenotime, zircon	783	87	12	7.9	[91]
Yunnan Chahe	Biotite monzonitic granite	Xenotime	257	202	55	3.67	[92]
Yunnan Lincang	Biotite monzonitic granite	Xenotime	361	300	64	5.55	[93]

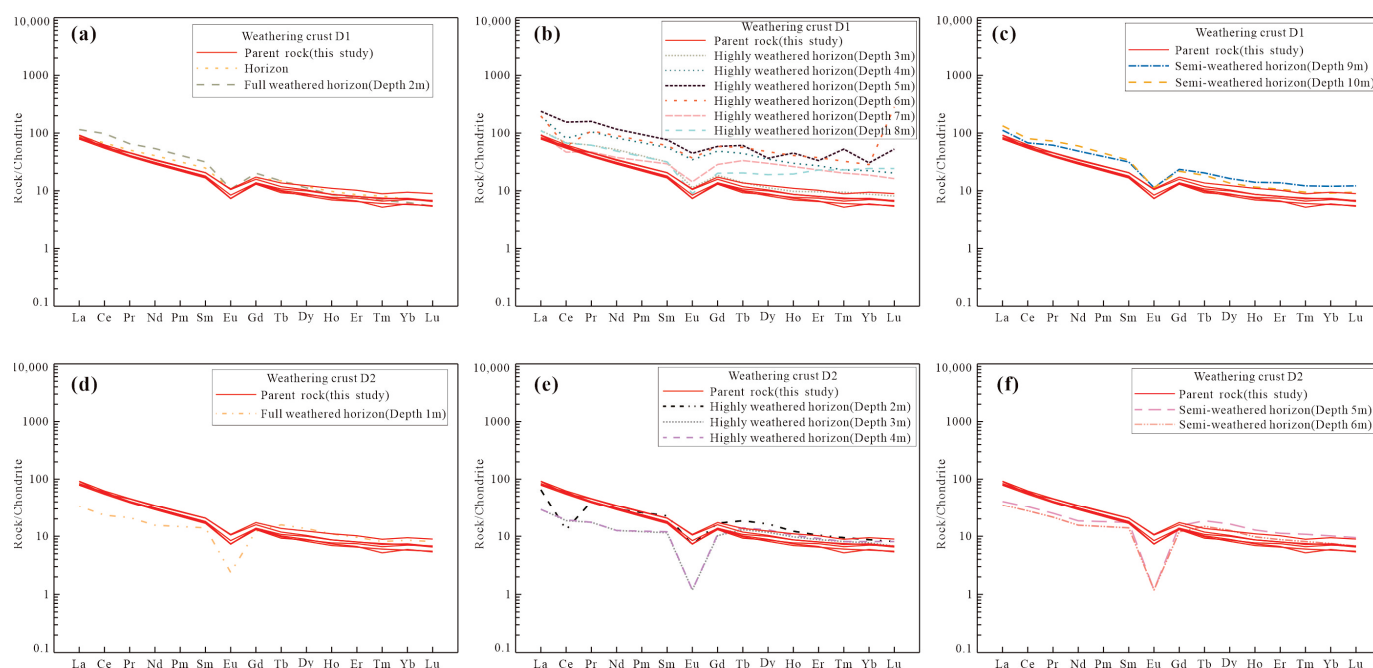
5.4.2. Geomorphology

The geomorphology of the study area mainly consists of mountains and hills. The rare-earth element contents from two weathering crust profiles showed that the top, upper, middle, and lower parts had REE contents of 329×10^{-6} and 178×10^{-6} , 369×10^{-6} – 929×10^{-6} and 155×10^{-6} – 226×10^{-6} , 402×10^{-6} – 436×10^{-6} and 184×10^{-6} – 224×10^{-6} , and 343×10^{-6} and 131×10^{-6} , respectively (Figure 18, Table 7). This indicates that different parts of the weathering crust profile show different rare-earth element contents. More specifically, the middle and upper parts showed the highest REE contents, whereas the top and lower parts were characterized by lower REE contents. This indicates that geomorphology is an important ore-controlling factor of the regolith-hosted REE deposits in the area, and the ridge area in the middle and upper parts is a favorable position for the enrichment of rare-earth elements. In contrast, the steep terrain lacks good conditions for the storage of rare-earth elements, and thus, it is difficult for deposits to be formed.

Table 7. REE compositions of granite and weathering crust from Darongshan–Shiwandashan, south-east Guangxi.

Type	Sample Number	REE	LREE	HREE	LREE/HREE	δEu	δCe
Parent rock	LS-1	245	222	23	9.66	0.16	1.06
	LS-2	248	221	27	8.34	0.15	1.03
	LS-3	246	223	24	9.33	0.18	1.00
	LS-4	234	210	24	8.60	0.16	1.05
	LS-7	273	245	28	8.66	0.19	1.03
	LS-8	265	231	33	6.92	0.19	1.02
Full weathered horizon	D1-1	329	262	67.6	8.48	0.50	0.99
	D1-2	421	360	63.0	11.75	0.41	1.10
Highly weathered horizon	D1-3	368	300	68.6	9.38	0.48	0.79
	D1-4	581	450	221	4.87	0.65	0.54
	D1-5	929	683	247	2.79	0.67	0.47
	D1-6	733	426	326	3.58	0.61	0.39
	D1-7	424	227	196	3.26	0.50	0.66
	D1-8	433	293	142	5.00	0.35	0.79
Semi-weathered horizon	D1-9	401	296	106	6.60	0.41	0.79
	D1-10	437	352	83.9	9.12	0.39	0.78
Full weathered horizon	D2-1	178	97	80.8	3.14	0.18	0.86
Highly weathered horizon	D2-2	226	130	95.6	3.57	0.35	0.25
	D2-3	155	80	74.8	2.99	0.13	0.80
	D2-4	159	81	77.7	2.84	0.09	0.85
Semi-weathered horizon	D2-5	223	126	98.0	3.38	0.08	1.00
	D2-6	184	106	77.6	3.74	0.09	0.97

Weathering crust data are from [72].

**Figure 18.** Chondrite-normalized REE distribution patterns of parent rocks and (a,d) full weathered horizon, (b,e) highly weathered horizon, and (c,f) semi-weathered horizon of weathering crust D1 and D2. Comparison data are sourced from [72].

5.4.3. Weathering

The development, integrity, and thickness of the weathering crust are all affected by the intensity of weathering [94]. Typical weathering crust profiles, from top to bottom, can be divided into a fully weathered horizon, highly weathered horizon, semi-weathered horizon, weakly weathered horizon, and parent rock. The rare-earth element contents in the fully weathered horizon, highly weathered horizon, and semi-weathered horizon of the two weathering profiles are 329×10^{-6} – 423×10^{-6} , 369×10^{-6} – 929×10^{-6} , and 402×10^{-6} – 436×10^{-6} and 178×10^{-6} , 155×10^{-6} – 226×10^{-6} , and 184×10^{-6} – 224×10^{-6} , respectively (Figure 18, Table 7). It can be seen that the maximum REE content in both profiles occurs in the highly weathered horizon. Theoretically, a higher degree of weathering is more conducive to the precipitation of rare-earth elements [95]. However, the maximum REE content did not occur in the fully weathered horizon, indicating that the degree of weathering is not directly proportional to the enrichment of REE. In addition, the fully weathered horizon in the study area is located at the top of the hillside, with a steep terrain and large slope, which is not conducive to the storage of rare-earth elements. In contrast, the highly weathered horizon is located at a relatively wide and slow terrain and undergoes strong vertical and lateral leaching, thus having the highest rare-earth element content.

The LREE/HREE ratio of the two weathering crust profiles gradually decreased from the fully weathered horizon to the semi-weathered horizon (Table 6; Figure 18), indicating that there is a differentiation of light and heavy rare-earth elements from the upper to lower parts of the weathering crust. The differentiation of light and heavy rare-earth elements may be related to the stability of rare-earth complexes and ligand complexation in soil solutions [96,97]. For instance, surface water contains anions such as carbon and phosphate ions. The complexation between these anions and heavy rare-earth elements leads to stronger mobility of heavy rare-earth elements, thus resulting in the accumulation of heavy rare-earth elements at the lower part of the weathering profile. Furthermore, prolonged and intense weathering and leaching facilitate the differentiation of light and heavy rare-earth elements, resulting in the accumulation of heavy rare-earth elements in the lower section of the weathering crust.

It is worth noting that the formation of regolith-hosted REE deposits is complex and results from the mutual influence and interaction of multiple factors. For example, geomorphology affects the migration and storage of rare-earth elements and the infiltration and leaching of surface water. This further affects the enrichment of rare-earth elements in the vertical section of the weathering crust profile. Moreover, it is difficult for mineralization to occur with a single factor; for example, the Darongshan and Yong'an plutons, both belonging to the Darongshan–Shiwandashan granite belt, have similar geomorphologies and climate conditions. However, only the former exhibits good regolith-hosted REE mineralization. The possible reasons are as follows: (1) The lithology and the degree of magma evolution are different. The Yong'an pluton is dominated by granodiorite and shows a low degree of magma evolution; (2) the degree of weathering is different. The weathered horizon of the Yong'an pluton is thin. Spherically weathered residual bodies are common, and even some fresh rock outcrops can be observed. In addition to the ore-controlling factors mentioned above, climate, hydrodynamic conditions, PH value, hydrothermal metamorphism, and microbial interactions are all influencing factors of regolith-hosted REE deposits [98,99]. These factors should be comprehensively considered in studies on the formation and differentiation mechanisms of regolith-hosted REE deposits.

6. Conclusions

(1) Geochemical data indicate that some Early Triassic (244–245 Ma) granite in the Darongshan–Shiwandashan granite belt belongs to A-type granite.

(2) The granite belongs to high-potassium calc-alkaline rock and is the product of the partial melting of sandy source rocks. Fractional crystallization of plagioclase, apatite, monazite, and epidote occurred during magma evolution. This formed in an extension tectonic background, which was related to the evolution of the Paleotethys.

(3) The granite is enriched in light rare-earth elements (LREE) and depleted in heavy rare-earth elements (HREE), and it contains certain REE-bearing minerals, such as xenotime, monazite, apatite, and zircon. These characteristics are comparable with those of the parent rocks of typical regolith-hosted REE deposits in South China. The highly weathered horizon located at the mountain ridge showed the highest concentration of rare-earth elements. The formation of regolith-hosted REE deposits in the Darongshan–Shiwandashan areas is primarily controlled by the degree of magma evolution, geomorphology, and weathering processes.

Supplementary Materials: Analytical methods can be downloaded at: <https://www.mdpi.com/article/10.3390/min15050530/s1>.

Author Contributions: Conceptualization, L.Y. and Y.C. (Yongfeng Cai); methodology, J.O. and F.X.; software, L.Y.; validation, Y.C. (Yongfeng Cai); formal analysis, J.O. and F.X.; investigation, L.Y., Y.C. (Yongfeng Cai), Y.C. (Yankun Chen) and F.X.; resources, Y.C. (Yongfeng Cai); data curation, L.Y.; writing—original draft preparation, L.Y.; writing—review and editing, L.Y., Y.Z. and Y.C. (Yongfeng Cai); supervision, Y.C. (Yongfeng Cai); project administration, Y.C. (Yongfeng Cai); funding acquisition, Y.C. (Yongfeng Cai) All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (Grant No. 42372102) and the Guangxi Key R&D Program (Grant No. Guike AB22035045).

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding author.

Acknowledgments: We appreciate the editor and reviewers for their valuable suggestions and constructive comments on this paper.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study, in the collection, analyses, or interpretation of data, in the writing of the manuscript, or in the decision to publish the results.

References

1. Suess, E. Are great ocean depths permanent. *Nat. Sci.* **1893**, *2*, 180–187.
2. Metcalfe, I. Gondwana Dispersion and Asian Accretion: An Overview. *J. Afr. Earth Sci.* **1999**, *29*, 8–28.
3. Metcalfe, I. Multiple Tethyan Ocean Basins and Orogenic Belts in Asia. *Gondwana Res.* **2021**, *100*, 87–130. [CrossRef]
4. Wang, Y.J.; Qian, X.; Cawood, P.A.; Liu, H.C.; Feng, Q.L.; Zhao, G.C.; Zhang, Y.H.; He, H.Y.; Zhang, P.Z. Closure of the East Paleotethyan Ocean and Amalgamation of the Eastern Cimmerian and Southeast Asia Continental Fragments. *Earth-Sci. Rev.* **2018**, *186*, 195–230. [CrossRef]
5. Stampfli, G.M. Tethyan oceans. *Geol. Soc. Lond. Spec. Publ.* **2000**, *173*, 1–23. [CrossRef]
6. Zhu, D.C.; Mo, X.X.; Zhao, Z.D.; Niu, Y.L.; Wang, L.Q.; Chu, Q.H.; Gui, T.P.; Xu, J.F.; Zhou, C.Y. Presence of Permian extension-and arc-type magmatism in southern Tibet: Paleogeographic implications. *Bulletin* **2010**, *122*, 979–993. [CrossRef]
7. Yang, J.; Du, Y.S.; Huang, H.; Yang, J.H.; Huang, H.W.; Huang, Z.Q. Devonian–Carboniferous Pillow OIB-Type Basalts in the Youjiang Basin, SW China: Implications for the Eastern Extension of the Paleo-Tethys Branch Ocean. *J. Earth Sci.* **2023**, *34*, 690–705. [CrossRef]
8. Liu, F.; Lin, W.; Wang, Y.; Meng, L.T.; Faure, M.; Nguyen, V.V.; Wu, Q.Y.; Chu, Y.; Wei, W.; Thu, H.L.T.; et al. Heterogeneity of the Ailaoshan–Song Ma ophiolitic mélange and its palaeogeographic implications for the evolution of Eastern Palaeo-Tethys. *Tectonophysics* **2023**, *858*, 229848. [CrossRef]
9. Qian, X.; Wang, Y.J.; Zhang, Y.Z.; Zhang, Y.H.; Vongpaseuth, S.; Zhang, A.M.; He, H.Y. Petrogenesis of Permian–Triassic Felsic Igneous Rocks along the Truong Son Zone in Northern Laos and Their Paleotethyan Assembly. *Lithos* **2019**, *328*, 101–114. [CrossRef]

10. Shi, M.F.; Wu, Z.B.; Liu, S.S.; Peng, Z.M.; Guo, L.N.; Nie, F.; Xu, S.W. Geochronology and Petrochemistry of Volcanic Rocks in the Xaignabouli Area, NW Laos. *J. Earth Sci.* **2019**, *30*, 37–51. [CrossRef]
11. Yang, L.; Yuan, W.M.; Zhu, X.Y.; Shi, Z. Late Triassic-Cenozoic Thermochronology in the Southern Sanjiang Tethys, SW China: New Insights from Zircon Fission Track Analysis. *J. Earth Sci.* **2019**, *30*, 996–1004. [CrossRef]
12. Zhai, Q.G.; Chung, S.L.; Tang, Y.; Hu, P.Y.; Jin, X.C.; Wang, J.; Wang, H.T.; Wang, K.L.; Lee, H.Y. Late Carboniferous Ophiolites from the Southern Lancangjiang Belt, SW China: Implication for the Arc-Back-Arc System in the Eastern Paleo-Tethys. *Lithos* **2019**, *344*, 134–146. [CrossRef]
13. Sone, M.; Metcalfe, I. Parallel Tethyan Sutures in Mainland Southeast Asia: New Insights for Palaeo-Tethys Closure and Implications for the Indosinian Orogeny. *Comptes Rendus Geosci.* **2008**, *340*, 166–179. [CrossRef]
14. Yu, Y.Q.; Qian, X.; Ghani, A.A.; Zhang, Y.Z.; Wang, Y.J. Triassic Felsic Magmatism in SE Peninsular Malaysia: Petrogenesis and Geodynamic Implications for the Eastern Paleotethyan Tectonic Transition. *Lithos* **2023**, *462*, 107399. [CrossRef]
15. Wang, Y.J.; He, H.Y.; Cawood, P.A.; Srithai, B.; Feng, Q.L.; Fan, W.M.; Zhang, Y.Z.; Qian, X. Geochronological, Elemental and Sr-Nd-Hf-O Isotopic Constraints on the Petrogenesis of the Triassic Post-Collisional Granitic Rocks in NW Thailand and Its Paleotethyan Implications. *Lithos* **2016**, *266*, 264–286. [CrossRef]
16. Wang, H.N.; Liu, F.L.; Santosh, M.; Wang, F. Subduction Erosion Associated with Paleo-Tethys Closure: Deep Subduction of Sediments and High Pressure Metamorphism in the SE Tibetan Plateau. *Gondwana Res.* **2020**, *82*, 171–192. [CrossRef]
17. Wang, H.N.; Liu, F.L.; Santosh, M.; Cai, J.; Wang, F.; Ji, L. Rapid Cold Slab Subduction of the Paleo-Tethys: Insights from Lawsonite-Bearing Blueschist in the Changning–Menglian Orogenic Belt, Southeastern Tibetan Plateau. *Gondwana Res.* **2020**, *85*, 189–223. [CrossRef]
18. Huang, H.; Jin, X.C.; Shi, Y.K.; Zhen, J.B.; Yan, Z. New Fusulinid Assemblages from the Changning–Menglian Belt in Western Yunnan, China and Their Paleogeographic Implications. *J. Asian Earth Sci.* **2023**, *256*, 105807. [CrossRef]
19. Hou, Z.Q.; Zhang, H.R. Geodynamics and metallogeny of the eastern Tethyan metallogenic domain. *Ore Geol. Rev.* **2015**, *70*, 346–384. [CrossRef]
20. Fu, X.N.; Yi, Z.B.; Fu, W.; Liu, J.C.; Han, Z.X.; Fang, G.C.; Sha, X.; Liu, X.; Xu, C. Mineralogy and weathering of REE minerals in the Liuchen granite, Guangxi, southern China: Implications for HREE enrichment in the granite regolith. *Ore Geol. Rev.* **2024**, *169*, 106099. [CrossRef]
21. Fu, X.N.; Bai, Y.P.; Fu, W.; Zhao, Q.; Li, P.Q.; Guo, X.H.; Tang, Z.H. Comparison of weathering enrichment effects of rare earth elements in the Liuchen and Darongshan granites in Southeastern Guangxi and their provenance study. *J. Guilin Univ. Technol.* **2025**, *45*, 1–15. (In Chinese with English Abstract)
22. Fu, W.; Dong, C.F.; Xu, C.; Wang, R.H.; Lu, J.P.; Zhou, H.; Han, Z.X.; Yi, Z.B.; Lv, Y.Z.; Huang, G.Q.; et al. Research on Prospecting Direction of Ion-Adsorption Type Heavy Rare Earth Element Resources in Guangxi and Progresses in Scientific Demonstration Exploration. *Earth Sci.* **2024**, *49*, 1931–1945. (In Chinese with English Abstract)
23. Zhao, Z.; Wang, D.H.; Pan, H.; Qu, W.J. REE Geochemistry of a Weathering Profile in Guangxi, Southern China, and Genesis of Ion-Adsorption Type REE Deposit. *Earth Sci.* **2017**, *42*, 1697–1706. (In Chinese with English Abstract)
24. Fu, W.; Luo, P.; Hu, Z.Y.; Feng, Y.Y.; Liu, L.; Yang, J.B.; Feng, M.; Yu, H.X.; Zhou, Y.Z. Enrichment of ion-exchangeable rare earth elements by felsic volcanic rock weathering in South China: Genetic mechanism and formation preference. *Ore Geol. Rev.* **2019**, *114*, 103120. [CrossRef]
25. Tian, M.Y. Petrological Assemblage and Geological Implications of the Indosinian Igneous Rocks in Southeastern Guangxi Province. Master's Thesis, China University of Geosciences, Beijing, China, 2021; pp. 1–67.
26. Zhou, Y.; Zhao, Y.S.; Cai, Y.F.; Hu, Q.F.; Wang, C. Permian-Triassic Magmatism in the Qin-Fang Tectonic Belt, SW China: New Insights into Tectonic Evolution of the Eastern Paleo-Tethys. *J. Earth Sci.* **2023**, *34*, 1704–1716. [CrossRef]
27. Zhao, L.; Guo, F.; Fan, W.M.; Li, C.W.; Qin, X.F.; Li, H.X. Crustal Evolution of the Shiwandashan Area in South China: Zircon U-Pb-Hf Isotopic Records from Granulite Enclaves in Indo-Sinian Granites. *Chin. Sci. Bull.* **2010**, *55*, 2028–2038. (In Chinese with English Abstract) [CrossRef]
28. Jiao, S.J.; Li, X.H.; Huang, H.Q.; Deng, X.G. Metasedimentary Melting in the Formation of Charnockite: Petrological and Zircon U-Pb-Hf-O Isotope Evidence from the Darongshan S-Type Granitic Complex in Southern China. *Lithos* **2015**, *239*, 217–233. [CrossRef]
29. Deng, X.G.; Chen, Z.G.; Li, X.H.; Liu, D.Y. SHRIMP U-Pb zircon dating of the Darongshan-Shiwandashan granitoid belt in southeastern Guangxi, China. *Geol. Rev.* **2004**, *50*, 426–432. (In Chinese with English Abstract)
30. Wang, W.B.; Li, J.H.; Xin, Y.J.; Sun, H.S.; Yu, Y.Q. Zircon LA-ICP-MS U-Pb dating and geochemical analysis of the Darongshan-Shiwandashan granitoids in southwestern South China and their geological implications. *Acta Geosci. Sin.* **2018**, *39*, 179–188. (In Chinese with English Abstract)
31. Chen, C.H.; Hsieh, P.S.; Lee, C.Y.; Zhou, H.W. Two Episodes of the Indosinian Thermal Event on the South China Block: Constraints from LA-ICPMS U-Pb Zircon and Electron Microprobe Monazite Ages of the Darongshan S-Type Granitic Suite. *Gondwana Res.* **2011**, *19*, 1008–1023. [CrossRef]

32. Li, J.H.; Zhao, G.C.; Johnston, S.T.; Dong, S.W.; Zhang, Y.Q.; Xin, Y.J.; Wang, W.B.; Sun, H.S.; Yu, Y.Q. Permo-Triassic structural evolution of the Shiwandashan and Youjiang structural belts, South China. *J. Struct. Geol.* **2017**, *100*, 24–44. [CrossRef]
33. Huang, C.; Shen, R.W.; Nan, Z.L.; Fu, L.G.; Liu, S.; Cai, D.Z.; Wang, H.; Yu, Y.Z. Zircon U-Pb Ages and Geochemical Characteristics of Early Indosinian Liuwanshan Granites, Guangxi. *Geol. Bull. China* **2017**, *36*, 209–223. (In Chinese with English Abstract)
34. Wang, M.F.; Zhang, X.B.; Pi, D.H.; Guo, X.N. Zircon U-Pb dating of Pubei granite and strontium isotope from sphalerite of the Xinhua Pb–Zn–(Ag) deposit, Yunkai area of Guangxi Province, South China. *Acta Geochim.* **2016**, *35*, 156–171. [CrossRef]
35. Qin, X.F.; Wang, Z.Q.; Cao, J.; Feng, Z.H.; Hu, G.A.; Pan, L.Z. Petrogenesis of early Indosinian granites from the southwestern segment of Qinfang tectonic belt, southern Guangxi: Constraints from zircon U-Pb chronology and geochemistry. *J. Jilin Univ. (Earth Sci. Ed.)* **2013**, *43*, 1471–1487. (In Chinese with English Abstract)
36. Qin, Y.; Cai, Y.F.; Liu, J.; Liu, X.J.; Zhou, Y.; Li, Z.L.; Yang, L.Y. Magmatism Records of Palaeo-Tethyan Evolution: Evidence from Indosinian Volcanic Rocks in Southeastern Guangxi. *Earth Sci.* **2024**, *49*, 3140–3154. (In Chinese with English Abstract)
37. Liu, D.; Kang, Z.Q.; Xu, J.F.; Chen, L.G.; Wei, N.S.; Wei, T.W.; Li, D.X.; Chen, H.; Cao, Y.; Liu, D.M.; et al. Chronology, geochemistry and genetic significance of Mashan basalt in southeast Guangxi. *J. Guilin Univ. Technol.* **2019**, *39*, 806–816. (In Chinese with English Abstract)
38. Qin, Y.; Zhou, Y.; Liu, X.J.; Zhao, Y.S.; Li, Z.L.; Yang, L.Y.; Li, C.; Cai, Y.F. Geochronology and Geochemistry of Igneous Rocks in the Qinfang Belt: Implications for Spatio-Temporal Framework of Paleo-Tethys. *Lithos* **2025**, *494–495*, 107900. [CrossRef]
39. Peccerillo, A.; Taylor, S.R. Geochemistry of Eocene Calc-Alkaline Volcanic Rocks from the Kastamonu Area, Northern Turkey. *Contrib. Mineral. Petrol.* **1976**, *58*, 63–81. [CrossRef]
40. Maniar, P.D.; Piccoli, P.M. Tectonic Discrimination of Granitoids. *Geol. Soc. Am. Bull.* **1989**, *101*, 635–643. [CrossRef]
41. Li, Y.J.; Wei, J.H.; Santosh, M.; Tan, J.; Fu, L.B.; Zhao, S.Q. Geochronology and Petrogenesis of Middle Permian S-Type Granitoid in Southeastern Guangxi Province, South China: Implications for Closure of the Eastern Paleo-Tethys. *Tectonophysics* **2016**, *682*, 1–16. [CrossRef]
42. Zhao, L.; Guo, F.; Fan, W.M.; Li, C.W.; Qin, X.F.; Li, H.X. Origin of the Granulite Enclaves in Indo-Sinian Peraluminous Granites, South China and Its Implication for Crustal Anatexis. *Lithos* **2012**, *150*, 209–226. [CrossRef]
43. Charoy, B.; Barbey, P. Ferromagnesian Silicate Association in S-Type Granites: The Darongshan Granitic Complex (Guangxi, South China). *Bull. Société Géologique France* **2008**, *179*, 13–27. [CrossRef]
44. Fang, D.Y. Geological, Geochemical Characteristics and Petrogenesis of the Wangchong Granitic Super Unit, Darongshan Area, Guangxi Province. Master's Thesis, East China University of Technology, Nanchang, China, 2012.
45. Yuan, Y.S.; Liu, S.; Nan, Z.L.; Zhan, H.S. U-Pb Age and Hf Isotopic Characteristics of Zircons from the Yong'an Granitoid Pluton in Southeastern Guangxi and Their Geological Implications. *Acta Petrol. Mineral.* **2018**, *37*, 869–883. (In Chinese with English Abstract)
46. Qin, H.F.; Huang, X.Q.; Jiang, J.; Tan, B.; Pan, J.G.; Xie, Z.G. Genesis of Indosinian Granites in Maoershan, Northern Guangxi: Evidence from Petrology, Geochemistry, Zircon U-Pb Ages and Hf Isotope. *J. Guilin Univ. Technol.* **2018**, *38*, 597–613. (In Chinese with English Abstract)
47. Yang, X.M.; Zhang, P.S. Study on the Occurrence State and Mass Balance of Rare Earth Elements in Granite. *Rare Earth* **1992**, *5*, 6–11. (In Chinese with English Abstract)
48. Zhao, Y.S.; Zhou, Y.; Xu, C.; Cai, Y.F.; Han, Z.X.; Fang, G.C.; Han, Z.C. Geochemical Characteristics and Rare Earth Metallogenic Indication of Yanshanian Granite in Southeast Guangxi. *Chin. J. Geol.* **2023**, *58*, 890–909. (In Chinese with English Abstract)
49. Li, C.N. *Petrology of Trace Elements in Igneous Rocks*; China University of Geosciences Press: Wuhan, China, 1992; pp. 1–195.
50. Chappell, B.W.; White, A.J.R. Two Contrasting Granite Types. *Pac. Geol.* **1974**, *8*, 173–174.
51. White, W.M.; Tapia, M.D.M.; Schilling, J.G. The Petrology and Geochemistry of the Azores Islands. *Contrib. Mineral. Petrol.* **1979**, *69*, 201–213. [CrossRef]
52. Whalen, J.B. Geochemistry of an island-arc plutonic suite: The Uasilau-Yau Yau intrusive complex, New Britain, PNG. *J. Petrol.* **1985**, *26*, 603–632. [CrossRef]
53. Wu, F.Y.; Li, X.H.; Yang, J.H.; Zheng, Y.F. Discussions on the Petrogenesis of Granite. *Acta Petrol. Sin.* **2007**, *23*, 1217–1238. (In Chinese with English Abstract)
54. Whalen, J.B.; Currie, K.L.; Chappell, B.W. A-Type Granites: Geochemical Characteristics, Discrimination and Petrogenesis. *Contrib. Mineral. Petrol.* **1987**, *95*, 407–419. [CrossRef]
55. Chappell, B.W. Aluminium saturation in I- and S-type granites and the characterization of fractionated haplogranites. *Lithos* **1999**, *46*, 535–551. [CrossRef]
56. Wang, Q.; Zhao, Z.H.; Xiong, X.L. The ascertainment of Late-Yanshanian A-type granite in Tongbai-Dabie orogenic belt. *Acta Petrol. Mineral.* **2000**, *19*, 297–306. (In Chinese with English Abstract)
57. Eby, G.N. Chemical Subdivision of the A-Type Granitoids: Petrogenetic and Tectonic Implications. *Geology* **1992**, *20*, 641–644. [CrossRef]
58. Loiselle, M.C.; Wones, D.R. Characteristics and Origin of Anorogenic Granites. *Geol. Soc. Am.* **1979**, *11*, 468.

59. Zi, J.W.; Cawood, P.A.; Fan, W.M.; Tohver, E.; Wang, Y.J.; Campbell McCuaig, T. Generation of Early Indosinian Enriched Mantle-Derived Granitoid Pluton in the Sanjiang Orogen (SW China) in Response to Closure of the Paleo-Tethys. *Lithos* **2012**, *140*, 166–182. [CrossRef]
60. Liu, C.; Deng, J.F.; Liu, J.L.; Shi, Y.L. The Characteristics of Volcanic Rocks from Late Permian to Early Triassic in Ailaoshan Tectono-Magmatic Belt and Implications for Tectonic Settings. *Acta Petrol. Sin.* **2011**, *27*, 3590–3602. (In Chinese with English Abstract)
61. Liu, H.C.; Wang, Y.J.; Cawood, P.A.; Fan, W.M.; Cai, Y.F.; Xing, X.W. Record of Tethyan Ocean Closure and Indosinian Collision along the Ailaoshan Suture Zone (SW China). *Gondwana Res.* **2015**, *27*, 1292–1306. [CrossRef]
62. Zhang, Y.Y.; Zhang, D.; Chen, Y.H.; Mo, X.X.; Zhao, Z.N.; Huo, H.L. U-Pb Chronology, Lithogeochemistry and Tectonic Significance of Late Permian Granite Porphyry in Zhenyuan Gold Deposit, the Middle Section of Ailaoshan. *Acta Petrol. Sin.* **2021**, *37*, 1674–1690. (In Chinese with English Abstract)
63. Roger, F.; Maluski, H.; Lepvrier, C.; Van, T.V.; Paquette, J.L. LA-ICPMS Zircons U/Pb Dating of Permo-Triassic and Cretaceous Magmatism in Northern Vietnam: Geodynamical Implications. *J. Asian Earth Sci.* **2012**, *48*, 72–82. [CrossRef]
64. Wang, J.L.; Ling, F.C.; Pen, Z.; Shi, M.F.; Wang, H. LA-ICP-MS Zircon U-Pb Isotopic Age of Porphyritic Hornblende-Biotite Monzonitic Granite of Phia Bioc Pluton in Truong Son Fold Belt, Laos-Vietnam and Its Geological Significance. *Geol. Sci. Technol. Bull.* **2014**, *33*, 66. (In Chinese with English Abstract)
65. Wang, X.D.; Sun, C.M.; Jia, X.H.; Zhang, L.G.; Zhou, D. Geochronology, Geochemistry, and Petrogenesis of the Mashan Basalt in Southeast Guangxi Province: Constraints on the Indosinian Tectonic Setting of South China. *Geol. China* **2023**, *50*, 573–585.
66. Xu, W.C.; Luo, B.J.; Xu, Y.J.; Wang, L.; Chen, Q. Geochronology, Geochemistry, and Petrogenesis of Late Permian to Early Triassic Mafic Rocks from Darongshan, South China: Implications for Ultrahigh-Temperature Metamorphism and S-Type Granite Generation. *Lithos* **2018**, *308–309*, 168–180. [CrossRef]
67. Zhou, M.F.; Li, X.X.; Wang, Z.C.; Li, X.C.; Liu, J.C. The Genesis of Regolith-Hosted Rare Earth Element and Scandium Deposits: Current Understanding and Outlook to Future Prospecting. *Chin. Sci. Bull.* **2020**, *65*, 3809–3824. (In Chinese with English Abstract) [CrossRef]
68. Huang, Y.F.; Tan, W.; Bao, Z.W.; He, H.P.; Liang, X.L.; Huang, J.; Wang, H. Constraints of Parent Rock on the Formation of Ion Adsorption HREE Deposit in the Weathering Crust of the Shangyou Granite Batholith. *Geotecton. Metallog.* **2022**, *46*, 303–317. (In Chinese with English Abstract)
69. Li, Y.H.M.; Zhao, W.W.; Zhou, M.F. Nature of Parent Rocks, Mineralization Styles and Ore Genesis of Regolith-Hosted REE Deposits in South China: An Integrated Genetic Model. *J. Asian Earth Sci.* **2017**, *148*, 65–95. [CrossRef]
70. He, H.P.; Yang, W.B. REE Mineral Resources in China: Review and Perspective. *Geotecton. Metallog.* **2022**, *46*, 1–13.
71. Zhang, D.; Yang, W.B.; Niu, H.C. Na-metasomatism and its contributions to REE enrichment in alkaline granite systems. *Acta Petrol. Sin.* **2024**, *40*, 864–872. (In Chinese with English Abstract) [CrossRef]
72. Fu, W.; Li, X.T.; Feng, Y.Y.; Feng, M.; Peng, Z.; Yu, H.X.; Lin, H. Chemical Weathering of S-Type Granite and Formation of Rare Earth Element (REE)-Rich Regolith in South China: Critical Control of Lithology. *Chem. Geol.* **2019**, *520*, 33–51. [CrossRef]
73. Wang, Y.X.; Lu, H.J.; Dai, X.; Duan, T.; Bai, X.J.; Cai, Y.W.; Yin, X.M.; Chen, L.H.; Diwu, J.; Du, S.Y. Facile and Efficient Decontamination of Thorium from Rare Earths Based on Selective Selenite Crystallization. *Inorg. Chem.* **2018**, *57*, 1880–1887. [CrossRef]
74. Neron, A.; Bédard, L.P.; Gaboury, D. The Saint-Honoré Carbonatite REE Zone, Québec, Canada: Combined Magmatic and Hydrothermal Processes. *Minerals* **2018**, *8*, 397. [CrossRef]
75. Yang, W.B.; Niu, H.C.; Shan, Q.; Luo, Y.; Yu, X.Y.; Qiu, Y.Z. Ore-Forming Mechanism of the Baierzhe Super-Large Rare and Rare Earth Elements Deposit. *Acta Petrol. Sin.* **2009**, *25*, 2924–2932. (In Chinese with English Abstract)
76. Zhang, B.T.; Hu, Z.G.; Sun, F.; Zhao, X.B.; Liu, S.; Zhang, Y.S.; Wang, X.Y.; Hu, J.B. Controlling Factors and Metallogenic Model of Ion-Adsorption Type REE Deposits in Middle Section of Lincang Granite Belt, Yunnan Province. *J. Chin. Soc. Rare Earths* **2024**, *42*, 179–194. (In Chinese with English Abstract)
77. He, Y.L.; Ma, L.Y.; Li, X.R.; Wang, H.; Liang, X.L.; Zhu, J.X.; He, H.P. Mobilization and fractionation of rare earth elements during experimental bio-weathering of granites. *Geochim. Cosmochim. Acta* **2023**, *343*, 384–395. [CrossRef]
78. Zhang, W.L. Petrogeochemistry and Tectonic Environment of Dafuzu Rock Mass in Southern Jiangxi Province. *Geotecton. Metallog.* **2006**, *30*, 98–107. (In Chinese with English Abstract)
79. Qiu, J.S.; McInnes, B.I.A.; Xu, X.S.; Allen, C.M. Zircon ELA-ICP-MS Dating for Wuliting Pluton at Dajishan, Southern Jiangxi and New Recognition about Its Relation to Tungsten Mineralization. *Geol. Rev.* **2004**, *50*, 125–133. (In Chinese with English Abstract)
80. Hang, Y.F. Controls of Bedrocks on the Formation of Ion-Adsorption Type REE Deposits in the Weathering Crusts. Ph.D. Thesis, University of Chinese Academy of Sciences (Guangzhou Institute of Geochemistry, Chinese Academy of Sciences), Guangzhou, China, 2021; pp. 1–149.
81. Wang, Y.; Zhao, B.B.; Yang, L.; Hu, B.Q.; Gao, H.D.; Qiu, L.F.; He, Z.B. Geochemical Characteristics and Metallogenic Implications of Extra Large-Scale Ion Adsorption Type Heavy Rare Earth Deposit in Zudong, Southern Jiangxi. *Rare Earth* **2024**, *44*, 51–63. (In Chinese with English Abstract)

82. Yang, Y.Y.; Li, N.B.; Jiang, Y.H.; Zhao, Y. Geochemical Differences of Parent Rocks for Ion-Adsorption LREE and HREE Deposits: A Case Study of the Guanxi and Dabu Granite Plutons. *Geotecton. Metallog.* **2024**, *48*, 232–247. (In Chinese with English Abstract)
83. Yang, W.Z.; He, C.; Wang, Y.; Li, M.G.; Wang, X.G.; Chen, Q.R.; Gong, L.X.; Zhong, W. Genesis of the Giant Shitouping Heavy Rare Earth Element Deposit, Ganzhou, Jiangxi: Constraints from Mineralogy and Geochemistry of Regolith. *Earth Sci.* **2025**, *50*, 1335–1352. (In Chinese with English Abstract)
84. Xie, M.J.; Zhou, J.; Wang, X.Q.; Qi, F.Y.; Zang, B.M.; Wu, H.; Liu, D.S.; Liu, Y.H.; Liu, F.T. Research of Elements' Migration and Enrichment Characteristics of Ion-Adsorption Type REE Deposits in Southern Jiangxi Province. *J. Chin. Soc. Rare Earths* **2022**, *40*, 697–710. (In Chinese with English Abstract).
85. Bao, Z.W.; Zhao, Z.H. Geochemistry of Mineralization with Exchangeable REY in the Weathering Crusts of Granitic Rocks in South China. *Ore Geol. Rev.* **2008**, *33*, 519–535. [CrossRef]
86. Huang, J.; Tan, W.; Liang, X.L.; He, H.P.; Ma, L.Y.; Bao, Z.W.; Zhu, J.X. REE Fractionation Controlled by REE Speciation during Formation of the Renju Regolith-Hosted REE Deposits in Guangdong Province, South China. *Ore Geol. Rev.* **2021**, *134*, 104172. [CrossRef]
87. Huang, J.; Tan, W.; Liang, X.L.; He, H.P.; Ma, L.Y.; Bao, Z.W.; Zhu, J.X.; Zhou, Q. Weathering Characters of REE-Bearing Accessory Minerals and Their Effects on REE Mineralization in Renju Regolith-Hosted REE Deposits in Guangdong Province. *Geochimica* **2022**, *51*, 684–695. (In Chinese with English Abstract)
88. Guo, M.; Huang, L.L.; Sun, S.L.; Huang, K.W.; He, Q.X.; Xiang, A.P. Geochemical Characteristics of Hongling Biotite Granite and Granite Ion-Adsorbed Rare Earth Deposits in Shaoguan, Guangdong. *J. Chengdu Univ. Technol. (Nat. Sci. Ed.)* **2024**, *51*, 561–578, 595. (In Chinese with English Abstract)
89. Fu, W.; Zhao, Q.; Luo, P.; Li, P.Q.; Lu, J.P.; Zhou, H.; Yi, Z.B.; Xu, C. Mineralization diversity of ion-adsorption type REE deposit in southern China and the critical influence of parent rocks. *Acta Geol. Sin.* **2022**, *96*, 3901–3925. (In Chinese with English Abstract)
90. Zhao, Z.; Chen, Z.H.; Zou, X.Y.; Wang, D.H.; Chen, Z.Y. REE Mineralization of Epimetamorphic Rocks from an Ion-Adsorption Type REE Deposit in Southern Jiangxi Province. *Earth Sci.* **2018**, *43*, 3652–3663. (In Chinese with English Abstract)
91. Zhang, B.; Ma, G.T.; Gao, R.D.; Zeng, Z.J.; Wang, L.; Zuo, Z.L.; Huang, S.K. Formation Conditions and Prospecting Prediction of Tuguanzhai Ion-Adsorption Type REE Deposit in Tengchong-Lianghe Area. *Earth Sci.* **2018**, *43*, 2628–2637. (In Chinese with English Abstract)
92. Wang, C.B.; Ni, G.Q.; Qin, Y.K.; Liao, Z.K.; Li, W.S.; Li, S.; Zang, L.; Guan, B. Petrogenesis and REE Enrichment Mechanism of Gejiu Alkaline Complex in Yunnan Province. *Acta Petrol. Mineral.* **2021**, *40*, 704–716. (In Chinese with English Abstract)
93. Zhang, M.; Li, Y.; He, X.C.; Feng, J.L.; Zheng, Y.; Wang, H.K.; Du, J.G.; Wang, S.S. Mineralization of the Ion Adsorption-Type REE Deposits in the Central Part of the Lincang Granites in Western Yunnan. *Sediment. Geol. Tethyan Geol.* **2018**, *38*, 37–47. (In Chinese with English Abstract)
94. Nesbitt, H.W.; Young, G.M. Early Proterozoic Climates and Plate Motions Inferred from Major Element Chemistry of Lutites. *Nature* **1982**, *299*, 715–717. [CrossRef]
95. Maulana, A.; Yonezu, K.; Watanabe, K. Geochemistry of Rare Earth Elements (REE) in the Weathered Crusts from the Granitic Rocks in Sulawesi Island, Indonesia. *J. Earth Sci.* **2014**, *25*, 460. [CrossRef]
96. Aubert, D.; Stille, P.; Probst, A. REE Fractionation during Granite Weathering and Removal by Waters and Suspended Loads: Sr and Nd Isotopic Evidence. *Geochim. Cosmochim. Acta* **2001**, *65*, 387–406. [CrossRef]
97. Yusoff, Z.M.; Ngwenya, B.T.; Parsons, I. Mobility and Fractionation of REEs during Deep Weathering of Geochemically Contrasting Granites in a Tropical Setting, Malaysia. *Chem. Geol.* **2013**, *349–350*, 71–86. [CrossRef]
98. Zhao, Y.; Yang, W.B.; Leng, C.B.; Shan, Q.; Niu, H.C.; Li, N.B. Exotic REE Behaviors of Zircon in the Koktokay No. 3 Granitic Pegmatite, Xinjiang, Northwest China. *Ore Geol. Rev.* **2023**, *154*, 105329. [CrossRef]
99. He, H.P.; Wang, H.; Li, X.R.; Ma, L.Y.; Zhu, J.X.; Yang, W.B. Remobilization and Transferring of Rare Earth Elements in the Formation of Regolith-Hosted REE Deposits. *J. Geomech.* **2024**, *30*, 707–722. (In Chinese with English Abstract)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Origin and Tectonic Implication of Cenozoic Alkali-Rich Porphyry in the Beiya Au-Polymetallic Deposit, Western Yunnan, China

Yun Zhong ¹, Yajuan Yuan ^{2,*}, Ye Lu ³ and Bin Xia ⁴

¹ School of Surveying and Mapping, Guangdong Polytechnic of Industry and Commerce, Guangzhou 510510, China; cloudzj@gdgm.edu.cn

² School of Geography, South China Normal University, Guangzhou 510631, China

³ Guangdong Marine Geological Survey Institute, Guangzhou 510075, China; luye3@mail3.sysu.edu.cn

⁴ School of Marine Sciences, Sun Yat-sen University, Zhuhai 519082, China; xiabin@mail.sysu.edu.cn

* Correspondence: yuanyajuan@m.scnu.edu.cn

Abstract: Cenozoic alkali-rich porphyries are widely distributed in the junction zone between the Sanjiang Orogenic belt and the Yangtze Plate. They are of great significance for understanding the regional geodynamics, tectonic evolution, and metallogenesis. However, the origin of these porphyries remains controversial. In this study, new petrological, geochemical, and geochronological data are presented for Cenozoic syenite porphyry from the Beiya porphyry Au-polymetallic deposit in western Yunnan. Zircon U-Pb dating results show that the Beiya syenite porphyries formed around 36.3–35.0 Ma, coinciding with the magmatic peak in the Jinshajiang-Red River (JSJ-RR) alkali-rich porphyry belt. Geochemical analyses indicate that the Beiya porphyries have potassic characteristics and an arc-like geochemical affinity, with C-type adakite affinity, suggesting a post-collisional setting. The JSJ-RR fault zone is unlikely to be the primary mechanism responsible for the formation of this alkali-rich porphyry magmatism. Instead, the development of the Beiya alkali-rich porphyries is likely associated with the convective removal of the lower part of the over-thickened lithospheric mantle and asthenospheric upwelling during the Eocene–Oligocene. Their magmas probably originated from the partial melting of Paleo–Mesoproterozoic garnet amphibolite facies rocks in the thickened lower continental crust, with the addition of shoshonitic mafic magmas produced by the partial melting of metasomatized lithospheric mantle triggered by asthenospheric upwelling. This study provides additional reliable evidence to further constrain the origin of Cenozoic alkali-rich porphyries in the JSJ-RR belt.

Keywords: alkali-rich porphyry; Paleo–Mesoproterozoic lower continental crust; metasomatized lithospheric mantle; Beiya porphyry Au-polymetallic deposit; Sanjiang area

1. Introduction

The Sanjiang Tethyan tectonic domain in southwest China, spanning southern Qinghai, eastern Tibet, western Sichuan, and western Yunnan, is defined by the convergent drainage of the Nujiang, Lancangjiang, and Jinshajiang rivers within the Hengduan Mountains [1] (Figure 1). It was formed by the Indo–Eurasian collision, is characterized by extensive Cenozoic magmatism, and hosts major Cu–Mo–Au deposits [1–4].

The NW-trending Jinshajiang (Ailao Shan)–Red River fault zone (JSJ-RRFZ, a shear zone), a significant tectonic boundary in the southeastern Tibetan Plateau (Figure 1), extends southward to Indochina. Influenced by the Cenozoic Indo–Australian plate’s south-eastward movement and post-collision extension in eastern Tibet [5], this shear zone

hosts a ~3700 km-long Cenozoic alkali-rich intrusive belt associated with late-collision orogeny [6,7]. This belt constitutes a major tectonic-magma-metallogenic province in the eastern Indo–Asian collision zone, containing diverse alkali-rich porphyries and significant deposits such as Yulong, Machangqing, and Beiya [6,7].

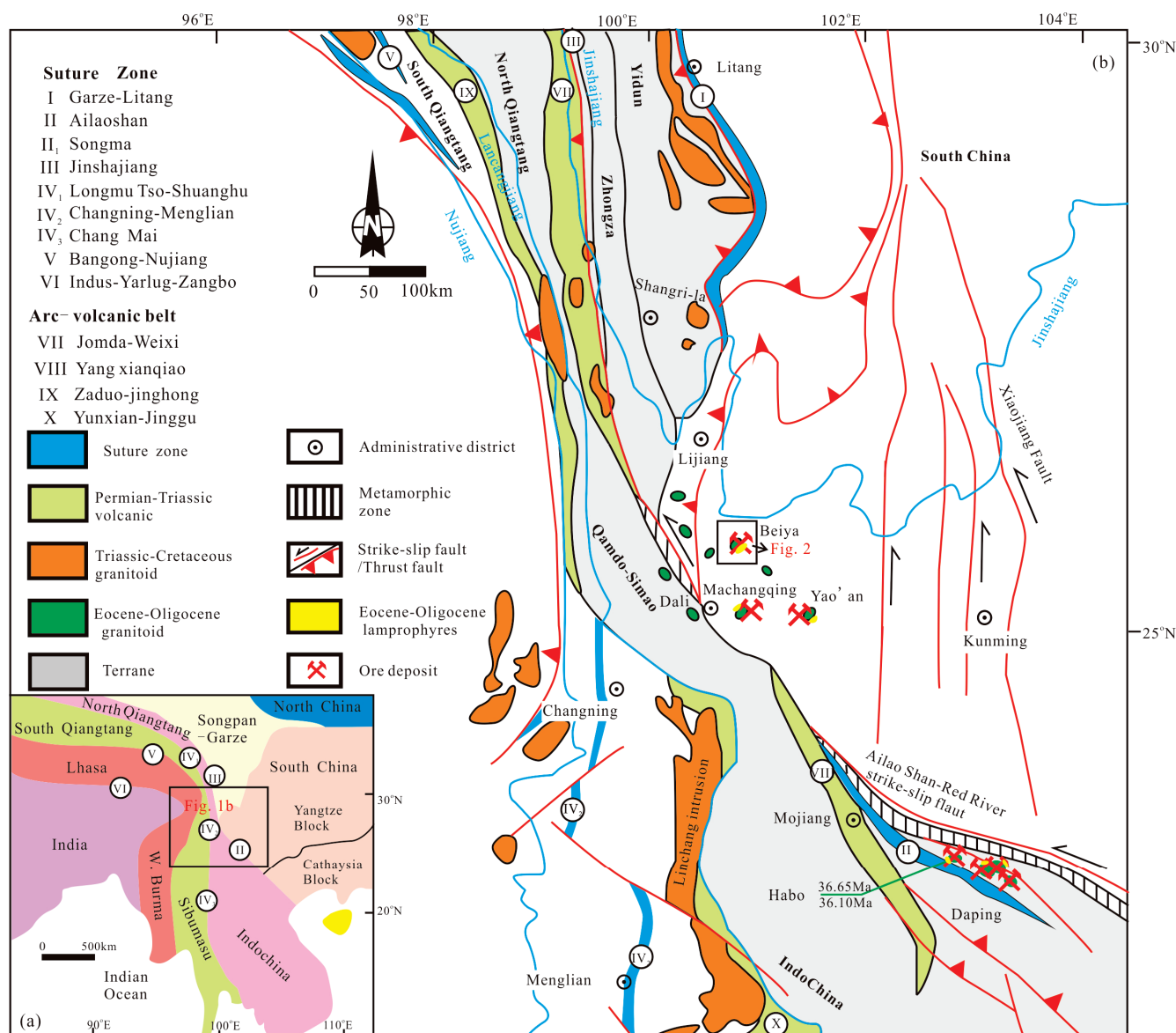


Figure 1. (a) A sketch map illustrating the tectonic framework of the Tibetan Plateau and surrounding areas [1,8,9] as well as the location of Figure 1b, and (b) a geological sketch map showing the distribution of Paleogene potassium-rich igneous rocks in western Yunnan [1–4] and the location of Figure 2.

Despite recent advancements, the petrogenesis of JSJ-RR alkali-rich intrusions remains a subject of debate [10–15]. The proposed genetic models include the following.

- (1) Metasomatized lithospheric mantle melting: Partial melting of metasomatized sub-continental lithospheric mantle due to the Indian plate's eastward subduction [16] though crustal assimilation may be required to explain LILE (large ion lithophile elements)/LREE (light rare earth element) enrichment and HFSE (high-field strength element) depletion in some porphyries [15,17,18].
- (2) Hybrid source origin: Mixed mantle–crustal magmatism involving juvenile crust, ancient crustal materials, OIB (Ocean Island Basalt)/MORB (Mid-Ocean Ridge Basalt),

or upper mantle components [17,19–23]. For instance, isotopic data from the Beiya gold district suggest a mixed source involving OIB, MORB, sedimentary rocks, and upper mantle [21]. Recent petrological and geochemical studies further confirm that the ore-bearing alkali-rich porphyries in the northern section of the JSJ-RR belt were likely derived from the partial melting of a Neoproterozoic lower crust with the input of enriched and depleted mantle-derived magmas [22].

- (3) Thickened mafic lower crust melting: Partial melting of thickened mafic lower crust, indicated by K_2O , Y, Yb, Sr/Y (56.1–109) and low MgO and Cr (or Ni) values in Western Yunnan Cenozoic potassic felsic igneous rocks [24].
- (4) Island-arc mantle activation: Partial melting of island-arc mantle triggered by Indo-Eurasian collision-driven strike-slip faulting [25] though temporal decoupling with JSJ-RRFZ shearing (33–20 Ma) challenges this model [17,24].

Additionally, post-collisional ore-forming porphyries in the JSJ-RR belt are frequently associated with recycled, metal-enriched lower crust ponded by Neoproterozoic arc magmas [13,15,26]. Nevertheless, zircon Hf isotope model ages (0.94–1.98 Ga) from Beiya, Wandongshan, and Bijiaoshan porphyries suggest a Paleo–Mesoproterozoic crustal source, conflicting with this hypothesis [27,28].

The Beiya porphyry Au-polymetallic deposit, located in western Yunnan, within the JSJ-RR alkali-rich intrusive belt (Figure 1), comprises multiple porphyry deposits [7,29,30] (Figure 2). Numerous studies have significantly advanced our understanding of the genesis of Cenozoic alkali-rich porphyry and its associated mineralization in the Beiya region [18,27,31–34]. However, previous studies have focused on Wandongshan and Hongnitang ore blocks; other blocks remain under-investigated [3,18,26,31,35]. Comprehensive geochemical datasets and zircon U–Pb age determinations for the Beiya porphyry across these different ore bodies remain incomplete.

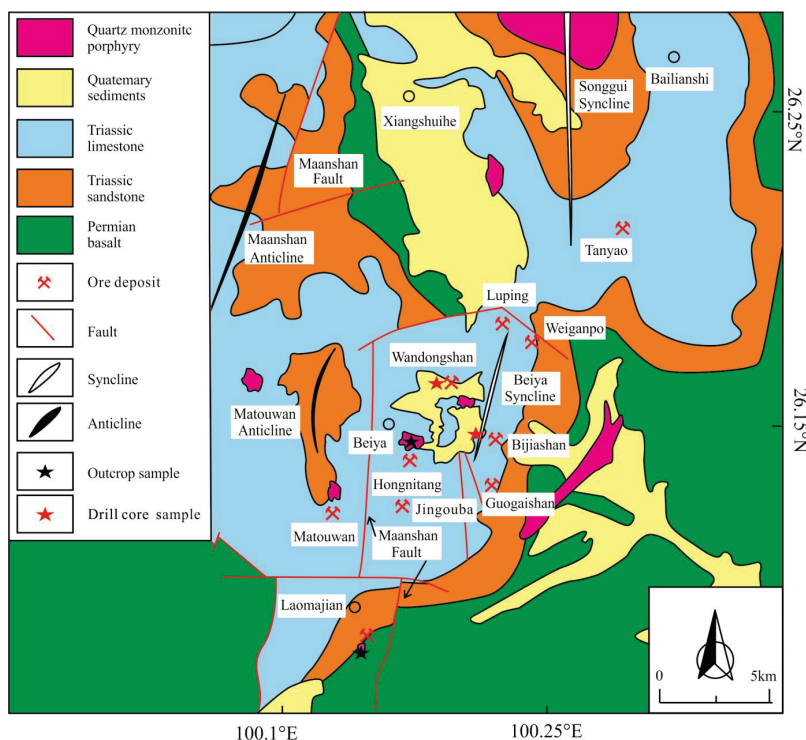


Figure 2. Simplified geological map of the Beiya porphyry Au-polymetallic deposit in western Yunnan [27,36].

This study systematically investigates the Cenozoic porphyries in the Bijiaoshan, Wandongshan, Laomajian, and Hongnitang ore blocks of the Beiya deposit (Figures 1 and 2).

It employs whole-rock geochemistry, Sr-Nd isotopes, zircon U-Pb dating, and Lu-Hf isotopes to reevaluate the petrogenesis, formation age, and source nature of these porphyries, thereby enhancing our understanding of the region's tectonic, magmatic, and metallogenic evolution.

2. Geological Background and Sample Descriptions

2.1. Geological Background

The Sanjiang area, a crucial component of the Tethyan tectonic domain, is situated at the eastern edge of the Alpine-Himalayan orogenic belt, near the convergence of the Pacific and Tethyan tectonic domains. This area experiences intense magmatic activity, resulting in the formation of ultramafic-acidic and alkaline rocks, which may be controlled by regional fault structures. The magmatic activity has three main periods: Variscan, Yanshanian, and Himalayan. The sedimentary strata here are relatively complete, with formation ages ranging from the Proterozoic to the Cenozoic [18].

The Indo-Eurasian collision in the Sanjiang area terminated ~40 Ma, initiating the post-collisional phase [37,38]. Following this, the continuous convergence and compression of the Indo-Eurasian continent caused intense intracontinental thrusting and strike-slip shearing in the Sanjiang area [7,29]. Cenozoic magmatism here is vigorous and extensive, driven by asthenospheric upwelling and significant mantle-derived magmatic activity, mainly from ~40–30 Ma [10,39,40]. The JSJ-RR Cenozoic magmatic rocks are mostly mafic (ca. 37–33 Ma lamprophyre dykes with minor mafic lava) and felsic rocks (ca. 38–33 Ma) [34]. These felsic rocks, emplaced within unmetamorphosed sedimentary sequences, are intermediate-acid alkali-rich porphyritic intrusions of ultra-shallow or shallow facies, associated with polymetallic deposits. They are mainly monzonite porphyry, quartz porphyry, syenite porphyry, and granite porphyry, often occurring as small stocks, rock walls, apophyses, and dykes [2,3,8,10].

The Beiya porphyry Au-polymetallic deposit, the largest gold deposit in southwest China, is situated in Beiya village, Heqing County, Dali Prefecture, Yunnan Province. It spans an area of about 800 km², primarily along the NNE-trending flank of the Beiya syncline. Geotectonically, it is connected to the NW-trending JSJ-RR fault, the NS-trending Binchuan-Chenghai fault, and the NE-trending Muli-Lijiang fault [3,8,21,30,36,41,42] (Figure 1).

Due to frequent Himalayan magmatic activities, the Beiya area has many Cenozoic magmatic rocks, especially shallow intermediate-acid intrusions. The main rocks are syenite porphyry, quartzite syenite porphyry, and granite porphyry, with minor biotite granite porphyry and lamprophyre [8,42]. These rock masses, controlled by the N-S trending Maanshan fault and E-W trending concealed fault, are exposed as stocks, sills, or dykes, typically less than 0.1 km² in area [8,42]. Microgranular enclaves (MMEs), including gabbroic and dioritic enclaves, are found in the porphyry [8].

Mineralization at the Beiya porphyry Au-polymetallic deposit is closely tied to the Himalayan alkali-rich porphyry [43]. Multiple tectonic activities in this area are facilitated hydrothermal alteration, leading to varying degrees of Cu, Au, Ag, Fe, Pb, and Zn mineralization along fault fracture zones or contacts between porphyry bodies and surrounding rocks. The deposit has a west ore belt (Hongnitang, Wandongshan, and Jingouba) and an east belt (Weiganpo, Bijiaoshan, and Guogaishan) (Figure 2). The Nandaping, Matouwan, Laomajian, and other ore blocks are located on the periphery of the main ore belt [36,42]. Paleogene sedimentary strata in the area consist primarily of red lacustrine sandy mudstones and piedmont coarse clastics [8,42].

2.2. Sample Descriptions

Fourteen representative fresh porphyritic samples were collected from the Bijiaoshan, Wandongshan, Laomajian, and Hongnitang ore blocks of the Beiya porphyry Au-polymetallic deposit. Samples from Bijiaoshan and Wandongshan represent drill cores (Figures 2 and 3). The coordinates for Laomajian and Hongnitang are 100.139° E, 26.041° N and 100.180° E, 26.145° N, respectively.



Figure 3. Photographs of hand specimens and photomicrographs of samples from the Bijiaoshan (a,b), Wandongshan (c,d), Laomajian (e,f), and Hongnitang (g,h) ore blocks. (i) Field occurrence of the Hongnitang ore blocks. Minerals are abbreviated as follows: plagioclase = Pl, K-feldspar = Kfs, quartz = Qz, and biotite = Bt.

All syenite porphyritic samples exhibit similar fine-grained porphyritic and block structures, with a cryptocrystalline matrix comprised mainly of feldspar and quartz (Figure 3; Supplementary Table S1). The phenocryst compositions show slight variations among different ore blocks. The Bijiaoshan and Wandongshan samples primarily contain orthoclase, with minor amounts of quartz and biotite, while the Laomajian and Hongnitang samples have more abundant quartz.

Specific lithological descriptions are as follows.

The Bijiaoshan syenite porphyry is characterized by hypidiomorphic granular texture and massive structure. It predominantly consists of orthoclase, quartz, biotite, and a small amount of opaque minerals. The orthoclase grains measure 0.4 to 0.8 mm and display fine semi-idiomorphic plate texture with developed cracks. Quartz grains, measuring 0.2 to 0.3 mm, are distributed between orthoclase grains. Biotite grains are patellar and

relatively euhedral, with a particle size ranging from 0.2 to 0.4 mm. Opaque minerals occur as semi-idiomorphic grains with a disseminated distribution.

The Wandongshan syenite porphyry displays hypidiomorphic granular texture and massive structure, primarily composed of orthoclase, quartz, and a small amount of opaque minerals. Orthoclase grains range from 0.3 to 1 mm in size, showing fine semi-idiomorphic plate texture with developed cracks. Quartz grains, sized 0.2 to 0.6 mm, are distributed between orthoclase grains. Opaque minerals are present as semi-idiomorphic grains with a disseminated distribution.

The Laomajian quartz syenite porphyry primarily consists of alkaline feldspar, plagioclase, quartz, and a few opaque minerals. Alkaline feldspars are predominantly orthoclase, which are fine, alloform-semi-idiomorphic granular with sizes ranging from 0.50 to 1.00 mm and are often metasomatized by quartz. Plagioclase is mainly oligoclase, with a particle size of 0.30 to 1.00 mm, exhibiting a semi-idiomorphic plate shape, fine polysynthetic twinning, slight sericitization, and silicification. Quartz grains, about 0.02 to 0.50 mm in size, have undergone recrystallization. Opaque minerals are about 0.02 to 0.10 mm in size, with a semi-hedral and hedral grain structure and disseminated structure.

The Hongnitang quartz syenite porphyry primarily consists of alkaline feldspar, plagioclase, quartz, and a small amount of opaque minerals. Alkaline feldspars are predominantly orthoclase, exhibiting a fine, alloform-semi-idiomorphic granular structure, sized 0.2 to 1.0 mm. Plagioclase is mainly oligoclase, with particle sizes ranging from 0.2 to 2.0 mm. It exhibits a semi-idiomorphic tabular habit and fine polysynthetic twinning, along with slight sericitization and silicification. Quartz grains, approximately 0.05 to 1.50 mm in size, have undergone recrystallization. Opaque minerals are about 0.02 to 0.50 mm in size, with a semi-hedral and hedral grain structure and disseminated structure.

3. Analytical Methods

Zircon U-Pb dating was conducted using laser ablation inductively, coupled with plasma mass spectrometry (LA-ICP-MS), at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS). The internal structure was examined using cathodoluminescence (CL) images prior to U-Pb isotopic analyses. The LA-ICP-MS system utilized consisted of an Agilent 7500a ICP-MS, coupled with a Resonetics RESOLUTION M-50 ArF Excimer laser source ($\lambda = 193$ nm), using laser energy of 80 mJ, a repetition rate of 10 Hz, a spot diameter of 31 μm , and an ablation time of 40 s. Helium served as a carrier gas to carry ablated aerosols to the ICP source [44]. NIST610 [45] and TEMORA ($^{206}\text{Pb}/^{238}\text{U} = 416.8$ Ma) [46] were utilized as external calibration standards, along with ^{29}Si as an internal standard. Common Pb was corrected by using observed ^{204}Pb . The ages cited in the text are $^{206}\text{Pb}/^{238}\text{U}$ ages (the older age is the $^{207}\text{Pb}/^{206}\text{Pb}$ age), which are the weighted mean at the 95% confidence level. The ICPMSDataCal 7.4 software and the ISOPLOT 3 add-in were used for data processing [47,48].

Major element abundances were analyzed using an X-ray fluorescence spectrometer (XRF) on glass disks at the GIGCAS [49], with analytical uncertainties ranging from 1% to 5%. Trace elements were determined using a Perkin-Elmer Sciex ELAN 6000 ICP-MS at the GIGCAS. The powdered samples (~50 mg) were dissolved in high-pressure Teflon bombs using a HF + HNO₃ mixture for 24 h. An internal standard Rh was used to monitor signal drift when counting. The methods are described in [49], with analytical accuracies ranging from 2% to 5%.

Sr and Nd isotopic analyses were conducted using a Neptune Plus Multi-Collector inductively, coupled with a plasma mass spectrometer (MC-ICP-MS), at the Guilin University of Technology (GUT). The analytical methods used are similar to those described in

reference [50]. In brief, approximately 100 mg sample powders were dissolved in Teflon bombs with HF + HNO₃ acid at 150 °C overnight. Separation of Nd was achieved by passing through cation columns, followed by HDEHP columns. Measured Sr and Nd isotopic ratios were normalized based on $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, respectively. Throughout the analyses, $^{87}\text{Sr}/^{86}\text{Sr}$ values of the NBS987 standard and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the JNdI-1 standard were 0.710267 ± 12 (2σ) and 0.512088 ± 4 (2σ), respectively. The parameters involved in the calculation are from references [51,52].

Zircon Hf isotope analysis, excluding sample WDS-01, was conducted in situ using an ArF excimer laser ablation system attached to a Neptune plasma MC-ICP-MS (LA-MC-ICP-MS) at the GIGCAS. Instrumental conditions and data acquisition are comprehensively described in reference [49]. A stationary spot was used for the present analyses, with a beam diameter of 44 μm , a laser energy density of 80 mJ/pulse, and a repetition rate of 8 Hz, depending on the sizes of the ablated domains. Helium was used as the carrier gas to transport the ablated samples from the ablation cell to the ICP-MS torch. To assess the quality of the analytical data, the Penglai standard zircon was analyzed, yielding a $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282898 ± 0.000008 (2σ , $n = 16$), which is consistent with the recommended value ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282906 \pm 0.000010$) [53]. The parameters involved in the calculation are from references [54–56].

Zircon Lu-Hf isotopic analyses of the sample WDS-01 were conducted using a Neptune Plus MC-ICP-MS in conjunction with an ESI NewWave 193 excimer ArF laser ablation system at the Guangxi Key Laboratory of Hidden Metallic Ore Deposits Exploration, GUT. A stationary spot with a beam diameter of 50 μm was used for the analyses. During routine analyses, zircon GJ1 was used as the reference standard, yielding a weighted mean $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282010 ± 0.000002 (2σ , $n = 8$). This is consistent with the weighted mean $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282013 ± 0.000003 (2σ) obtained through a solution analysis method, as reported in reference [57].

4. Results

4.1. Zircon U-Pb Dating

Zircon grains of four syenite porphyritic samples collected from the Bijiashan, Wandongshan, Laomajian, and Hongnitang ore blocks are mostly euhedral, transparent, and columnar, ranging in length from 80 to 180 μm with length-to-width ratios of 1:1 to 1:3 (Figure 4). The zircons display oscillatory zoning in CL images, a feature characteristic of zircons from magmatic rocks [58]. The Th/U values of the analyzed zircons are mostly greater than 0.1 (Supplementary Table S2), with the exception of three spots in samples WDS01 (Wandongshan) and LMJ-01 (Laomajian), indicating a typical magmatic origin for the zircons [59].

The average age of zircon U-Pb was calculated after discarding data with a concordant degree less than 85%. Sample BJS07 (Bijiashan) yielded $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 36.6 to 33.7 Ma, with a weighted average age of 35.0 ± 0.6 Ma ($n = 9$, MSWD = 1.2; Figure 5a). Sample WDS01 (Wandongshan) produced $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 37.2 to 35.1 Ma, with a weighted average age of 36.2 ± 0.3 Ma ($n = 13$, MSWD = 0.92; Figure 5b). The $^{206}\text{Pb}/^{238}\text{U}$ ages of sample LMJ-01 (Laomajian) range from 37.0 to 33.9 Ma, with a weighted average of 35.5 ± 0.6 Ma ($n = 10$, MSWD = 2.4; Figure 5c). Additionally, sample HNT-01 (Hongnitang) provided $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 37.8 to 34.9 Ma, with a weighted average of 36.3 ± 0.7 Ma ($n = 7$, MSWD = 2.4; Figure 5d). All ages from the samples represent the formation age.



Figure 4. Cathodoluminescence images for zircons from the Beiya syenite porphyritic samples from the Bijiashan (a), Wandongshan (b), Laomajian (c), and Hongnitang (d) ore blocks.

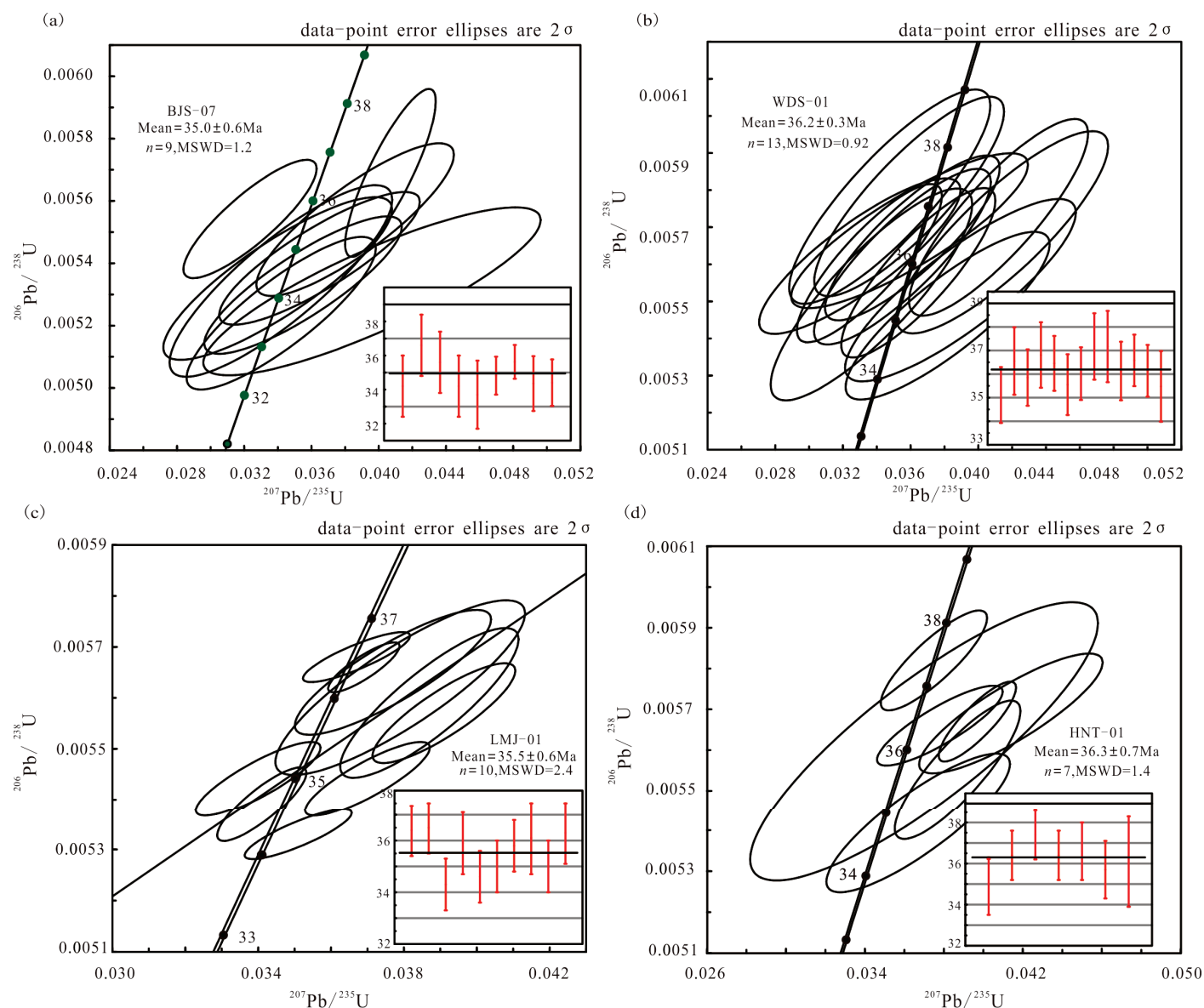


Figure 5. The zircon U-Pb concordia diagrams and weighted $^{206}\text{Pb}/^{238}\text{U}$ mean age diagrams of the Beiya syenite porphyritic samples from the Bijiashan (a), Wandongshan (b), Laomajian (c), and Hongnitang (d) ore blocks.

4.2. Whole-Rock Geochemical Compositions

Whole-rock major and trace element data for the Beiya alkali-rich porphyry from the Bijiashan, Wandongshan, Laomajian, and Hongnitang ore blocks are presented in Supplementary Table S3 (including 24 samples collected from open published literature [3,8,31,35,60]). These rocks have SiO_2 contents ranging from 65.40 to 72.82 wt.%, indicating their intermediate-acidic to acidic nature. The Rittmann indexes ($\sigma = [\omega(\text{K}_2\text{O} + \text{Na}_2\text{O})]^2 / [\omega(\text{SiO}_2 - 43)]$) vary from 2.40 to 6.11 with a mean of 4.09, resembling those of alkaline rocks. Their K_2O contents range from 5.68 to 11.32 wt.%, with total alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) values of 8.03–12.31 wt.% and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios of 1.51–24.91, thus classifying them as potassium rocks. On the QAP diagram, these rocks are within alkali-feldspar granite porphyry, quartz alkali feldspar syenite porphyry, syeno-granite porphyry, quartz syenite porphyry, monzo-granite porphyry, and quartz monzonite porphyry fields (Figure 6a). They plot within the shoshonite series on the K_2O vs. SiO_2 diagram (Figure 6b). The Al_2O_3 contents are relatively high, ranging from 13.45 to 17.00 wt.%, with A/CNK values of 0.75–1.56. These data suggest

that the Beiya alkali-rich porphyries primarily belong to metaluminous to peraluminous rocks (Figure 6c).

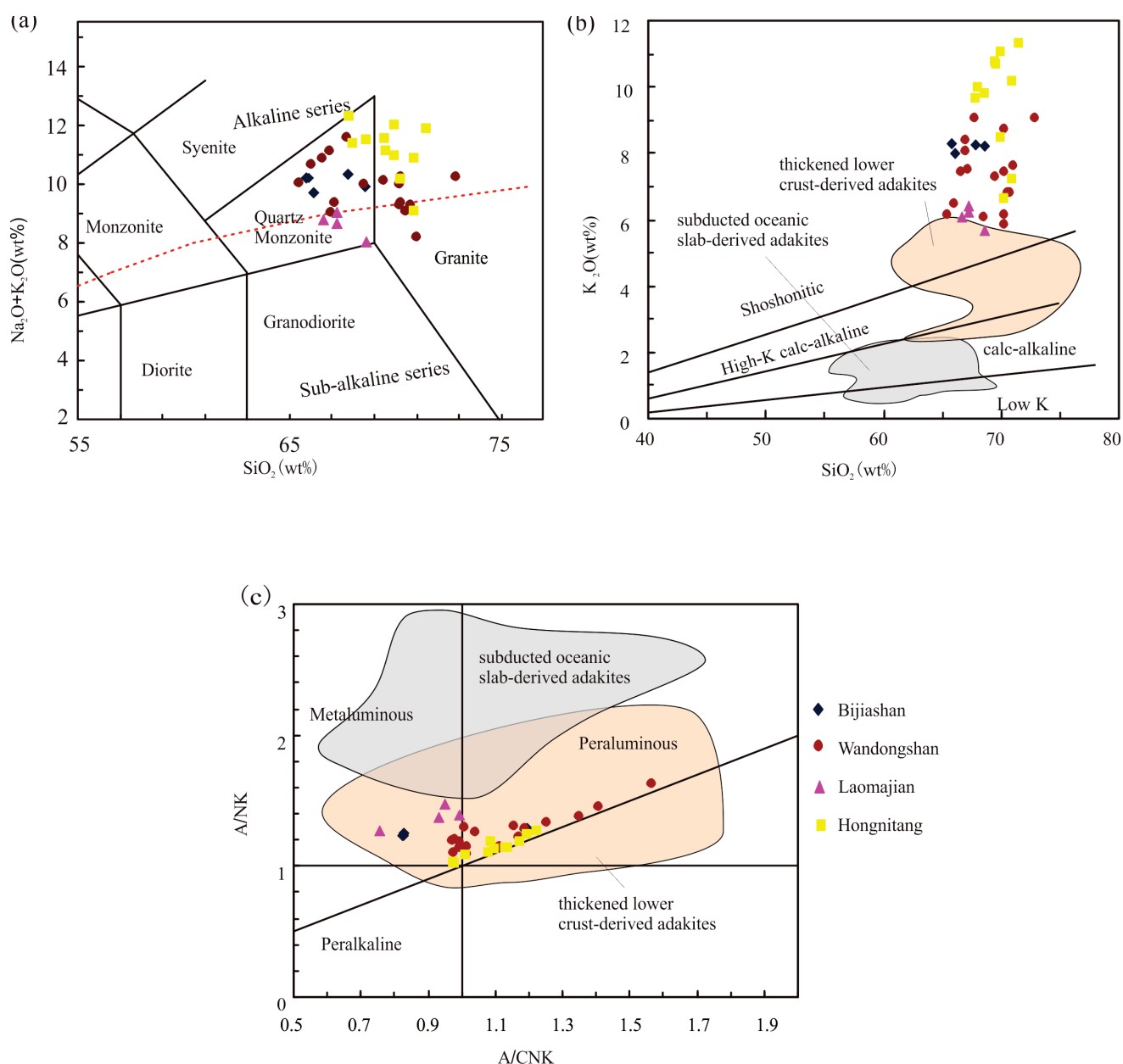


Figure 6. Chemical classification diagrams for the Beiya alkali-rich porphyry in western Yunnan. (a) QAP diagram [61], (b) K_2O vs. SiO_2 diagram [62,63], and (c) A/NK vs. A/CNK diagram [64]. A = Al_2O_3 , N = Na_2O , K = K_2O , and C = CaO (all in molar proportion). The fields of literature data for adakite are from [65].

On the primitive mantle-normalized diagram (Figure 7a), the partition curves of the Beiya alkali-rich porphyry exhibit identical right-leaning trends. Generally, the porphyries are enriched in LILEs such as Rb, Ba, K, and Sr, and depleted in HFSEs including Ta, Nb, and Ti, comparable to arc calc-alkaline magmas derived from melting of a wedge mantle metasomatized by fluids from a subducted oceanic slab [29]. The total REE (ΣREE) contents of the rocks are low, ranging from 36.3 to 138.82 ppm. The chondrite-normalized REE patterns display LREE enrichment and heavy rare earth element (HREE) depletion (Figure 7b), with $(\text{La}/\text{Yb})_{\text{N}}$ ratios of 5–37. The δEu values of the samples range from 0.43 to 1.26 with a mean of 0.88, displaying weak negative Eu anomalies overall. These

characteristics differ from those of coeval lamprophyres in western Yunnan (Figure 7), which were derived from a metasomatized lithospheric mantle [66].

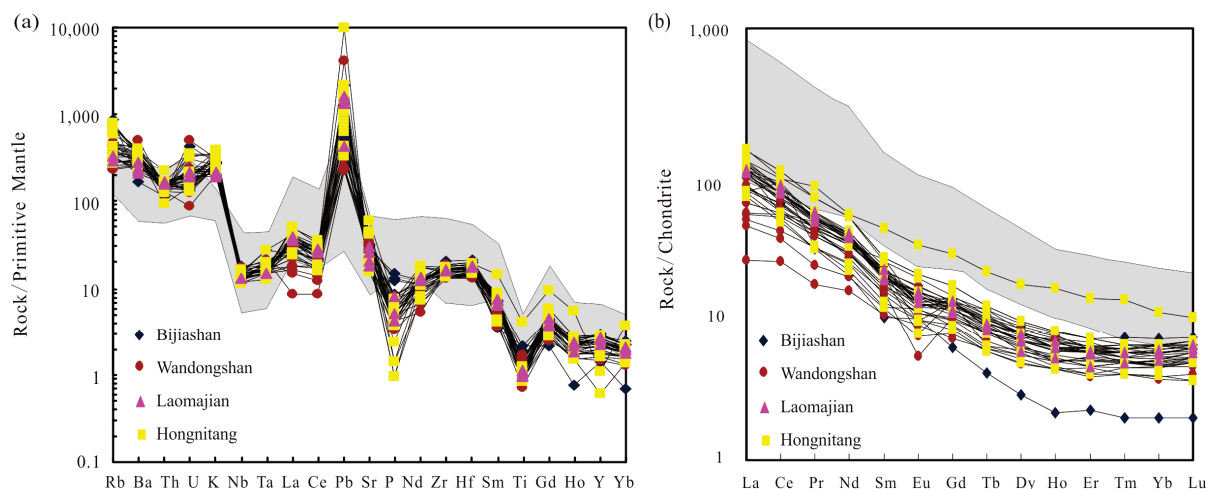


Figure 7. (a) Primitive mantle-normalized diagrams and (b) chondrite-normalized REE patterns for the Beiya alkali-rich porphyry in western Yunnan. The gray bands represent data from the literature on Paleogene lamprophyres exposed in the study area [66–71]. The chondrite and primitive mantle normalization values are from [72].

4.3. Whole-Rock Sr-Nd and Zircon Hf Isotopic Compositions

The whole-rock Sr and Nd isotopic results for the Beiya alkali-rich porphyry are presented in Supplementary Table S4. The $(^{87}\text{Sr}/^{86}\text{Sr})_i$ ratios for the samples, ranging from 0.707478 to 0.709280, exceed the mantle's initial value (0.7044) and are akin to those of the Beiya monzogranite porphyry (0.7060–0.7081) [8,35]. The Nd composition and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of the rocks show relative stability. The $(^{143}\text{Nd}/^{144}\text{Nd})_i$ ratios vary from 0.512327 to 0.512407, while the $\epsilon_{\text{Nd}}(t)$ values range from -5.6 to -4.1 , which are similar to those of the Beiya monzogranite and syenite porphyries (-6.7 to -1.5) [8,35].

In Figure 8, these rocks plot between the MORB and enriched mantle (EM) end-members, closer to the MORB and the EM I fields. They occupy the same area as the Cenozoic post-collisional potassic-ultrapotassic volcanic rocks in northern Tibet and the Cenozoic potassic felsic intrusions in western Yunnan, implying a similar genetic mechanism.

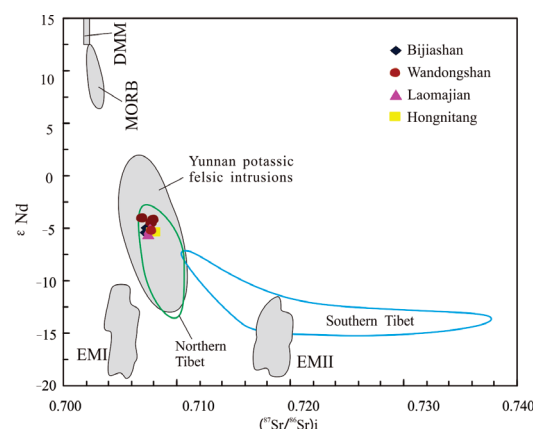


Figure 8. Initial $^{87}\text{Sr}/^{86}\text{Sr}(t)$ vs. $\epsilon_{\text{Nd}}(t)$ diagram for samples from the Beiya alkali-rich porphyry in western Yunnan. The field for Eocene–Oligocene potassic felsic intrusions in western Yunnan is from [8,35,40]. The field for Cenozoic post-collisional potassic-ultrapotassic volcanic rocks in northern Tibet is from [73–75]. The field for Cenozoic post-collisional potassic-ultrapotassic volcanic rocks in southern Tibet is from [76–79]. The MORB, EM I, and EM II mantle end-members are sourced from [80,81].

The zircon $^{176}\text{Lu}/^{177}\text{Hf}$ ratios for the Beiya alkali-rich porphyry range from 0.000265 to 0.001688 (Supplementary Table S5), indicating the absence of significant accumulation of radiation-induced Hf after zircon crystallization [82]. The zircon $^{176}\text{Hf}/^{177}\text{Hf}$ ratios range from 0.282475 to 0.282710, whereas the $f_{\text{Lu/Hf}}$ values are from -0.99 to -0.95 . Based on the concordia age-adjusted calculation for zircon U-Pb dating, the $\varepsilon_{\text{Hf}}(t)$ values vary from -9.7 to -0.6 (Figure 9), which are distinct from those of the Beiya monzogranite porphyry (-2.4 to 2.1) [8]. The crustal model ages (T_{DM2}) of the zircons are concentrated between 1152 and 1734 Ma, older than those of the Beiya monzogranite porphyry (0.8–1.1 Ga) [8]. These ages are comparable to those reported for the Eocene mineralized porphyry in Bijiaoshan, with zircon Hf isotope model ages ranging from 0.94 to 1.98 Ga (primarily 1.05–1.55 Ga) [28], as well as the Eocene mineralized porphyry in Wandongshan, which yielded zircon Hf isotope model ages ranging from 0.11 to 1.59 Ga [27].

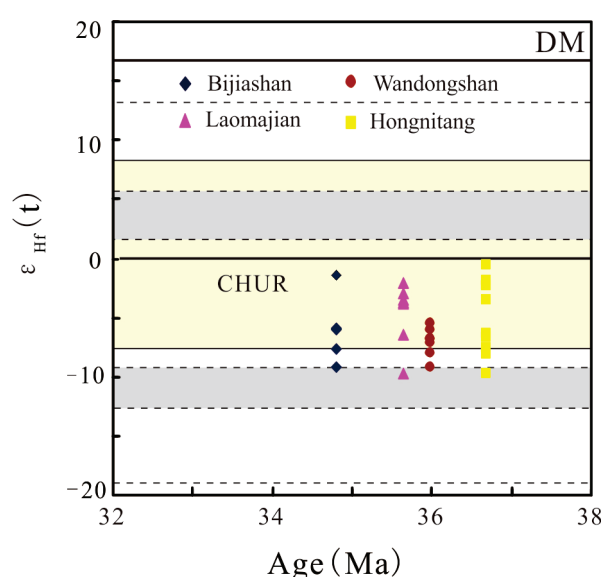


Figure 9. Variation of initial Hf isotope values vs. the U-Pb ages of the zircons for the Beiya alkali-rich porphyry in western Yunnan. DM is depleted mantle, and CHUR is chondritic uniform reservoir. The gray fields represent episodes of major juvenile crustal growth in the Yangtze Craton [83–85], and yellow fields represent episodes of other Eocene–Oligocene porphyry deposits in western Yunnan [8,35,36].

5. Discussion

5.1. Chronological Significance of the Beiya Syenite Porphyry

The chronological significance of the Beiya alkali-rich porphyry is critical for elucidating Cenozoic tectono-magmatic evolution in the Sanjiang region. Previous chronological studies in this area have yielded inconsistent results due to method limitations and sample selection. Early K-Ar and Ar-Ar dating on porphyry rocks from Wandongshan (65.6–25.5 Ma), Hongnitang (50.9–24.6 Ma), and Bijiaoshan (37.8 Ma) revealed broad age ranges [19,86,87]. Recent zircon U-Pb analyses narrowed these to 36.5–36.2 Ma for Hongnitang, 37.0–33.3 Ma for Wandongshan, and 35.2 Ma for Bijiaoshan [27,31,42,88]. Our LA-ICP-MS zircon U-Pb dating of four Beiya samples give ages of 36.3–35.0 Ma, aligning with regional magmatic records. Collectively, these results indicate the alkali-rich porphyry emplacement in the Beiya area predominantly occurred from 37–33 Ma.

Collisional orogens, such as the Tibetan orogen, typically undergo three principal stages: initial collisional convergence with crustal shortening and thickening; late-collisional transformation with strike-slip faulting, thrust systems, and potassic magmatism; and post-collisional extension involving lithospheric thinning, deep crustal shortening, and

shallow extension [25]. The Indian and Eurasian continents collided around 65 Ma, and the Sanjiang area's Indo–Eurasian collision ended at about 40 Ma, marking the post-collision phase's beginning [25,37,38]. This study suggests the Beiya alkali-rich porphyry formed around 37–33 Ma, placing it within this post-collision setting. This inference is supported by the conclusion delineated in Section 5.3.

Spatially, the age of the Beiya porphyry overlaps with coeval alkali-rich porphyries in the JSJ-RR metallogenic belt, including those at Machangqing, Yao'an, Laojiezi, and Habo [89–91]. This cluster corresponds to the peak of Himalayan potassium magmatism (42–32 Ma) along the JSJ-RR alkali-rich porphyry belt [10], suggesting a common tectonic driver. Temporally, the Beiya porphyry's emplacement coincides with major Cu–Mo–Au mineralization events (40–35 Ma) in the belt, such as Yulong (40 Ma), Beiya skarn (37 Ma), and Machangqing (36–35 Ma) [3]. These synchronous magmatic and metallogenic processes indicate a shared tectono-thermal origin.

While previous models attribute JSJ-RR belt magmatism to strike-slip tectonics [9,29], an increasing number of geochronological constraints challenge this interpretation. U–Pb and Ar–Ar dating of leucogranites in the JSJ-RRFZ indicate that the sinistral shear movement occurred around 33–22 Ma [92–95]. More recent dating of metamorphic massifs within and around the JSJ-RR shear zone has demonstrated large-scale left-lateral shearing, which was dominant and ranged in age from 31 Ma to 20 Ma [96–99]. Significantly, the youngest Beiya porphyry age (33.3 Ma, Figure 4) predates major shear zone activity, and most zircon U–Pb ages exceed 34 Ma. This temporal decoupling suggests that the JSJ-RRFZ may not account for the alkali-rich porphyry magmatism in the Beiya porphyry Au–polymetallic deposit.

5.2. Petrogenesis

5.2.1. Fractional Crystallization, Partial Melting, and Crustal Assimilation

The magmatic evolution of the Beiya alkali-rich porphyry was investigated through an integrated analysis of major-trace element systematics and isotopic signatures. Fractional crystallization processes are evidenced by systematic variations in major element compositions. The Beiya alkali-rich porphyries display systematic negative correlations between SiO_2 and MgO , TiO_2 , $\text{Fe}_2\text{O}_3\text{T}$, CaO , and P_2O_5 on the Harker diagrams (Figure 10), indicating successive fractionation of Fe–Ti oxides and apatite. This interpretation is reinforced by the depletion of compatible elements ($\text{Cr} = 0.99\text{--}22.80$ ppm; $\text{Ni} = 0.96\text{--}12.00$ ppm), consistent with the removal of olivine and pyroxene during early-stage differentiation. However, the absence of pronounced negative Eu anomalies ($\delta\text{Eu} = 0.42\text{--}1.26$, mean = 0.88) suggests limited plagioclase fractionation.

Incompatible element ratios, such as those between La and La/Yb or La and La/Sm, serve as effective indicators for distinguishing whether the rock formation originated from fractional crystallization or partial melting processes [100]. The positive correlations in La vs. La/Yb and La vs. La/Sm plots (Figure 11) demonstrate that partial melting processes have a dominant control over fractional crystallization. This aligns with the tendency of intermediate-acid potassium rocks to form via partial melting rather than fractional crystallization [101]. Thus, the Beiya alkali-rich porphyries likely originated primarily from partial melting, with fractional crystallization playing a secondary role.

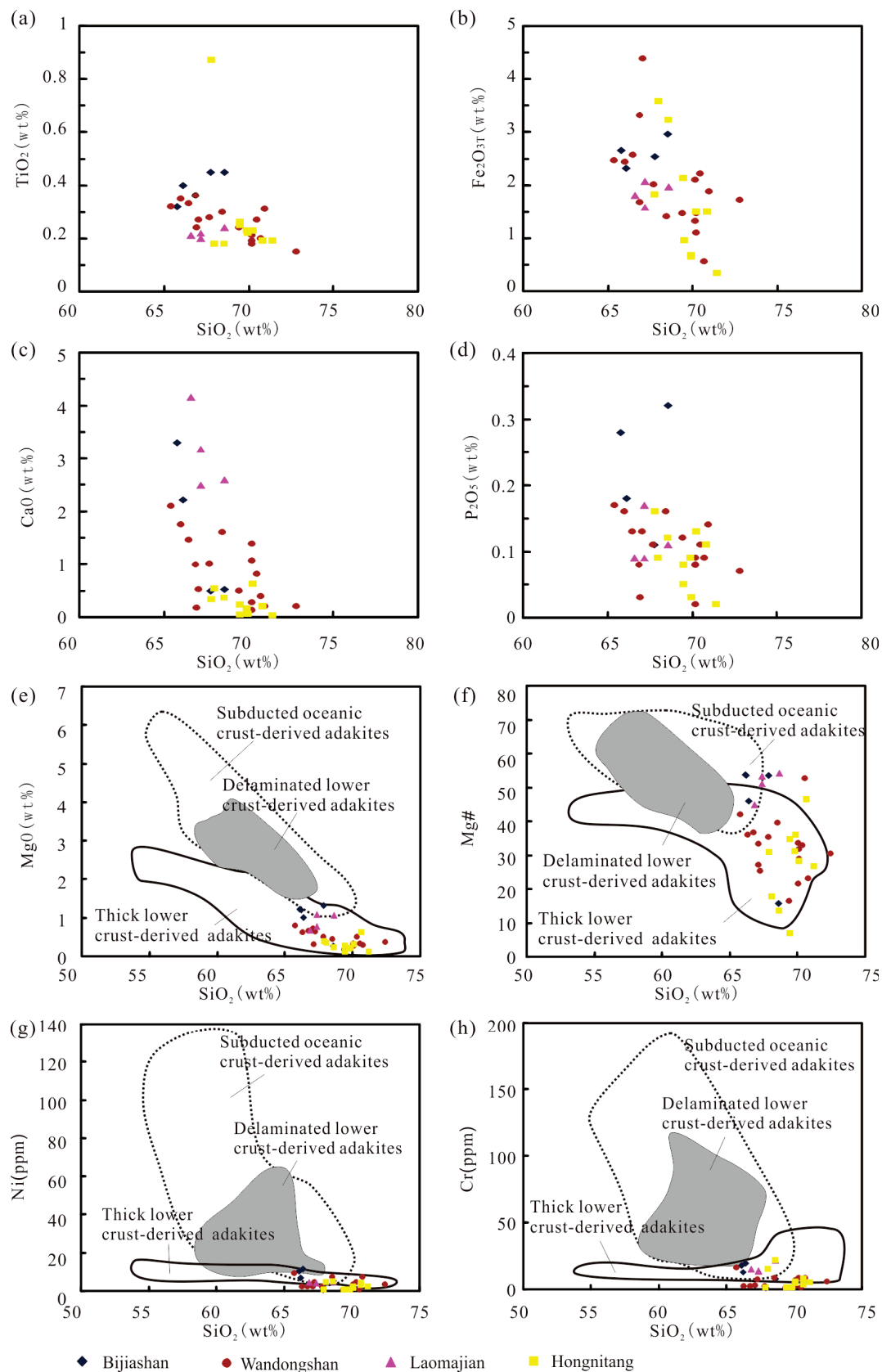


Figure 10. Variations in (a) TiO_2 vs. SiO_2 , (b) Fe_2O_{3T} vs. SiO_2 , (c) CaO vs. SiO_2 , (d) P_2O_5 vs. SiO_2 , (e) MgO vs. SiO_2 , (f) $\text{Mg\#}$ vs. SiO_2 , (g) Ni vs. SiO_2 , and (h) Cr vs. SiO_2 for the Beiya alkali-rich porphyry in western Yunnan. The classification curves of adakite are from [65].

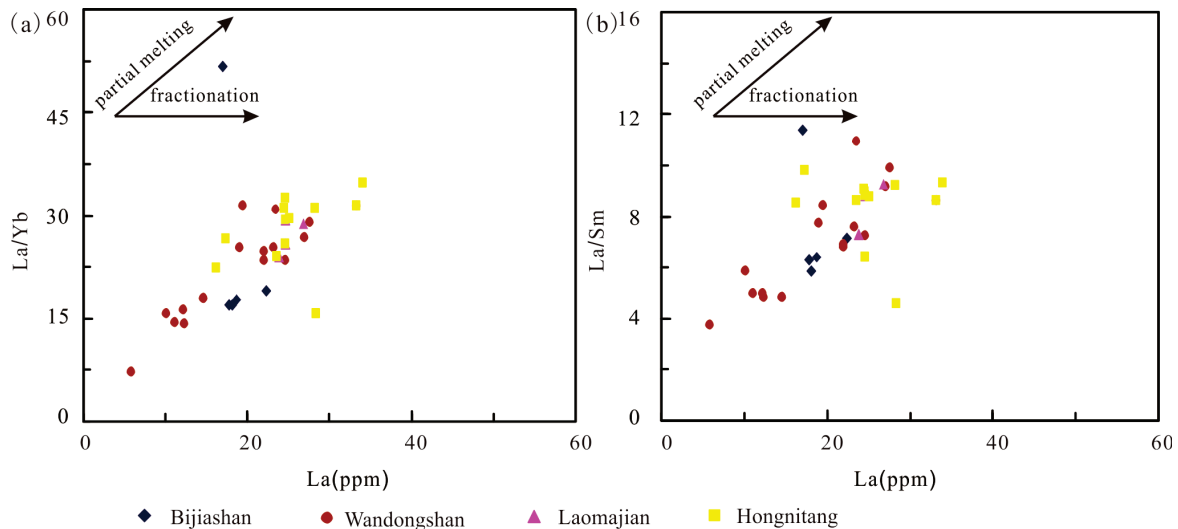


Figure 11. Variations in (a) La vs. La/Yb and (b) La vs. La/Sm [100] for the Beiya alkali-rich porphyry in western Yunnan.

Crustal contamination during magma ascent can modify original compositions of magmatic rocks. The Beiya alkali-rich porphyries exhibit enrichment in LILEs and LREEs, depletion in Nb-Ta-Ti, and enrichment in Zr-Hf relative to neighboring elements (Figure 7). Combined with $(^{87}\text{Sr}/^{86}\text{Sr})_i$ (0.707478–0.709280) and $\epsilon_{\text{Nd}}(t)$ ranges (−5.6 to −4.1) (Supplementary Table S3), these geochemical characteristics suggest potential crustal contamination. The presence of older zircons in some samples (WDS01: 791 Ma, 305 Ma, 218 Ma, 161 Ma; BJS07: 124 Ma) (Supplementary Table S2) further implies this process. Ratios of elements with similar distribution coefficients are unaffected by fractional crystallization or the degree of partial melting. Correlations between different elemental ratios can serve as effective indicators of crustal contamination [102–104]. In the study area, the Beiya alkali-rich porphyries exhibit horizontal linear relationships for the La/Yb-Nb-Ta, Ce/Pb-La/Nb, and Ta/Yb-Th/Yb ratios, while Th/Nb-Ce/Nb shows no significant correlation. These patterns do not indicate significant crustal contamination. Additionally, the Nb/U ratio (0.86–5.13, mean 2.62) is lower than the upper crust's (≈ 9) [105], further implying no significant crustal contamination.

5.2.2. Nature of Magma Sources

The Beiya alkali-rich porphyry is classified as a potassium rock, with its petrogenesis constrained by three established genetic models for Sanjiang potassic-ultrapotassic rocks: (1) fractional crystallization of enriched lithospheric mantle-derived mafic melts [35,106]; (2) partial melting of thickened lower continental crust [107,108]; and (3) magma mixing of mantle-crustal components in varying proportions [9,109–112].

Geochemically, the Beiya alkali-rich porphyry shows a wide range of geochemical values: SiO_2 = 65.40–72.82 wt.% (with a mean of 68.71 wt.%), Al_2O_3 = 13.70–17.00 wt.% (with a mean of 14.95 wt.%), MgO = 0.04–1.39 wt.% (with a mean of 0.50 wt.%), Sr = 320–1240 ppm, La/Yb = 7.17–51.61 (with a mean of 24.74), and Sr/Y = 35.94–332.22 (with a mean of 68.49) (Supplementary Table S3). These values, combined with positive Sr anomalies, weak δEu anomalies, HREE depletion (Figure 7), and alignment within the adakite field in Figure 12, indicate an adakitic affinity for the Beiya alkali-rich porphyry. Adakites are categorized into O-type (oceanic subduction-related) and C-type (typically crustal thickening-related) [113]. O-type adakites are characterized by low K_2O , high $\text{Na}_2\text{O}/\text{K}_2\text{O}$, low $(^{87}\text{Sr}/^{86}\text{Sr})_i$, and positive $\epsilon_{\text{Nd}}(t)$ values, distinguishing them from C-type adakites [114]. Based on these features, the Beiya alkali-rich porphyry is likely C-type adakite.

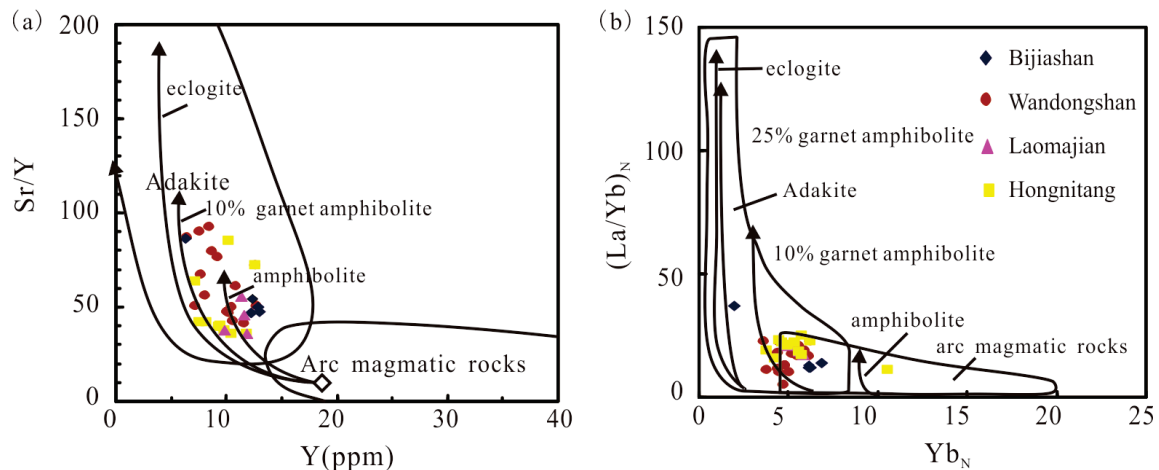


Figure 12. Variations in (a) Sr/Y vs. Y and (b) $(La/Yb)_N$ vs. Yb_N [114] for the Beiya alkali-rich porphyry in western Yunnan.

C-type adakites typically form via partial melting of: (1) ancient mafic rocks in the thickened lower crust (>50 km) underplated by lithospheric mantle-derived mafic magmas [115], (2) intermediate-basic rocks in the thickened lower crust [6,116], (3) newly underplated basaltic crust [117,118], or (4) delaminated lower crust [119]. The Beiya alkali-rich porphyry's geochemistry suggests a hybrid origin involving both mantle and crustal components. Key evidence for crustal dominance includes the following.

(1) The high SiO_2 contents > 66 wt.% of felsic rocks suggests they cannot be directly derived from partial mantle source melting, which would cause the magmas to have no more silica than andesitic in composition [120–122]. The Beiya alkali-rich porphyry's SiO_2 content (65.40–72.82 wt.%, with a mean of 68.71 wt.%) rules out this model. (2) Mantle-derived magmas typically exhibit peralkaline characteristics [123–125], whereas partial melting of supracrustal sediments results in strongly peraluminous melts [126]. The geochemical trend from peralkaline to peraluminous in Figure 6c suggests a crustal source influenced by mantle-derived magma. This is supported by the porphyry's low Nd/Th (0.51–2.28) and Nb/Ta (9.60–17.67) ratios, which are closer to crustal values (~3 and ~12) than mantle-derived rocks (>15 and ~22) [127]. (3) Zircon Hf isotope data, featuring $\epsilon_{Hf}(t)$ values of −9.7 to −0.6 and two-stage Hf model ages (T_{DM2}) of 1152–1734 Ma (Supplementary Table S4), along with $\epsilon_{Nd}(t)$ values of −5.6 to −4.1 (Supplementary Table S3), indicate a Paleo-Mesoproterozoic crustal source with a certain number of mantle-derived components to the source region. This aligns with previous studies on Eocene mineralized porphyries in Bijiaoshan and Wandongshan, which show zircon Hf model ages of 0.94–1.98 Ga [27,28]. The $\epsilon_{Hf}(t)$ values overlap with the Yangtze Block basement (Figure 9), where a Paleo- to Neoproterozoic (or even earlier) metamorphosed basement exists in the western margin [128,129]. Thus, the Beiya alkali-rich porphyries likely originated from this ancient, metamorphosed basement.

Major element diagrams, including the SiO_2 vs. MgO (Figure 10e), SiO_2 vs. Mg# (Figure 10f), SiO_2 vs. K_2O (Figure 6b), and A/NK vs. A/CNK (Figure 6c), suggest a thickened lower crust origin for the Beiya alkali-rich porphyry, consistent with SiO_2 vs. Cr and SiO_2 vs. Ni plots (Figure 10g,h). This aligns with previous studies on Cenozoic ore-forming porphyry intrusions in Tibet and western Yunnan, which were predominantly derived from partial melting of the subduction-modified, thickened mafic lower crust [15]. The Sr/Y vs. Y and $(La/Yb)_N$ vs. Yb_N diagrams (Figure 12) place the Beiya alkali-rich porphyry near the 10% garnet amphibolite melting curve, indicating derivation from partial melting of the thickened lower crust, likely in the garnet amphibolite facies. Previous studies have shown

that amphibole breakdown in thickened lower crust (e.g., garnet amphibolite, amphibole eclogite) during melting releases fluids into fertile magmas, promoting the oxidation state and H₂O content necessary for porphyry Cu-Mo-Au systems [29].

Considering the evidence and post-collisional setting (see Sections 5.1 and 5.3) of the Beiya alkali-rich porphyry, we conclude that it is a C-type adakite, most likely resulting from the partial melting of Paleo–Mesoproterozoic garnet amphibolite facies rocks within the thickened lower continental crust, influenced by mantle-derived magma. It is noteworthy that while some previous studies propose that ore-forming porphyry intrusions in the Gangdese and JSJ-RR belts originated solely from the partial melting of garnet-bearing amphibolite in the subduction-modified thickened lower crust [13,130], experimental evidence suggests that partial melts of garnet amphibolite typically exhibit adakitic characteristics and are calc-alkalic, but they are deficient in potassium and LILEs (Rb, Ba, Th, U) [131], which is inconsistent with the adakite-like rocks in our study (Figure 7). This indicates a mixed magma source.

5.3. Genetic Model

Tectonic discrimination diagram locates the Beiya porphyry within and around post-collisional granite field (Figure 13), consistent with the regional closure of the Tethyan and Jinshajiang–Ailao Shan Oceans at 37–33 Ma [25,37,38,132]. The presence of gabbroic/dioritic microgranular enclaves (MMEs), which are diagnostic of post-collisional magmatism [133], further supports this setting [8,133]. This inference aligns with the characteristics of adakite-like potassic rocks from post-collisional settings, which typically exhibit high Sr/Y ratios (35.94–332.22 ppm, this paper) and negative Nb, Ta, and Ti anomalies, but lack obvious Eu anomalies (Figure 7) [134–136].

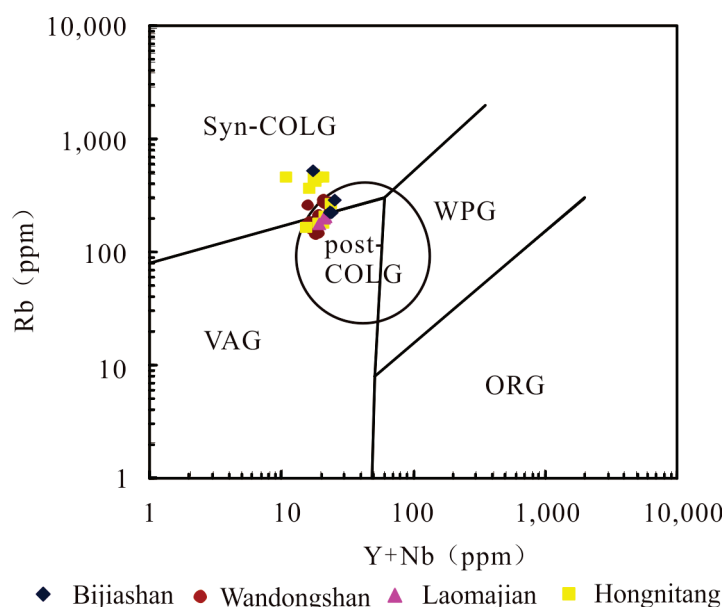


Figure 13. Tectonic discrimination diagram (Y + Nb) vs. Rb plot [131] for the Beiya alkali-rich porphyry in western Yunnan. VAG = volcanic arc granite, syn-COLG = syn-collisional granite, WPG = within-plate granite, ORG = ocean-ridge granite, and post-COLG = post-collisional granite.

The lower-crustal melting model is frequently used to interpret the geochemical features of porphyry intrusions in the Gangdese, Yulong, and JSJ-RR belts, especially their subduction-related and adakite-like characteristics [13,130]. Nevertheless, a two-stage model for post-collisional porphyry copper deposits in these belts has gained widespread acceptance [15,26]. This model involves the generation of post-collisional ore-forming porphyry intrusions through partial melting of subduction-modified, thickened mafic lower

crust (underplated Neoproterozoic arc magmas), with contributions from metasomatized lithospheric mantle-derived ultrapotassic magmas [15]. This conflicts with our conclusion that the Beiya alkali-rich porphyry primarily originated from partial melting of a Paleo–Mesoproterozoic garnet amphibolite facies source in the thickened lower continental crust [18–27].

The post-collision phase represents an extensional environment with tectonic relaxation [137]. Cenozoic potassic adakite-like and shoshonitic felsic intrusions in western Yunnan are linked to lithospheric thinning [24,35]. Prevailing models for lithosphere thinning include thermal erosion and/or chemical metasomatism transforming the lower part of the lithospheric mantle into asthenosphere, and delamination of the lithospheric mantle, possibly including the lowermost crust [138].

The lamprophyres and mafic volcanic rocks in western Yunnan are interpreted as originating from a metasomatized lithospheric mantle [66–71], suggesting incomplete lithospheric mantle delamination in the study area. Regionally, the limited extent of potassic magmatism and the absence of asthenospheric-sourced magmatism in western Yunnan make the delamination model unsuitable [69]. More plausibly, convective erosion of the lower lithospheric mantle, coupled with lithospheric thinning and subsequent asthenospheric upwelling, induced partial melting of the residual lithospheric mantle [69]. The Cenozoic asthenospheric upwelling in western Yunnan is evidenced by geophysical data revealing a ~300 km-wide mantle diapir derived from depths of ~450 km beneath western Yunnan [139]. Furthermore, an alternative model involving partial melting of delaminated mafic lower crust suggests that the resulting melts would exhibit anomalously high Sr/Y ratios (>100) due to the elevated garnet content in the restites [131], which contrasts with the mean Sr/Y ratio of 68.49 in the adakite-like rocks studied here.

Experimental studies reveal that Tibetan post-collisional adakite-like potassic rocks with arc geochemical signatures originate from partial melting of a hybrid source (80% garnet amphibolite + 20% primitive shoshonite) [131]. This mantle–crust interaction model explains both incompatible element enrichment and thermal energy required for crustal anatexis [131].

Cenozoic shoshonitic rocks in eastern Tibet occur along the Ailao Shan–Jinsha River fault zone and adjacent areas, comprising ultrabasic to acidic intrusive and extrusive varieties [140]. Sr–Nd–Pb isotopes indicate their derivation from metasomatized lithospheric mantle [140]. Lower crustal xenoliths hosted by Eocene–Oligocene potassic felsic intrusions suggest crustal thickness of ~55 km beneath western Yunnan [107]. Collectively, these observations support the genetic model proposed by Wang et al. [131], which can be applied to explain the origin of the Beiya alkali-rich porphyry (Figure 14).

- (1) Proterozoic subduction modification: Since the Neoarchean era, the continental margin of the Yangtze Craton has undergone multiple tectono-magmatic cycles associated with the supercontinents Columbia, Rodinia, Gondwana, and the Emeishan mantle plume [26]. Subsequent Proterozoic oceanic subduction beneath the craton introduced fluids into the lithospheric mantle, leading to the formation of hydrous mineral-enriched metasomatic domains crucial for subsequent magma formation [26].
- (2) Lithospheric thickening and erosion: Post-65 Ma India–Eurasia collision thickened the western Yunnan lithosphere [25], triggering gravitational instability that induced convective erosion of the lower lithospheric mantle. The consequent asthenospheric upwelling and extensional thinning provided thermodynamic conditions for mantle melting [69].
- (3) Mantle magma generation: Decompressional melting of upwelling asthenosphere transferred heat to the metasomatized subcontinental lithospheric mantle, generating shoshonitic/potassic mafic magmas [131].

- (4) Hybrid crustal melting: These mafic magmas underplated the ~55 km-thick lower crust, providing both incompatible element enrichment and thermal energy for partial melting of garnet amphibolite. The resulting hydrous melts ascended to form the Beiya porphyry at 37–33 Ma.

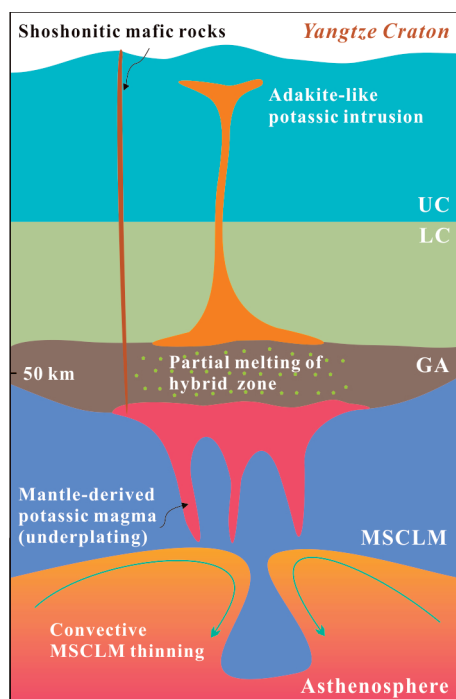


Figure 14. Genetic model for the Beiya alkali-rich porphyry, modified after Yang and Cao [15] and Wang et al. [131]. Shoshonitic/potassic mafic magma originates from the partial melting of a metasomatized sub-continental lithospheric mantle and underplates the lower crust. Subsequent continuous underplating triggers partial melting of the hybrid lower crust (comprising mantle-derived mafic underplates and pre-existing crust), forming adakite-like potassic rocks. MSCLM = metasomatized subcontinental lithospheric mantle; UC = Upper crust; LC = Lower crust; and GA = garnet amphibolite.

Throughout this process, the lithospheric mantle, which has been modified by paleo-subduction, supplies fluids and metal sources for Cenozoic non-arc Au-Cu-Mo mineralization, while lithospheric thinning provides the necessary thermodynamic conditions [26].

6. Conclusions

(1) LA-ICP-MS U-Pb zircon dating of four syenite porphyry samples from the Beiya porphyry Au-polymetallic deposit indicates ages ranging from 36.3 to 35.0 Ma, aligning with the magmatic peak in the JSJ-RR alkali-rich porphyry belt.

(2) The Beiya alkali-rich porphyry exhibits C-type adakite characteristics and was formed in a post-collisional environment.

(3) It likely formed as the lower continental lithospheric mantle was convectively removed and the asthenosphere rose upwards. The magmas probably originated from the partial melting of Paleo–Mesoproterozoic garnet amphibolite facies rocks in the thickened lower continental crust, with some shoshonitic mafic magma mixed in.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/min15050531/s1>: Table S1. LA-ICP-MS zircon U-Pb analytical results of the syenite porphyry samples from Beiya gold-polymetallic ore field; Table S2. Major (wt.%) and trace element compositions (ppm) and calculated parameters of the syenite porphyry samples from Beiya gold-polymetallic ore field; Table S3. Sr-Nd isotopic compositions of the syenite porphyry

samples from Beiya gold-polymetallic ore field; and Table S4. Lu-Hf isotopic data of zircons from the syenite porphyry samples in Beiya gold-polymetallic ore field. Table S5. Lu-Hf isotopic data of zircons from the syenite porphyry samples in Beiya gold-polymetallic ore field.

Author Contributions: Conceptualization, Y.Z. and Y.Y.; methodology, Y.Z., Y.Y., and Y.L.; software, Y.Z. and Y.Y.; validation, Y.Z., Y.Y., and Y.L.; formal analysis, Y.Z. and Y.Y.; investigation, Y.Z., Y.Y., and Y.L.; resources, B.X.; data curation, Y.Z. and Y.Y.; writing—original draft preparation, Y.Z. and Y.Y.; writing—review and editing, Y.Z. and Y.Y.; visualization, Y.Z., Y.Y., and Y.L.; supervision, Y.Y.; project administration, Y.Z., Y.Y., and B.X.; funding acquisition, Y.Z., Y.Y., and B.X. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (No. 42102256); Natural Science Foundation of Guangdong Province (Nos. 2017A030310395, 2018B030311030); Young Innovative Talent Project of Department of Education of Guangdong Province (Natural Science; grant 2022KQNCX184); Natural Research Project of Guangdong Polytechnic of Industry & Commerce (grant 2022-ZKT-01); High-level Talent Special Support Program of Guangdong Polytechnic of Industry & Commerce (grant 2023-gc-03); and Guangdong Key Scientific Research Platform and Projects for Higher-educational Institutions (grant 2023GCZX010).

Data Availability Statement: Data are available on request from the corresponding author of the manuscript.

Acknowledgments: We express our sincere gratitude to Bigyan for polishing the paper, Zhang Yuquan for his help with the discussion, Xianglin Tu with the chronology analysis, and Yin Liu for the geochemical analysis. We thank the journal editor and three anonymous reviewers for their careful revisions and constructive comments, which helped us improve the manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Deng, J.; Wang, Q.F.; Li, G.J.; Li, C.; Wang, C.M. Tethys tectonic evolution and its bearing on the distribution of important mineral deposits in the Sanjiang region, SW China. *Gondwana Res.* **2014**, *26*, 419–437. [CrossRef]
- Huang, X.L.; Niu, Y.L.; Xu, Y.G.; Chen, L.L.; Yang, Q.J. Mineralogical geochemical constraints on the petrogenesis of post-collisional potassic ultrapotassic rocks from western Yunnan SWChina. *J. Petrol.* **2010**, *51*, 1617–1654. [CrossRef]
- He, W.Y.; Mo, X.X.; He, Z.H.; White, N.C.; Chen, J.B.; Yang, K.H.; Wang, R.; Yu, X.H.; Dong, G.C.; Huang, X.F. The geology and mineralogy of the Beiya skarn gold deposit in Yunnan, Southwest China. *Soc. Econ. Geol.* **2015**, *110*, 1625–1641. [CrossRef]
- Yang, Z.; Yang, L.Q.; He, W.Y.; Gao, X.; Liu, X.D.; Bao, X.S.; Lu, Y.G. Control of magmatic oxidation state in intracontinental porphyry mineralization: A case from Cu (Mo-Au) deposits in the Jinshajiang-Red River metallogenic belt, SW China. *Ore Geol. Rev.* **2017**, *90*, 827–846. [CrossRef]
- Liu, J.L.; Chen, X.Y.; Tang, Y.; Tran, M.D.; Nguyen, Q.L.; Wu, W.B.; Zhang, Z.C.; Zhao, Z.D. New tectono-geochronological constraints on timing of shearing along the Ailao Shan-Red River shear zone: Implications for genesis of Ailao Shan gold mineralization. *J. Asian Earth Sci.* **2015**, *103*, 70–86. [CrossRef]
- Hou, Z.Q.; Zhong, D.L.; Deng, W.M.; Khin, Z. A tectonic model for porphyry copper-molybdenum-gold deposits in the eastern Indo-Asian collision zone//PORTERTM. In *Super Porphyry Copper and Gold Deposits: A Global Perspective*; PGC Publishing: Adelaide, Australia, 2004; pp. 423–440.
- Hou, Z.Q.; Zaw, K.; Pan, G.T.; Mo, X.X.; Xu, Q.; Hu, Y.Z.; Li, X.Z. Sanjiang Tethyan metallogenesis in SW China: Tectonic setting, metallogenic epochs and deposit types. *Ore Geol. Rev.* **2007**, *31*, 48–87. [CrossRef]
- He, W.Y.; Mo, X.X.; Yang, L.Q.; Xing, Y.L.; Dong, G.C.; Yang, Z.; Gao, X.; Bao, X.S. Origin of the Eocene porphyries and mafic microgranular enclaves from the Beiya porphyry Au polymetallic deposit, western Yunnan, China: Implications for magma mixing/mingling and mineralization. *Gondwana Res.* **2016**, *40*, 230–248. [CrossRef]
- Bao, X.S.; He, W.Y.; Mao, J.W.; Liang, T.; Wang, H.; Zhou, Y.M.; Wang, J.J. Redox states and genesis of Cu- and Au-mineralized granite porphyries in the Jinshajiang Cu-Au metallogenic belt, SW China: Studies on the zircon chemistry. *Miner. Depos.* **2023**, *58*, 1123–1142. [CrossRef]
- Xu, X.W.; Jiang, N.; Yang, K.; Zhang, B.L.; Liang, G.H.; Mao, Q.; Li, J.X.; Du, S.J.; Ma, Y.G.; Zhang, Y.; et al. Accumulated phenocrysts and origin of feldspar porphyry in the Chanhao area, western Yunnan, China. *Lithos* **2009**, *113*, 595–611. [CrossRef]
- Liang, H.Y.; Campbell, I.H.; Allen, C.; Sun, W.D.; Zhang, Y.Q. Zircon Ce^{4+}/Ce^{3+} ratios and ages for Yulong ore-bearing porphyries in eastern Tibet. *Miner. Depos.* **2006**, *41*, 152–159. [CrossRef]

12. Zhang, Y.Q.; Xie, Y.W. Geochronology of Ailaoshan-Jinshajiang alkalirich intrusive rocks and their Sr and Nd isotopic characteristic. *Sci. China Earth Sci.* **1997**, *40*, 524–529. [CrossRef]
13. Hou, Z.Q.; Zhou, Y.; Wang, R.; Zheng, Y.C.; Zhao, M.; Evans, N.J.; Weinberg, R.F. Recycling of metal-fertilized lower continental crust: Origin of non-arc Au-rich porphyry deposits at cratonic edges. *Geology* **2017**, *45*, 563–566. [CrossRef]
14. Sun, C.D.; Wu, P.; Wang, D.; Guan, S.J.; Jiang, X.J.; Jiang, L.Y.; Wang, L.Y. Geochemistry and Zircon U-Pb age of the Yao'an pseudoleucite porphyry, Yunnan Province, China. *Acta Geochim.* **2017**, *2*, 194–206. [CrossRef]
15. Yang, Z.M.; Cao, K. Post-collisional porphyry copper deposits in Tibet: An overview. *Earth-Sci. Rev.* **2024**, *258*, 104954. [CrossRef]
16. Wang, J.; Yin, A.; Harrison, T.M.; Marty, G.; Zhang, Y.Q.; Xie, G.H. A tectonic model for Cenozoic igneous activities in the eastern Indo-Asian collision zone. *Earth Planet. Sci. Lett.* **2001**, *188*, 123–133. [CrossRef]
17. Li, S.K.; Zhang, S.T.; Zhao, Q.H.; Li, M. Zircon U-Pb Chronology and Petrogeochemistry of Cenozoic Alkali-Rich Porphyry in Zaojiaochang, Lanping, Western Yunnan. *J. Jilin Univ. (Earth Sci. Ed.)* **2021**, *51*, 169–184. (In Chinese with English Abstract)
18. Li, Z.Q.; Zhang, P.P.; Zhou, K.W.; Zhang, J.W.; Yang, S.Z.; Wang, S.B.; Zou, Q.P.; Ma, Q.C.; Jiang, B.; Zhen, Y.L.; et al. Origin and geochemical characteristics of the porphyries in Beiya gold polymetallic deposit, Yunnan. *Miner. Explor.* **2023**, *14*, 849–860. (In Chinese with English Abstract)
19. Deng, W.M.; Huang, X.; Zhong, D.L. Alkali-rich porphyry and its relation with intraplate deformation of north part of Jinsha River. *Sci. China (Ser. D Earth Sci.)* **1998**, *41*, 297–305.
20. Zhong, D.L.; Ding, L.; Liu, F.T.; Liu, J.H.; Zhang, J.J.; Ji, J.Q.; Chen, H. Multi-oriented and layered structures of lithosphere in orogenic belt and their effects on Cenozoic magmatism—A case study of western Yunnan and Sichuan, China. *Sci. China (Ser. D Earth Sci.)* **2000**, *30*, 122–133. (In Chinese with English Abstract) [CrossRef]
21. Xu, X.W.; Cai, X.P.; Song, B.C.; Zhang, B.L.; Ying, H.L.; Xiao, Q.B.; Wang, J. Petrologic, chronological and geochemistry characteristics and formation mechanism of alkaline porphyries in the Beiya gold district, western Yunnan. *Acta Petrol. Sin.* **2006**, *22*, 631–642. (In Chinese with English Abstract)
22. Yang, H.; Wang, D.; Wu, P.; Wang, F.; Chen, F.C. Petrogenesis of alkali-rich porphyry and its Cu-Mo-Au deposit formation—A case study of the Jinsha River-Honghe River porphyry metallogenic belt. *Geol. Rev.* **2023**, *69*, 1669–1693.
23. Wu, J.; Zhao, Z.D.; Li, X.W.; Tu, X.W.; Li, C.; Lei, H.S.; Ma, Q.; Miao, Z.; Yang, Y.Y.; Liu, D.; et al. Re-melting of the Neoproterozoic juvenile mafic lower crust: The origin of adakitic and non-adakitic felsic suites in the southwest margin of Yangtze Craton. *Lithos* **2024**, 474–475, 107601. [CrossRef]
24. Tang, W.L.; Chen, J.L.; Tan, R.Y. Chronological and Geochemical Study of the Cenozoic Potassic Felsic Igneous Rocks in Western Yunnan, SE Tibet: Implications for their Tectonic Mechanisms. *Acta Geol. Sin. (Engl. Ed.)* **2022**, *96*, 904–918. [CrossRef]
25. Hou, Z.Q.; Cook, N.J. Metallogenesis of the Tibetan collisional orogen: A review and introduction to the special issue. *Ore Geol. Rev.* **2009**, *36*, 2–24. [CrossRef]
26. Xin, W. Research on Cenozoic Au-Cu-Mo Metallogenesis in Ailaoshan-Honghe Metallogenic Belt, Yunnan Province. Ph.D. Thesis, Jilin University, Jilin, China, 2020; pp. 1–216. (In Chinese with English Abstract)
27. Fu, Y.; Sun, X.M.; Lin, H.; Zhou, H.Y.; Li, X.; Ouyang, X.Q.; Jiang, L.Y.; Shi, G.Y.; Liang, Y.H. Geochronology of the giant Beiya gold-polymetallic deposit in Yunnan Province, Southwest China and its relationship with the petrogenesis of alkaline porphyry. *Ore Geol. Rev.* **2015**, *71*, 138–149. [CrossRef]
28. Zhou, J.; Li, S.; Li, S.Z.; Wang, G.H.; Santosh, M.; Zhang, L.; Yu, S.Y.; Liu, Y.M.; Li, X.Y. Petrogenesis of Eocene mineralized porphyry in bijiashan, eastern margin of Tibet plateau: Constraints from geochronology, geochemistry and Hf isotopes. *Lithos* **2018**, 316–317, 1–18.
29. Hou, Z.Q.; Zhang, H.R.; Pan, X.F.; Yang, Z.M. Porphyry Cu (-Mo-Au) deposits related to melting of thickened mafic lower crust: Examples from the eastern Tethyan metallogenic domain. *Ore Geol. Rev.* **2011**, *39*, 21–45. [CrossRef]
30. Mao, J.W.; Pirajno, F.; Lehmann, B.; Luo, M.C.; Berzina, A. Distribution of porphyry deposits in the Eurasian continent their corresponding tectonic settings. *J. Asian Earth Sci.* **2014**, *79* (Pt B), 576–584. [CrossRef]
31. Xu, X.W.; Cai, X.P.; Xiao, Q.B.; Peters, S.G. Porphyry Cu-Au and associated polymetallic Fe-Cu-Au deposits in the Beiya area, western Yunnan Province, South China. *Ore Geol. Rev.* **2007**, *31*, 224–246. [CrossRef]
32. Fu, Y.; Sun, X.M.; Zhou, H.Y.; Lin, H.; Yang, T.J. In-situ LA-ICP-MS U-Pb geochronology and trace elements analysis of polygenetic titanite from the giant Beiya gold-polymetallic deposit in Yunnan Province, Southwest China. *Ore Geol. Rev.* **2016**, *77*, 43–56. [CrossRef]
33. Zhou, J.X.; Dou, S.; Huang, Z.L.; Cui, Y.L.; Ye, L.; Li, B.; Gan, T.; Sun, H.R. Origin of the Luping Pb deposit in the Beiya area, Yunnan Province, SW China: Constraints from geology, isotope geochemistry and geochronology. *Ore Geol. Rev.* **2016**, *72*, 179–190. [CrossRef]
34. Quan, H.H.; Chai, P.; Yuan, L.L.; Jiao, S.T. Petrogenesis Mineralization and Tectonic Implications of Paleoproterozoic Potassic-Ultrapotassic Magmatic Rocks in Western Yunnan. *Gold Sci. Technol.* **2024**, *32*, 220–240. (In Chinese with English Abstract)

35. Lu, Y.J.; Kerrich, R.; McCuaig, T.C.; Li, Z.X.; Hart, C.J.R.; Cawood, P.A.; Hou, Z.Q.; Bagas, L.; Cliff, J.; Belousova, E.A.; et al. Geochemical Sr-Nd-Pb zircon Hf-O isotopic compositions of Eocene-Oligocene shoshonitic potassic adakite-like felsic intrusions in Western Yunnan SW China: Petrogenesis tectonic implications. *J. Petrol.* **2013**, *54*, 1309–1348. [CrossRef]
36. Liu, B.; Liu, H.; Zhang, C.Q.; Mao, Z.H.; Zhou, Y.M.; Huang, H.; He, Z.H.; Su, G.S. Geochemistry and geochronology of porphyries from the Beiya gold-polymetallic orefield, western Yunnan, China. *Ore Geol. Rev.* **2015**, *69*, 360–379. [CrossRef]
37. Yin, A.; Harrison, T.M. Geologic Evolution of the Himalayan-Tibetan Orogen. *Annu. Rev. Earth Planet. Sci.* **2000**, *28*, 211–280. [CrossRef]
38. Mo, X.X.; Dong, G.C.; Zhao, Z.D.; Guo, T.Y.; Wang, L.L.; Chen, T. Timing of magma mixing in the Gangdise magmatic belt during the India-Asia collision: Zircon shrimp U-Pb dating. *Acta Geol. Sin. (Engl. Ed.)* **2005**, *79*, 66–76.
39. Chung, S.L.; Lo, C.H.; Lee, T.Y.; Zhang, Y.Q.; Xie, Y.W.; Li, X.H.; Wang, K.L.; Wang, P.L. Diachronous uplift of the Tibetan plateau starting 40 Myr ago. *Nature* **1998**, *349*, 769–773. [CrossRef]
40. Lu, Y.J.; Kerrich, R.; Kemp, A.I.S.; McCuaig, T.C.; Hou, Z.Q.; Hart, C.J.R.; Li, Z.X.; Cawood, P.A.; Bagas, L.; Yang, Z.M.; et al. Intracontinental Eocene-Oligocene porphyry Cu mineral systems of Yunnan, Western Yangtze Craton, China: Compositional characteristics, sources, and implications for continental collision metallogeny. *Soc. Econ. Geol.* **2013**, *108*, 1541–1576. [CrossRef]
41. Liu, H.; Wang, Q.F.; Li, G.J.; Wan, L. Characterization of multi-type mineralizations in the Wandongshan gold poly-metallic deposit, Yunnan (China), by fractal analysis. *J. Geochem. Explor.* **2012**, *122*, 20–33. [CrossRef]
42. Deng, J.; Wang, Q.F.; Li, G.J.; Hou, Z.Q.; Jiang, C.Z.; Leonid, D. Geology and genesis of the giant Beiya porphyry-skarn gold deposit, northwestern Yangtze Block, China. *Ore Geol. Rev.* **2015**, *70*, 457–485. [CrossRef]
43. Li, W.C.; Wang, J.H.; He, Z.H.; Dou, S. Formation of Au-polymetallic ore deposits in alkaline porphyries at Beiya, Yunnan, Southwest China. *Ore Geol. Rev.* **2015**, *73*, 241–252. [CrossRef]
44. Yuan, Y.J.; Yin, Z.X.; Liu, W.L.; Huang, Q.T.; Li, J.F.; Liu, H.F.; Wan, Z.F.; Cai, Z.R.; Xia, B. Tectonic evolution of the Meso-Tethys in the western segment of Bangonghu-Nujiang suture zone: Insights from geochemistry and geochronology of the Lagkor Tso ophiolite. *Acta Geol. Sin. (Engl. Ed.)* **2015**, *89*, 369–388.
45. Pearce, N.J.G.; Perkins, W.T.; Westgate, J.A.; Gorton, M.P.; Jackson, S.E.; Neal, C.R.; Chenery, S.P. A compilation of new and published major and trace element data for NIST 852 SRM 610 and NIST 853 SRM 612 glass reference materials. *Geostand. News.* **1997**, *21*, 115–144. [CrossRef]
46. Black, L.P.; Kamo, S.L.; Allen, C.M.; Aleinikoff, J.N.; Davis, D.W.; Korsch, R.J.; Foudoulis, C. TEMORA 1: A new zircon standard for Phanerozoic U-Pb geochronology. *Chem. Geol.* **2003**, *200*, 155–170. [CrossRef]
47. Ludwig, K. *User's Manual for Isoplot 3.00: A Geochronological Toolkit for Microsoft Excel*; Special Publication; Berkeley Geochronology Center: Berkeley, CA, USA, 2003; pp. 1–70.
48. Liu, Y.S.; Hu, Z.C.; Gao, S.; Gunther, D.; Xu, J.; Gao, C.G.; Chen, H.H. In situ analysis of 812 major and trace elements of anhydrous minerals by LA-ICP-MS without applying an internal standard. *Chem. Geol.* **2008**, *257*, 34–43. [CrossRef]
49. Huang, F.; Xu, J.F.; Zeng, Y.C.; Chen, J.L.; Wang, B.D.; Yu, H.X.; Chen, L.; Huang, W.L.; Tan, R.Y. Slab Breakoff of the Neo-Tethys Ocean in the Lhasa Terrane Inferred from Contemporaneous Melting of the Mantle and Crust. *Geochem. Geophys. Geosystems* **2017**, *18*, 4074–4095. [CrossRef]
50. Huang, F.; Zhang, Z.; Xu, J.; Li, X.; Zeng, Y.; Wang, B.; Li, X.; Xu, R.; Fan, Z.; Tian, Y. Fluid flux in the lithosphere beneath southern Tibet during Neo-Tethyan slab breakoff: Evidence from an apatite-granite suite. *Lithos* **2019**, *344–345*, 324–338. [CrossRef]
51. Jacobsen, S.B.; Wasserburg, G.J. Sm-Nd Isotopic Evolution of Chondrites. *Earth Planet. Sci.* **1980**, *50*, 139–155. [CrossRef]
52. Lugmair, G.W.; Marti, K. Lunar initial $^{143}\text{Nd}/^{144}\text{Nd}$: Differential evolution of the lunar crust and mantle. *Earth Planet. Sci.* **1978**, *39*, 349–357. [CrossRef]
53. Li, X.H.; Long, W.G.; Li, Q.L.; Liu, Y.; Zheng, Y.F.; Yang, Y.H.; Chamberlain, K.R.; Wan, D.F.; Guo, C.H.; Wang, X.C.; et al. Penglai Zircon Megacrysts: A Potential New Working Reference Material for Microbeam Determination of Hf-O Isotopes and U-Pb Age. *Geostand. Geoanalytical Res.* **2010**, *34*, 117–134. [CrossRef]
54. Blichert-Toft, J.; Albarède, F. The Lu-Hf geochemistry of chondrites and the evolution of the mantle-crust system. *Earth Planet. Sci.* **1997**, *148*, 243–258. [CrossRef]
55. Griffin, W.L.; Pearson, N.J.; Belousova, E.; Jackson, S.E.; O'Reilly, S.Y.; Achterberg, E.; Shee, S.R. The Hf-isotope composition of cratonic mantle: LAM-MC-ICPMS analysis of zircon megacrysts in kimberlites. *Geochim. Cosmochim. Acta* **2000**, *64*, 133–147. [CrossRef]
56. Söderlund, U.; Patchett, P.J.; Vervoort, J.D.; Isachsen, C.E. The ^{176}Lu decay constant determined by Lu-Hf and U-Pb isotope systematics of Precambrian mafic intrusions. *Earth Planet. Sci.* **2004**, *219*, 311–324. [CrossRef]
57. Yuan, H.L.; Gao, S.; Dai, M.N.; Zong, C.L.; Gunther, D.; Fontaine, G.H.; Liu, X.M.; Diwu, C. Simultaneous determinations of U-Pb age, Hf isotopes and trace element compositions of zircon by excimer laser-ablation quadrupole and multiple-collector ICP-MS. *Chem. Geol.* **2008**, *247*, 100–118. [CrossRef]
58. Corfu, F.; Hanchar, J.M.; Hoskin, P.W.O.; Kinny, P. Atlas of zircon textures. *Rev. Mineral. Geochem.* **2003**, *53*, 469–500. [CrossRef]

59. Wu, Y.B.; Zheng, Y.F. Genesis of zircon and its constraints on interpretation of U-Pb age. *Chin. Sci. Bull.* **2004**, *49*, 1554–1569. [CrossRef]
60. Xu, S.M. Metallogenie Modeling of the Beiya Gold Deposit in Western Yunnan and Its Relation to the Cenozoic Alkali-Rich Porphyries: Beijing, China. Ph.D. Thesis, China University of Geosciences, Beijing, China, 2007; pp. 1–125. (In Chinese with English Abstract)
61. Streckeisen, A. To each plutonic rock its proper name. *Earth-Sci. Rev.* **1976**, *12*, 1–33. [CrossRef]
62. Rickwood, P.C. Boundary lines within petrologic diagrams which use oxides of major and minor elements. *Lithos* **1989**, *22*, 247–263. [CrossRef]
63. Le Maitre, R.W.; Bateman, P.; Dudek, A.; Keller, J.; Lameyre, J.; Le Bas, M.J.; Sabine, P.A.; Schmid, R.; Sorensen, H.; Streckeisen, A.; et al. *A Classification of Igneous Rocks and Glossary of Terms: Recommendations of the International Union of Geological Sciences Subcommission on the Systematics of Igneous Rocks*; Blackwell: Oxford, UK, 1989.
64. Maniar, P.D.; Piccoli, P.M. Tectonic discrimination of granitoids. *Geol. Soc. Am. Bull.* **1989**, *101*, 635–643. [CrossRef]
65. Wang, Q.; Xu, J.F.; Jian, P.; Bao, Z.W.; Zhao, Z.H.; Li, C.F.; Xiong, X.L.; Ma, J.L. Petrogenesis of adakitic porphyries in an extensional tectonic setting Dexing South China: Implications for the genesis of porphyry copper mineralization. *J. Petrol.* **2006**, *47*, 119–144. [CrossRef]
66. Lu, Y.J.; McCuaiga, T.C.; Li, Z.X.; Jourdan, F.; Hart, C.J.R.; Hou, Z.Q.; Tang, S.H. Paleogene post-collisional lamprophyres in western Yunnan, western Yangtze Craton: Mantle source and tectonic implications. *Lithos* **2015**, *233*, 139–161. [CrossRef]
67. Zhu, X.P.; Mo, X.X.; White, N.C.; Zhang, B.; Sun, M.X.; Wang, S.X.; Zhao, S.L.; Yang, Y. Petrogenesis metallogenic setting of the Habo porphyry Cu-(Mo-Au) deposit Yunnan China. *J. Asian Earth Sci.* **2013**, *66*, 188–203. [CrossRef]
68. Chen, Y.; Yao, S.; Pan, Y. Geochemistry of lamprophyres at the Daping gold deposit Yunnan Province China: Constraints on the timing of gold mineralization evidence for mantle convection in the eastern Tibetan Plateau. *J. Asian Earth Sci.* **2014**, *93*, 129–145. [CrossRef]
69. He, W.Y.; Mo, X.X.; Yu, X.H.; Dong, G.C.; He, Z.H.; Huang, X.F.; Li, X.W.; Jiang, L.L. Genesis and geodynamic settings of lamprophyres from Beiya, western Yunnan: Constraints from geochemistry, geochronology and Sr-Nd-Pb-Hf isotopes. *Acta Petrol. Sin.* **2014**, *30*, 3287–3300. (In Chinese with English Abstract)
70. Jia, L.Q.; Mo, X.X.; Dong, G.C.; Xu, W.Y.; Wang, L.; Guo, X.D.; Wang, Z.H.; Wei, S.G. Genesis of lamprophyres from Machangqing, western Yunnan: Constraints from geochemistry, geochronology and Sr-Nd-Pb-Hf isotopes. *Acta Petrol. Sin.* **2013**, *29*, 1247–1260. (In Chinese with English Abstract)
71. Gan, T.; Huang, Z. Platinum-group element and Re-Os geochemistry of lamprophyres in the Zhenyuan gold deposit, Yunnan province, China: Implications for petrogenesis and mantle evolution. *Lithos* **2017**, *282–283*, 228–239. [CrossRef]
72. Sun, S.S.; McDonough, W.F. Chemical and isotopic systematics of oceanic basalt: Implications for mantle composition and processes. *Geol. Soc. Lond. Spec. Publ.* **1989**, *42*, 313–345. [CrossRef]
73. Arnaud, N.O.; Vidal, P.; Tapponnier, P.; Matte, P.; Deng, W.M. The high K₂O volcanism of northwestern Tibet: Geochemistry and tectonic implications. *Earth Planet. Sci. Lett.* **1992**, *111*, 351–367. [CrossRef]
74. Turner, S.; Arnaud, N.; Liu, J.; Rogers, N.; Hawkesworth, C.; Harris, N.; Kelley, S.; van Calsteren, P.; Deng, W.M. Postcollisional, shoshonitic volcanism on the Tibetan plateau: Implications for convective thinning of the lithosphere and the source of ocean island basalts. *J. Petrol.* **1996**, *37*, 45–71. [CrossRef]
75. Guo, Z.F.; Wilson, M.; Liu, J.Q.; Mao, Q. Post-collisional potassic ultrapotassic magmatism of the northern Tibetan plateau: Constraints on characteristics of the mantle source geodynamic setting uplift mechanisms. *J. Petrol.* **2006**, *47*, 1177–1220. [CrossRef]
76. Miller, C.; Schuster, R.; Klotzli, U.; Frank, W.; Purtscheller, F. Post-collisional potassic ultrapotassic magmatism in SW Tibet: Geochemical Sr-Nd-Pb-O isotopic constraints for mantle source characteristics petrogenesis. *J. Petrol.* **1999**, *40*, 1399–1424. [CrossRef]
77. Ding, L.; Kapp, P.; Zhong, D.L.; Deng, W.M. Cenozoic volcanism in Tibet: Evidence for a transition from oceanic to continental subduction. *J. Petrol.* **2003**, *44*, 1833–1865. [CrossRef]
78. Zhao, Z.D.; Mo, X.X.; Dilek, Y.; Niu, Y.L.; DePaolo, D.J.; Robinson, P.; Zhu, D.C.; Sun, C.G.; Dong, G.C.; Zhou, S.; et al. Geochemical and Sr-Nd-Pb-O isotopic compositions of the post-collisional ultrapotassic magmatism in SW Tibet: Petrogenesis and implications for India intra-continental subduction beneath southern Tibet. *Lithos* **2009**, *113*, 190–212. [CrossRef]
79. Guo, Z.F.; Wilson, M.; Zhang, M.L.; Cheng, Z.H.; Zhang, L.H. Post-collisional ultrapotassic mafic magmatism in South Tibet: Products of partial melting of pyroxenite in the mantle wedge induced by roll-back delamination of the subducted Indian continental lithosphere slab. *J. Petrol.* **2015**, *56*, 1365–1406. [CrossRef]
80. Zindler, A.; Hart, S. Chemical geodynamics. *Annu. Rev. Earth Planet. Sci.* **1986**, *14*, 493–571. [CrossRef]
81. Hofmann, A.W. Mantle geochemistry: The message from oceanic volcanism. *Nature* **1997**, *385*, 219–229. [CrossRef]
82. Wu, F.Y.; Li, X.H.; Zheng, Y.F.; Gao, S. Lu-Hf isotopic systematics and their applications in petrology. *Acta Petrol. Sin.* **2007**, *23*, 185–220. (In Chinese with English Abstract)

83. Sun, X.M.; Zhang, Y.; Xiong, D.X.; Sun, W.D.; Shi, G.Y.; Zhai, W.; Wang, S.W. Crust and mantle contributions to gold-forming process at the Daping deposit, Ailaoshan gold belt, Yunnan, China. *Ore Geol. Rev.* **2009**, *36*, 235–249. [CrossRef]
84. Zhao, X.F.; Zhou, M.F.; Li, J.W.; Sun, M.; Gao, J.F.; Sun, W.H.; Yang, J.H. Late Paleoproterozoic to early Mesoproterozoic Dongchuan Group in Yunnan, SW China: Implications for tectonic evolution of the Yangtze Block. *Precambrian Res.* **2010**, *182*, 57–69. [CrossRef]
85. Wang, X.C.; Li, X.H.; Li, Z.X.; Li, Q.L.; Tang, G.Q.; Gao, Y.Y.; Zhang, Q.R.; Liu, Y. Episodic Precambrian crust growth: Evidence from U-Pb ages and Hf-O isotopes of zircon in the Nanhua Basin, central South China. *Precambrian Res.* **2012**, *222–223*, 386–403. [CrossRef]
86. Wang, D.H.; Chen, Y.C.; Xu, J.; Yang, J.M.; Xue, C.J.; Yan, S.H. Characteristic and metallogenic series of Cenozoic metallogeny in China. In Proceedings of the 31st International Geological Congress: Chinese Contributions to the Congress, Rio de Janeiro, Brazil, 6–17 August 2001; pp. 264–269. (In Chinese).
87. Yang, J.M.; Xue, C.J.; Xu, J.; Chen, Y.C.; Wang, D.H. *Geology and Metallogenesis of Himalayan Alkali-Rich Porphyries in Northwestern Yunnan*; Himalayan Endogenic Mineralization Research; Chen, Y.C., Wang, D.H., Eds.; Geological Publishing House: Beijing, China, 2001; pp. 57–68. (In Chinese)
88. Lu, Y.J.; Kerrich, R.; Cawood, P.A.; McCuaig, T.C.; Hart, C.J.R.; Li, Z.X.; Hou, Z.Q.; Bagas, L. Zircon SHRIMP U-Pb geochronology of potassic felsic intrusions in western Yunnan, SW China: Constraints on the relationship of magmatism to the Jinsha suture. *Gondwana Res.* **2012**, *22*, 737–747. [CrossRef]
89. Chung, S.L.; Chu, M.F.; Zhang, Y.Q.; Xie, Y.W.; Lo, C.H.; Lee, T.Y.; Lan, C.Y.; Li, X.H.; Zhang, Q.; Wang, Y.Z. Tibetan tectonic evolution inferred from spatial and temporal variations in post-collisional magmatism. *Earth-Sci. Rev.* **2005**, *68*, 173–196. [CrossRef]
90. Xia, B.; Lu, Y.; Yuan, Y.J.; Chen, W.Y.; Zhang, X.; Xu, C.; Yu, S.R.; Wan, Z.F. Mixing of Enriched Lithospheric Mantle-Derived and Crustal Magmas: Evidence from the Habo Cenozoic Porphyry in Western Yunnan. *Acta Geol. Sin. (Engl. Ed.)* **2018**, *92*, 1753–1768. [CrossRef]
91. Yan, Q.G.; Jiang, X.J.; Li, C.; Zhou, L.M.; Wang, Z.Q.; Sher, S.B.; Qu, W.J.; Du, A.D. Geodynamic background of intracontinental Cenozoic Alkaline volcanic rocks in Laojiezi, Western Yangtze Craton: Constraints from Sr-Nd-Hf-O isotopes. *Acta Geol. Sin.-Engl. Ed.* **2018**, *92*, 2098–2119.
92. Schärer, U.; Tapponnier, P.; Lacassin, R.; Leloup, P.H.; Zhong, D.; Ji, S. Intraplate tectonics in Asia: A precise age for large-scale Miocene movement along the Ailao Shan-Red River shear zone, China. *Earth Planet. Sci. Lett.* **1990**, *97*, 65–77. [CrossRef]
93. Schärer, U.; Zhang, L.C.; Tapponnier, P. Duration of strike-slip movements in large shear zones: The Red River belt, China. *Earth Planet. Sci. Lett.* **1994**, *126*, 379–397. [CrossRef]
94. Harrison, T.M.; Chen, W.; Leloup, P.H.; Ryerson, F.J.; Tapponnier, P. An early Miocene transition in deformation regime within the Red River fault zone Yunnan its significance for the Indo-Asian tectonics. *J. Geophys. Res.* **1992**, *97*, 7159–7182. [CrossRef]
95. Zhang, L.S.; Schärer, U. Age and origin of magmatism along the Cenozoic Red River shear belt. *China. Contrib. Mineral. Petrol.* **1999**, *134*, 67–85. [CrossRef]
96. Gilley, L.D.; Harrison, T.M.; Leloup, P.H.; Ryerson, F.J.; Lovera, O.M.; Wang, J.H. Direct dating of left-lateral deformation along the Red River shear zone China Vietnam. *J. Geophys. Res.* **2003**, *108*, 14–21. [CrossRef]
97. Sassier, C.; Leloup, P.H.; Rubatto, D.; Galland, O.; Yahui, Y.; Ding, L. Direct measurement of strain rates in ductile shear zones: A new method based on syntectonic dikes. *J. Geophys. Res.* **2009**, *114*, B01406. [CrossRef]
98. Searle, M.; Yeh, M.; Lin, T.H.; Chung, S.L. Structural constraints on the timing of left-lateral shear along the Red River shear zone in the Ailao Shan and Diancang Shan ranges, Yunnan, SW China. *Geosphere* **2010**, *6*, 316–338. [CrossRef]
99. Cao, S.Y.; Liu, J.L.; Leiss, B.; Neubauer, F.; Genser, J.; Zhao, C.Q. Oligo-Miocene shearing along the Ailao Shan-Red River shear zone: Constraints from structural analysis and zircon U/Pb geochronology of magmatic rocks in the Diancang Shan massif, SE Tibet, China. *Gondwana Res.* **2011**, *19*, 975–993. [CrossRef]
100. Chung, S.L.; Chu, M.F.; Ji, J.Q.; O'Reilly, S.Y.; Pearson, N.J.; Liu, D.Y.; Lee, T.Y.; Lo, C.H. The nature and timing of crustal thickening in southern Tibet: Geochemical and zircon Hf isotopic constraints from post-collisional adakites. *Tectonophysics* **2009**, *477*, 36–48. [CrossRef]
101. Li, X.Z.; Yin, C.Q.; Gao, P.; Davis, D.W.; Li, S.; Zhang, J.; Qian, J.H.; Zhang, Y.L. Petrogenesis tectonic implications of Eocene-Oligocene potassic felsic porphyries in the Sanjiang region southeastern Tibetan Plateau. *J. Asian Earth Sci.* **2022**, *232*, 105209. [CrossRef]
102. Campbell, I.H.; Griffiths, R.W. The evolution of mantle's chemical structure. *Lithos* **1993**, *30*, 389–399. [CrossRef]
103. Baker, J.A.; Menzies, M.A.; Thirlwall, M.F.; Macpherson, C.G. Petrogenesis of quaternary intraplate volcanism Sana's Yemen: Implication polybaric melt hybridization. *J. Petrol.* **1997**, *38*, 1359–1390. [CrossRef]
104. Macdonald, R.; Rogers, N.W.; Fitton, J.G. Plume-lithosphere interaction in the generation of the basalts of the Kenya rift east Africa. *J. Petrol.* **2001**, *42*, 877–900. [CrossRef]
105. Taylor, S.R.; McLennan, S.M. The continental crust: Its composition evolution. *J. Geol.* **1985**, *94*, 57–72.

106. Liu, Z.; Liao, S.Y.; Wang, J.R.; Ma, Z.; Liu, Y.X.; Wang, D.B.; Tang, Y.; Yang, J. Petrogenesis of late Eocene high Ba-Sr potassic rocks from western Yangtze Block SE Tibet: Amagmatic response to the Indo-Asian collision. *J. Asian Earth Sci.* **2017**, *135*, 95–109. [CrossRef]
107. Zhao, X.; Yu, X.H.; Mo, X.X.; Zhang, J.; Lv, B.X. Petrological and geochemical characteristics of Cenozoic alkali-rich porphyries and xenoliths hosted in western Yunnan province. *Geoscience* **2004**, *18*, 217–228.
108. Xin, T.; Zhao, Z.D.; Niu, Y.L.; Zhang, S.Q.; Cousens, B.; Liu, D.; Zhang, Y.; Han, M.Z.; Zhao, Y.X.; Lei, H.S.; et al. Petrogenesis and tectonic implications of the Eocene–Oligocene potassic felsic suites in western Yunnan, eastern Tibetan Plateau: Evidence from petrology, zircon chronology, elemental and Sr–Nd–Pb–Hf isotopic geochemistry. *Lithos* **2019**, *340–341*, 287–315.
109. Zhou, Y.; Xu, B.; Hou, Z.Q.; Wang, R.; Zheng, Y.C.; He, W.Y. Petrogenesis of Cenozoic high-Sr/Y shoshonites and associated mafic microgranular enclaves in an intracontinental setting: Implications for porphyry Cu–Au mineralization in western Yunnan, China. *Lithos* **2019**, *324/325*, 39–54. [CrossRef]
110. Zhou, Y.; Hou, Z.Q.; Wang, R.; Xu, B.; Evans, N.J.; He, W.Y.; Zheng, Y.C.; Zhou, J.X. Origin of biotite-rich xenoliths in the Eocene Beiya porphyry: Implications for upper-crustal Au remobilization and formation of giant porphyry Au systems in a collisional setting. *Lithos* **2023**, *442*, 107063. [CrossRef]
111. Yang, M.M.; Zhao, F.F.; Liu, X.F.; Qing, H.R.; Chi, G.X.; Li, X.Y.; Duan, W.J.; Lai, C. Contribution of magma mixing to the formation of porphyry-skarn mineralization in a post-collisional setting: The Machangqing Cu–Mo–(Au) deposit, Sanjiang tectonic belt, SW China. *Ore Geol. Rev.* **2020**, *122*, 103518. [CrossRef]
112. Xu, L.L.; Zhu, J.J.; Huang, M.L.; Pan, L.C.; Hu, R.Z.; Bi, X.W. Genesis of hydrous-oxidized parental magmas for porphyry Cu (Mo, Au) deposits in a postcollisional setting: Examples from the Sanjiang region, SW China. *Miner. Depos.* **2023**, *58*, 161–196. [CrossRef]
113. Zhang, Q.; Jin, W.J.; Xiong, X.L.; Li, C.D.; Wang, Y.L. Characteristics and implication of O-Type Adakite in China during different geological periods. *Geotecton. Et Metallog.* **2009**, *33*, 432–447. (In Chinese with English Abstract)
114. Defant, M.J.; Drummond, M.S. Derivation of some modern arc magmas by melting of young subducted lithosphere. *Nature* **1990**, *347*, 662–665. [CrossRef]
115. Zhang, Q.; Wang, Y.; Liu, W.; Wang, L.W. Adakite: Its characteristics and implications. *Geol. Bull. China* **2002**, *21*, 431–435. (In Chinese with English Abstract)
116. Chung, S.L.; Liu, D.; Ji, J.Q.; Chu, M.F.; Lee, T.Y.; Wen, D.J.; Zhang, Q. Adakites from continental collision zones: Melting of thickened lower crust beneath southern Tibet. *Geology* **2003**, *31*, 1021–1024. [CrossRef]
117. Atherton, M.P.; Petford, N. Generation of sodium-rich magmas from newly underplated basaltic crust. *Nature* **1993**, *362*, 144–146. [CrossRef]
118. Muir, R.J.; Weaver, S.D.; Bradshaw, J.D.; Eby, G.N.; Evans, J.A. The Cretaceous Separation Point batholith New Zealand: Granitoid magmas formed by melting of mafic lithosphere. *J. Geol. Soc.* **1995**, *152*, 689–701. [CrossRef]
119. Xu, J.F.; Shinjo, R.; Defant, M.J.; Wang, Q.; Rapp, R.P. Origin of Mesozoic adakitic intrusive rocks in the Ningzhen area of East China: Partial melting of delaminated lower continental crust? *Geology* **2002**, *30*, 1111–1114. [CrossRef]
120. Jahn, B.M.; Zhang, Z.Q. Archean granulite gneisses from eastern Hebei Province, China: Rare earth geochemistry and tectonic implications. *Contrib. Mineral. Petrol.* **1984**, *85*, 224–243. [CrossRef]
121. Baker, M.B.; Hirschmann, M.M.; Ghiorso, M.S.; Stolper, E.M. Compositions of near-solidus peridotite melts from experiments and thermodynamic calculations. *Nature* **1995**, *375*, 308–311. [CrossRef]
122. Valley, J.W.; Lackey, J.S.; Cavosie, A.J.; Clechenko, C.C.; Apicuzza, M.J.; Basei, M.A.S.; Bindeman, I.N.; Ferreira, V.P.; Sial, A.N.; King, E.M.; et al. 4.4 billion years of crustal maturation: Oxygen isotope ratios of magmatic zircon. *Contrib. Mineral. Petrol.* **2005**, *150*, 561–580. [CrossRef]
123. King, P.L.; White, A.J.R.; Chappell, B.W.; Allen, C.M. Characterization origin of aluminous A-type granites from the Lachlan Fold Belt southeastern Australia. *J. Petrol.* **1997**, *38*, 371–391. [CrossRef]
124. Patiño Douce, A.E. Generation of metaluminous A-type granites by low pressure melting of calc-alkaline granitoids. *Geology* **1997**, *25*, 743–746. [CrossRef]
125. Wu, F.Y.; Sun, D.Y.; Li, H.M.; Jahn, B.M.; Wilde, S.A. A-type granites in northeastern China: Age and geochemical constraints on their petrogenesis. *Chem. Geol.* **2002**, *187*, 143–173. [CrossRef]
126. Yang, L.Q.; Deng, J.; Dilek, Y.; Meng, J.Y.; Gao, X.; Santosh, M.; Wang, D.; Yan, H. Melt source and evolution of I-type granitoids in the SE Tibetan Plateau: Late Cretaceous magmatism and mineralization driven by collision-induced transtensional tectonics. *Lithos* **2016**, *245*, 258–273. [CrossRef]
127. Bea, F.; Fershtater, G.B.; Montero, P.; Whitehouse, M.; Levin, V.Y.; Scarrow, J.H.; Austrheim, H.; Pushkariev, E.V. Recycling of continental crust into the mantle as revealed by Kytlym dunite zircons, Ural Mts, Russia. *Terra Nova* **2001**, *13*, 407–412. [CrossRef]
128. Chen, Q.; Sun, M.; Zhao, G.C.; Zhao, J.H.; Zhu, W.L.; Long, X.P.; Wang, J. Episodic crustal growth and reworking of the Yudongzi terrane, South China: Constraints from the Archean TTGs and potassic granites and Paleoproterozoic amphibolites. *Lithos* **2019**, *326–327*, 1–18. [CrossRef]

129. Zheng, Y.F.; Zhao, G. Two styles of plate tectonics in Earth's history. *Sci. Bull.* **2020**, *65*, 329–334. [CrossRef] [PubMed]
130. Guo, Z.F.; Wilson, M.; Liu, J. Post-collisional adakites in South Tibet: Products of partial melting of subduction-modified lower crust. *Lithos* **2007**, *96*, 205–224. [CrossRef]
131. Wang, X.; Zhang, J.F.; Rushmer, T.; Adam, J.; Turner, S. Adakite-Like Potassic Magmatism Crust-Mantle Interaction in a Postcollisional Setting: An Experimental Study of Melting Beneath the Tibetan Plateau. *J. Geophys. Res. Solid Earth* **2019**, *124*, 12782–12798. [CrossRef]
132. Pearce, J.A. Sources and settings of granitic rocks. *Episodes* **1996**, *19*, 120–125. [CrossRef]
133. Gomez-Frutos, D.; Castro, A. Mafic microgranular enclaves (MMEs) trace the origin of post-collisional magmas. *Geology* **2023**, *8*, 51. [CrossRef]
134. Conticelli, S.; Guarnieri, L.; Farinelli, A.; Mattei, M.; Avanzinelli, R.; Bianchini, G.; Boari, E.; Tommasini, S.; Tiepolo, M.; Prelević, D.; et al. Trace elements and Sr-Nd-Pb isotopes of K-rich, shoshonitic, and calc-alkaline magmatism of the Western Mediterranean Region: Genesis of ultrapotassic to calc-alkaline magmatic associations in a post-collisional geodynamic setting. *Lithos* **2009**, *107*, 68–92. [CrossRef]
135. Topuz, G.; Altherr, R.; Schwarz, W.H.; Siebel, W.; Satır, M.; Dokuz, A. Post-collisional plutonism with adakite-like signatures: The Eocene Saraycık granodiorite (Eastern Pontides, Turkey). *Contrib. Mineral. Petrol.* **2005**, *150*, 441–455. [CrossRef]
136. Wang, R.; Weinberg, R.F.; Collins, W.J.; Richards, J.P.; Zhu, D.C. Origin of postcollisional magmas and formation of porphyry Cu deposits in southern Tibet. *Earth-Sci. Rev.* **2018**, *181*, 122–143. [CrossRef]
137. Liégeois, J.P.; Navez, J.; Hertogen, J.; Blank, R. Contrasting origin of post-collisional high-K calc-alkaline and shoshonitic versus alkaline and peralkaline granitoids. Use Sliding normalization. *Lithos* **1998**, *45*, 1–28. [CrossRef]
138. Deng, J.; Su, S.; Niu, Y.; Liu, C.; Zhao, G.C.; Zhao, X.G.; Zhou, S.; Wu, Z.X. A possible model for the lithospheric thinning of North China Craton: Evidence from the Yanshanian (Jura-Cretaceous) magmatism and tectonism. *Lithos* **2007**, *96*, 22–35. [CrossRef]
139. Liu, J.Q. *Volcanoes in China*; Science Press: Beijing, China, 1999; pp. 1–219. (In Chinese)
140. Zhang, Y.Q.; Xie, Y.W.; Li, X.H.; Qiu, H.N.; Zhao, Z.H.; Liang, H.Y.; Chung, S. Isotopic characteristics of shoshonitic rocks in eastern Qinghai-Tibet Plateau: Petrogenesis and its tectonic implication. *Sci. China (Ser. D)* **2001**, *44*, 1–6. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Genesis and Mineralization Process of the Lanuoma Sediment-Hosted Pb–Zn Deposit, Sanjiang Metallogenic Belt, Southwestern China: Constraints from Zn, Pb, and S Isotopes

Chunxia Xu ¹, Jiantang Peng ^{2,*}, Jianjun Gan ¹, Chun Tang ¹, Zhiming Yin ¹ and Cheng Huang ¹

¹ School of Hydraulic Engineering, Jiangxi University of Water Resources and Electric Power, Nanchang 330099, China; xuchunxia_nit@163.com (C.X.); ganjianjun@juwp.edu.cn (J.G.); tangchun@juwp.edu.cn (C.T.); yinzhiming2025@163.com (Z.Y.); huangcheng_nit@126.com (C.H.)

² State Key Laboratory of Critical Mineral Research and Exploration, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550001, China

* Correspondence: jtpeng@126.com

Abstract

The Lanuoma sediment-hosted lead–zinc (Pb–Zn) deposit, situated in the central part of the Sanjiang base metal metallogenic belt (SMB) within the Changdu Basin, is hosted by Triassic Bolila Formation limestone. The source of metals and sulfur (S), as well as the ore-forming processes for the deposits in this belt, are contentious. To constrain the metal and sulfur sources and to define the ore-forming mechanism, we analyzed Zn, Pb, and S isotopes of sphalerite and robinsonite, as well as Zn isotopes of the host limestone and the metamorphic basement. Sphalerite shows homogeneous $\delta^{66}\text{Zn}$ values (-0.31‰ to -0.12‰ ; mean = -0.20‰). The calculated $\delta^{66}\text{Zn}$ of the ore-forming fluid ($\sim 0.00\text{‰}$) matches that of the Triassic limestone, indicating a sedimentary Zn source ($\delta^{66}\text{Zn} = -0.11\text{‰}$ to -0.09‰ ; average 0.00‰). Robinsonite displays a wider $\delta^{66}\text{Zn}$ range (-0.22‰ to 0.44‰), reflecting a mixture of sedimentary and metamorphic sources ($\delta^{66}\text{Zn} = 0.12\text{‰}$ to 0.42‰ ; average 0.22‰). Lead isotopes of sphalerite are uniform ($^{206}\text{Pb}/^{204}\text{Pb} = 19.041\text{--}19.079$) and indicative of a sedimentary rock source, whereas robinsonite shows wide variation ($^{206}\text{Pb}/^{204}\text{Pb} = 19.070\text{--}19.156$) and linear trends between low- and high-radiogenic end-members, indicating mixed Pb sources from sedimentary rocks and metamorphic basement. Sulfur isotopic compositions of sulfides ($\delta^{34}\text{S} = -1.4\text{‰}$ to 2.6‰ ; mean = -0.1‰) cluster near 0‰ , consistent with a deep magmatic origin. A strong linear correlation between $^{206}\text{Pb}/^{204}\text{Pb}$ and $\delta^{66}\text{Zn}$, coupled with a lack of correlation between both $^{206}\text{Pb}/^{204}\text{Pb}$ and $\delta^{34}\text{S}$ and $\delta^{66}\text{Zn}$ and $\delta^{34}\text{S}$ in the sulfides, indicates that Pb and Zn were derived from a common metal source, whereas sulfur originated from a distinct reservoir. Combined with previously published fluid inclusion, rare earth element, and multi-isotopic constraints, these results suggest that Pb–Zn mineralization at Lanuoma was controlled by a mixing between metal-rich basinal brines and sulfur-rich deep-sourced fluids, leading to sulfide precipitation dominated by open-space filling. This study provides new insights into the genesis and mineralization process of sediment-hosted Pb–Zn deposits in the Sanjiang metallogenic belt.

Keywords: Lanuoma deposit; sediment-hosted Pb–Zn deposit; ore genesis; mineralization process; fluid mixing; Zn–Pb–S isotopes

1. Introduction

Sediment-hosted Pb–Zn deposits are common in the Sanjiang metallogenic belt (SMB) and constitute one of the most important base-metal resources in China [1]. These deposits are mainly hosted in foreland basin successions and are commonly regarded as Mississippi Valley-type (MVT-like) systems formed during basin evolution associated with Cenozoic orogeny [2]. Owing to their economic significance and complex tectonic setting, SMB sediment-hosted Pb–Zn deposits have been the subject of extensive geological, geochemical, and isotopic investigations.

Previous studies have made substantial progress in constraining the timing, fluid characteristics, and possible metal sources of these deposits. Geochronological data indicate that most sediment-hosted Pb–Zn deposits in the SMB formed during the Oligocene (ca. 27–33 Ma; [3]), broadly synchronous with regional tectonic deformation and magmatic activity [4]. Fluid inclusion, trace element, and multi-isotopic (e.g., C–O–Sr–Nd–Hg–He) studies suggest that basinal brines played a major role in metal transport, and that fluid mixing involving meteoric, metamorphic, and/or magmatic components may have occurred in different segments of the belt [5–7].

Despite these advances, several fundamental issues remain unresolved. The sources of Pb and Zn are still debated. Many studies favor derivation from basinal sedimentary strata. Others propose contributions from metamorphic basement or deeper crustal components, based mainly on Pb isotopic heterogeneity and mixing trends [8,9]. The source and redox state of sulfur remain controversial. Both thermochemical sulfate reduction (TSR) and bacterial sulfate reduction (BSR) have been invoked [10,11], and in some cases magmatic sulfur has been proposed [12]. However, these interpretations are commonly based on sulfur isotopes alone and lack integration with metal isotopic constraints. Third, although fluid mixing has been widely recognized [13], the mechanisms linking fluid evolution to metal precipitation are still poorly constrained, particularly in terms of whether metals and sulfur were sourced from the same or distinct reservoirs.

The Lanuoma sediment-hosted Pb–Zn–Sb deposit, located in the Changdu Basin in the central SMB, is a good candidate for addressing these issues. Previous studies have suggested that Lanuoma mineralization involved mixing between basinal brines and magmatic-related fluids, and that sulfur was reduced through TSR [12,14]. Mercury isotope data further indicate contributions from both sedimentary strata and metamorphic basement [15]. However, the precise sources of Pb and Zn, and their relationship to sulfur sources and precipitation processes, remain insufficiently constrained.

Recent advances in Zn isotope geochemistry provide a powerful tool to trace metal sources and fluid–rock interaction processes in hydrothermal systems ([16] and references therein). When combined with Pb and S isotopes, Zn isotopes can help distinguish between sedimentary, basement, and magmatic contributions, and be used to evaluate whether metals and sulfur were derived from common or decoupled reservoirs [17–21].

In this study, we integrate Zn, Pb, and S isotopes of sphalerite and robinsonite with Zn isotopes of ore-hosting strata and metamorphic basement from the Lanuoma deposit. By combining these new data with previously published Pb isotopic and fluid geochemical constraints, we aim to (1) identify the sources of Pb, Zn, and reduced sulfur, (2) evaluate the role of fluid mixing in metal transport and precipitation, and (3) provide new insights into the metallogenic mechanism of sediment-hosted Pb–Zn deposits in the Sanjiang metallogenic belt.

2. Regional Geology

The Sanjiang base metal metallogenic belt (SMB) is located along the eastern and northern margins of the Qinhai-Tibet Plateau, bounded by the Jinshajiang Sutures (JS)

to the north and the Bangognhu-Nujiang Sutures (BNS) to the south (Figure 1a). The SMB was profoundly influenced by the collisional orogeny between the Indian and Eurasian continents during Cenozoic, which resulted in the development of large-scale strike-slip fault system, thrust-nappe structural systems, and associated Tertiary foreland basins [22,23]. More than one hundred Pb–Zn–Cu–Ag deposits and occurrences have been identified within the SMB, predominantly hosted in sedimentary rocks. From north to south of the SMB, these deposits are distributed within a series of Tertiary foreland basins, including the Tuotuohe, Yushu, Changdu, and Lanping-Simao basins, collectively forming a more than 1000 km-long base-metal metallogenic belt.

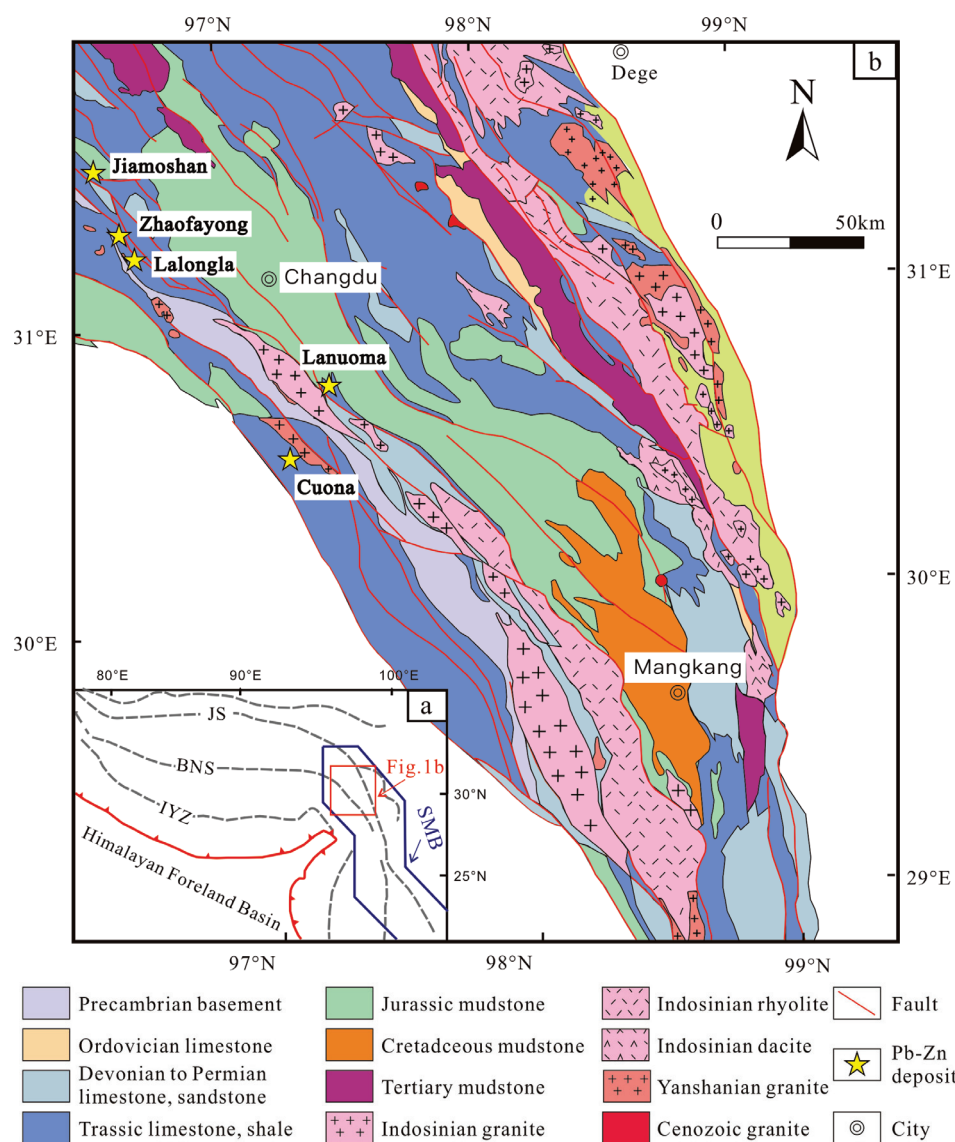


Figure 1. (a) Simplified tectonic map, showing the SMB within the Tibetan Plateau. (b) Geological map of the Changdu area showing the Lanuoma deposit (Modified after [14]).

The Changdu Basin is bounded by the Jinshajiang suture to the east and the Nujiang suture to the west, forming a NW-trending belt that widens toward the north and converges toward the south. The Precambrian Jitang Group, which is composed of schist, gneiss and granulite, constitutes the metamorphic basement of Changdu Basin (Figure 1b). Paleozoic strata, including Ordovician, Devonian, Carboniferous, and Permian systems, are sporadically distributed and mainly composed of clastic rocks and carbonates. Mesozoic strata are widely distributed in the mining area. The Triassic is dominated by marine carbonate

rocks and sandy mudstone. The Jurassic consists of marine–terrestrial to terrestrial clastic rocks, while the Cretaceous is characterized by continental clastic rocks. Tertiary strata are composed of clastic rocks and gypsum [24].

Extensive tectonism occurred in the basin in response to the collision of the Indian and Asian continents in the Cenozoic. During the middle to late Eocene, the Jinshajiang and Lancangjiang orogenic belts on both sides of the Changdu Basin thrust toward the basin, forming a convergent thrust tectonic pattern. In the late Eocene to Oligocene, the basin experienced strike-slip extension, developing a series of en échelon structures along pre-existing deep faults [1].

Igneous rocks in the Changdu Basin comprise Late Triassic volcanic and intrusive rocks. The volcanic rocks mainly consist of basalt, andesitic tuff, and rhyolite [6]. The main intrusive rocks are represented by the Jitang pluton, which intrudes into the Jitang Group metamorphic rocks and Carboniferous strata. They are mainly composed of S-type biotite granite and granodiorite [25].

3. Geology of the Lanuoma Deposit

The Lanuoma deposit is located approximately 10 km north of the town of Jitang and is hosted in the Upper Triassic Strata. The mining area of the Lanuoma deposit exposes four sedimentary formations: the Jiapila, Bolila, Adula, and Duogaila formations (Figure 2). From bottom to top, the Jiapila Formation distributed in western and north-western mining area is a clastic rock assemblage composed mainly of lithic and feldspathic quartz sandstones interbedded with gypsum layers. The Bolila Formation exposed in the central part of the mining area is the ore-hosting strata for Pb–Zn ore bodies; the lithology of the formation is mainly gray to white limestone, which was formed in a coastal environment representing a transitional marine–terrestrial facies. The Adula Formation is outcropped in the north-central part of the mining area and has a funnel-shaped morphology, with the lithology of mudstone and shale interbedded with minor quartz sandstone. The Duogaila Formation on the top can be divided into two members. The lower member is mainly composed of carbonaceous mudstone whereas the upper member is dominated by feldspathic sandstone. Quaternary residual, colluvial, and alluvial–proluvial deposits occur in the eastern part of the mining area.

Three major faults occur in the Lanuoma deposit. The F_1 and F_2 reverse faults, located in the central-western part and eastern part of the mining area, are the main ore-controlling structure. The F_1 marks the boundary between the Jiapila Formation and the Bolila Formation. It generally dips westward with an inclination of $45\text{--}60^\circ$. The F_2 fault dips eastward with an inclination of $60\text{--}78^\circ$. The footwall consists of the Bolila Formation, while the hanging wall is composed of the Duogaila Formation. The F_3 strike-slip fault is a post-ore structure. An anticline structure is developed in the central part of the mining area, plunging northward. The western limb is steeply dipping ($55\text{--}85^\circ$), while the eastern limb is gently dipping ($35\text{--}65^\circ$). No. I and No. II ore bodies are distributed within the Bolila Formation on the limbs of the anticline.

The ore body hosted in limestone of the Bolila Formation occurs as stratified or lenticular in morphology (Figures 3 and 4a) and is controlled by structural fracture zones. Mineralization is dominated by open-space filling, with replacement playing a subordinate role. Ore minerals mainly occur in vein-like, brecciated, and massive forms. Based on exploration data, two ore bodies (No. I and No. II) have been delineated. The F_3 fault separates the two ore bodies, with ore Body No. I located to the north and ore Body No. II to the south.

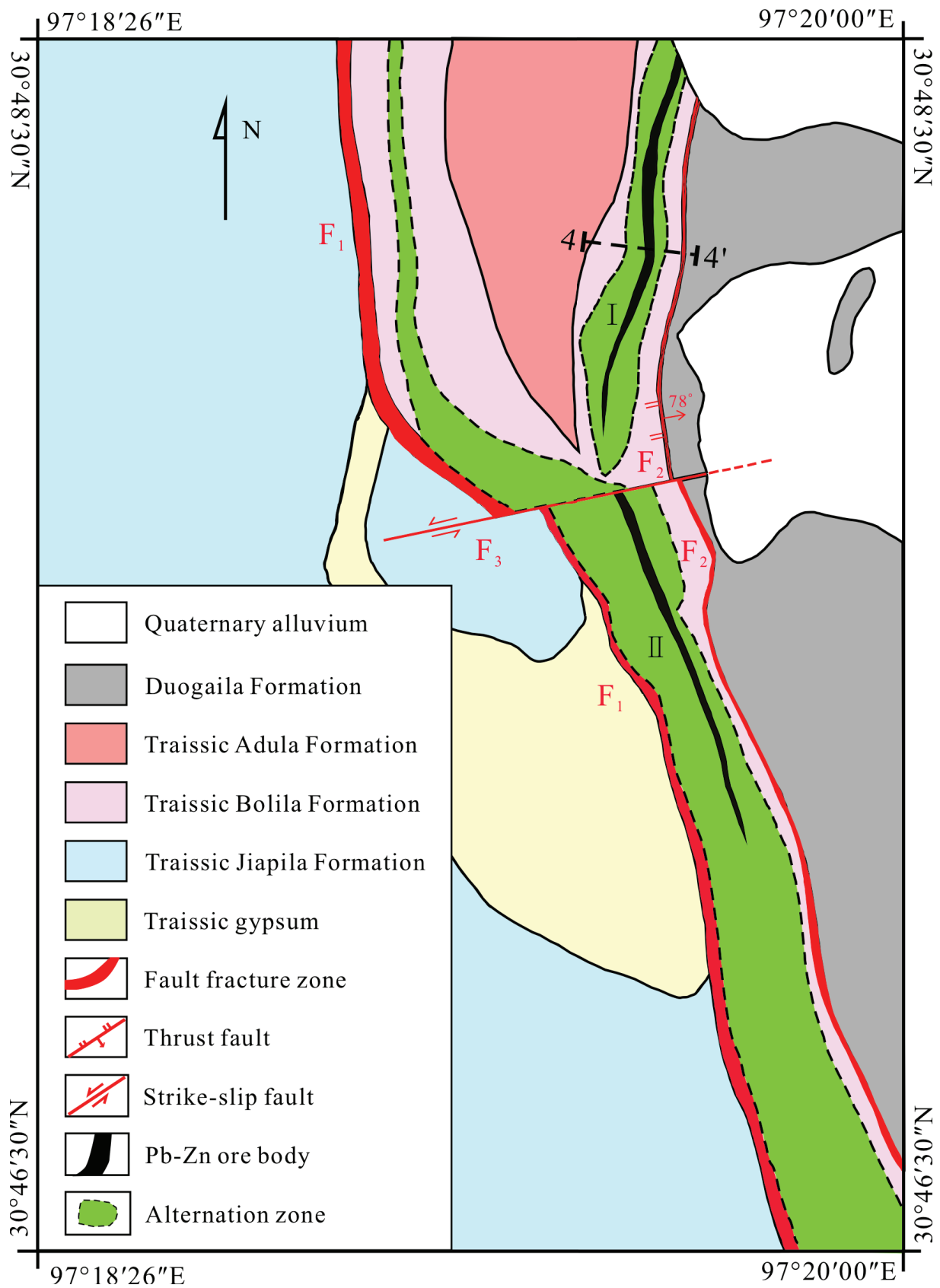


Figure 2. Simplified geological map of the Lanuoma deposit (modified after [14]).

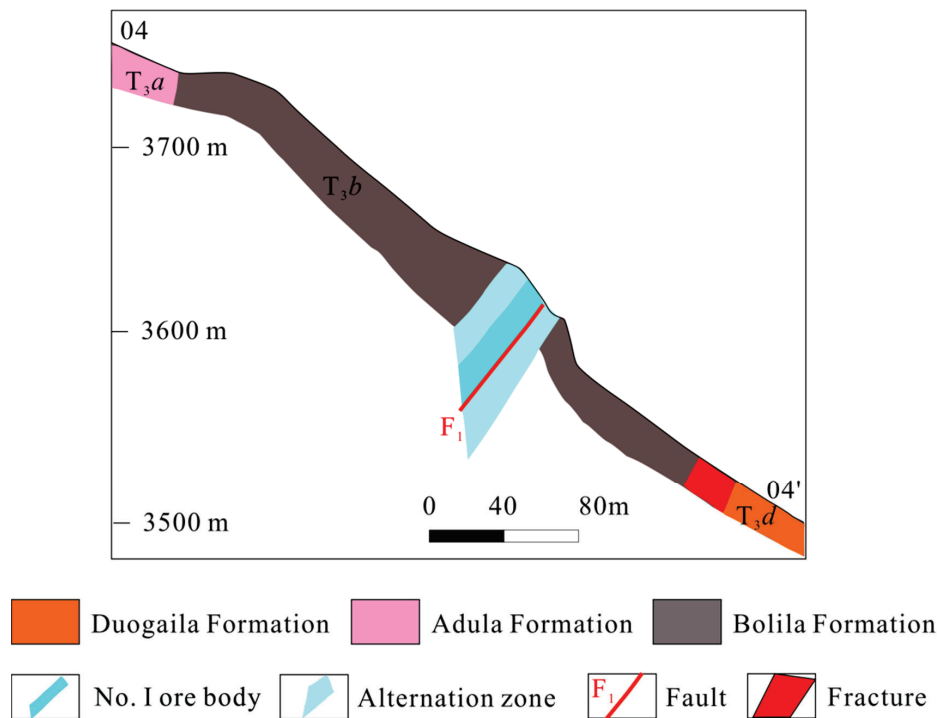


Figure 3. Cross section along 4-4' exploration lines (Modified after [12,26]).

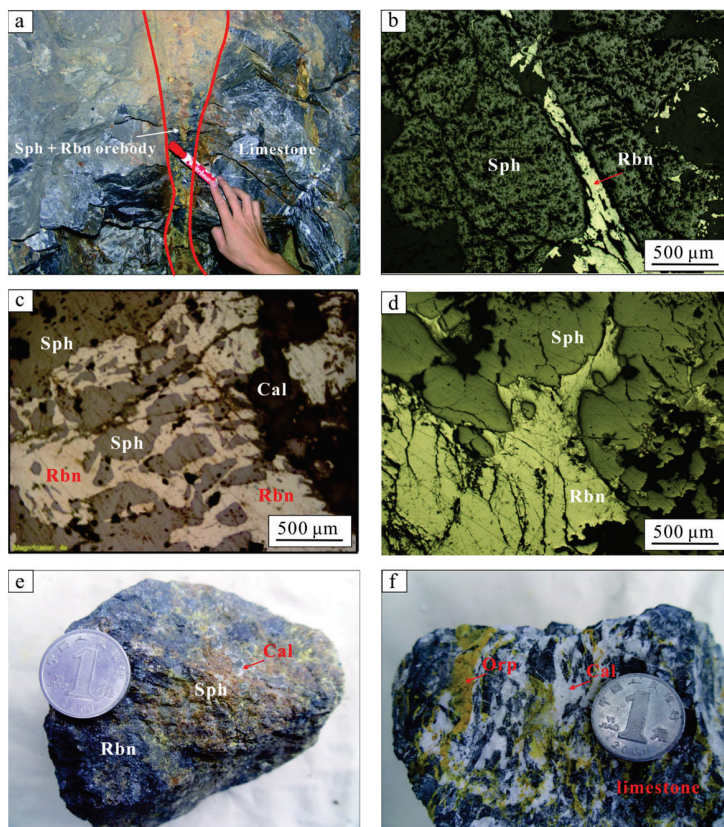


Figure 4. Photographs of representative orebodies; ore samples from the Lanuoma deposit. (a) Lenticular Zn-Pb-Sb orebody hosted by limestone; the red lines outline the boundary of the orebody; (b) sphalerite replaced by fine veinlet-type robinsonite; (c) robinsonite replacing sphalerite and showing a replacement relict texture; (d) Sphalerite occurred as isolated and embayed patches; (e) massive ore composed of sphalerite, robinsonite, and calcite; (f) orpiment and calcite occurred as a veinlet network structure within limestone.

The ore Body No. I strikes NNW and dips westward with a dip angle of 40–50°. It extends 1100 m in length, has an average thickness of 12 m, and reaches a maximum down-dip extension of 175 m. The average grades are 2.41 wt.% Pb, 3.02 wt.% Zn, and 1.92 wt.% Sb. The ore Body No. II generally dips eastward at angles of 60–70°, with a strike length of approximately 1025 m and an average thickness of 6.48 m. The average ore grades are 1.86 wt.% Pb and 1.08 wt.% Zn.

Wall-rock alteration is characterized mainly by calcitization, pyritization, silicification, and orpiment mineralization. Calcitization is expressed by micritic calcite replacement of limestone and marl, as well as by the widespread development of calcite veins. Cross-cutting relationships among calcite veins indicate that calcitization occurred during multiple stages. Micritic calcite replacement of limestone and marl is commonly accompanied by pyritization. Orpiment mineralization occurs mainly within fault-related breccia zones. Orpiment (locally associated with realgar) is abundant in carbon-rich, brittle marls, where it occurs in vein-like and massive forms.

Robinsonite and sphalerite are the main ore minerals, which commonly occur as granular aggregates. Robinsonite also occurs intergrown with sphalerite, either as banded or fine vein-like replacements (Figure 4b). The latter shows a replacement relict (Figure 4c), or isolated or embayed texture (Figure 4d). The ores are mainly characterized by massive (Figure 4e), disseminated, stockwork (Figure 4f), vein-type, porous, and brecciated textures.

The Lanuoma Pb–Zn deposit is hosted in limestone of the Triassic Bolila Formation, which was deposited in a shallow-marine carbonate platform environment. The host rocks are locally brecciated and fractured, providing favorable open spaces for fluid circulation and mineral precipitation. Mineralization reflects a transition from diagenetic to hydrothermal conditions, as indicated by dominant open-space filling accompanied by subordinate replacement of the carbonate host rocks. These structural and lithological features facilitated fluid focusing and fluid–rock interaction, forming a suitable physicochemical environment for Pb–Zn–Sb sulfide deposition.

Based on mineral assemblages and textural relationships, the mineralization can be divided into three stages [14], including a pre-mineral stage (Stage 1), a syn-mineral stage (Stage 2), and a post-mineral stage (Stage 3). The paragenetic sequence of minerals for the Lanuoma deposit is summarized in Figure 5. The pre-mineral stage (Stage 1) is characterized by early pyrite and gangue minerals, dominated by oolitic pyrite, calcite, and minor sulfate minerals (e.g., gypsum and barite), which are disseminated within limestone and predate significant Pb–Zn mineralization. The syn-mineral stage (Stage 2) represents the main period of sulfide deposition. The early stage (Stage 2a) corresponds to the principal Pb–Zn–Sb mineralization and is characterized by pyrite, sphalerite, galena, and robinsonite, occurring mainly as vein fillings and breccia fillings, commonly associated with calcite. The late stage (Stage 2b) is dominated by orpiment and realgar, with minor late-stage sulfides hosted in calcite veins. The post-mineral stage (Stage 3) is marked by the emplacement of barren, coarse-grained calcite veins that cut earlier mineral assemblages and contain little to no sulfide minerals.

Minerals	Stage 1	Stage 2a	Stage 2b	Stage 3
Robinsonite				
Sphalerite				
Pyrite				
Galena				
Quartz				
Orpiment				
Realgar				
Barite				
Gypsum				
Calcite				

Figure 5. Paragenetic sequence of minerals in the Lanuoma deposit.

4. Sampling and Analytical Methods

4.1. Sample Collection

Sphalerite and robinsonite samples used for zinc, lead, and sulfur isotopic analyses in this study were collected from underground galleries of the Lanuoma mine at elevations between 3280 and 3396 m asl. These samples are from Stage 2 and represent mineralization-stage products. Host limestone samples were taken from exposed outcrops in the ore district, whereas metamorphic rocks were sampled from distal regional outcrops near the town of Jitang.

4.2. Zinc Isotopic Analyses

About 50 mg of each powdered sample was dissolved in concentrated HNO₃-HF (1:3) and then refluxed in 6 N HCl to remove fluorides, following the dissolution procedure described by [27]. Zinc was purified by anion-exchange chromatography using AGI-X8 resin, after the method of [28]. The resin was conditioned with 1.5 N HBr, and Zn was eluted with 0.5 N HNO₃. Total Zn blanks were <10 ng, and recovery exceeded 99%. The purified Zn solutions were evaporated to dryness and re-dissolved in 0.1 N HNO₃ for isotopic measurement. Zinc isotope compositions were measured on a Thermo Scientific Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Bremen, Germany) at Washington University in St. Louis, following the analytical conditions of [29]. Isotope ratios were expressed in delta notation ($\delta^{66}\text{Zn}$, $\delta^{68}\text{Zn}$) relative to the JMC 3-0749 L Zn standard, with mass bias corrected using exponential law. Analytical reproducibility (2σ) was better than $\pm 0.05\text{‰}$ for $\delta^{66}\text{Zn}$.

4.3. Sulfur Isotopic Analyses

Powdered sulfide (sphalerite and robinsonite) analyses were conducted at the Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. Sulfur isotope analyses were completed using a Finnigan MAT-253 continuous flow isotope ratio mass spectrometer coupled to an elemental analyzer (EA-IRMS) (Thermo Fisher Scientific, Bremen, Germany)

according to the method of [30]. Sulfide samples were converted to SO_2 for isotopic analysis by burning in the reactor under a constant temperature of about 1000 °C using a stream of purified oxygen. The sulfur dioxide was then carried by helium into the mass spectrometer. Measurements are reported using standard δ -notation relative to V-CDT international standard. The analytical error was better than 0.2‰ (1 σ) calculated from replicate analyses of the IAEA international standards: IAEA S1 (−0.30‰), IAEA S2 (+22.62‰) and IAEA S3 (−32.49‰). The precision calculated from replicate analyses of unknown samples is better than 0.2‰ (1 σ).

4.4. Lead Isotopic Analyses

Lead isotope analyses were performed at the Analytical Laboratory of Beijing Research Institute of Uranium Geology by IsoProbe-T thermal ionization mass spectrometer (TIMS) (GV Instruments, Manchester, UK). Detailed procedures were described by [31]. Briefly, small quantities of powdered sulfide samples (sphalerite and robinsonite) were dissolved in acid, chemically separated and purified by ion exchange (AG1 $\times$ 8, 200–400 resin) with diluted HBr used as eluant, loaded on Re filaments using phosphoric acid and silica gel, thermally ionized, and then analyzed by mass spectrometry. The $^{208}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$, and $^{204}\text{Pb}/^{206}\text{Pb}$ ratios of the Standard NBS 981 were 2.16810 ± 0.0008 (2 σ), 0.91464 ± 0.00033 (2 σ), and 0.059042 ± 0.000037 (2 σ), respectively. They are consistent with their corresponding recommended values of 2.16701 ± 0.00013 (2 σ), 0.91459 ± 0.00009 (2 σ), and 0.059047 ± 0.000024 (2 σ) [32].

5. Results

5.1. Zinc Isotopes

The $\delta^{66}\text{Zn}$ values of sphalerite range from −0.31‰ to −0.12‰ (average −0.20‰; $n = 5$) with narrow variations. Robinsonite has a wide range of $\delta^{66}\text{Zn}$ values from −0.22‰ to +0.44‰ with an average value of 0.06‰ ($n = 5$). The $\delta^{66}\text{Zn}$ values of the Triassic Bolila formation limestone and the Jitang Group metamorphic rocks are between −0.11‰ and +0.09‰ (average 0.00‰; $n = 3$) and 0.12‰ and +0.42‰ (average 0.22‰; $n = 5$), respectively (Table 1).

Sphalerite has the lowest $\delta^{66}\text{Zn}$ values. Metamorphic rocks of the Jitang Group have the highest $\delta^{66}\text{Zn}$ values. The $\delta^{66}\text{Zn}$ values of robinsonite overlap between Jitang Group metamorphic rocks and the Triassic Bolila formation limestone.

5.2. Sulfur Isotopes

The $\delta^{34}\text{S}$ values of sphalerite vary between −0.7‰ and 0.6‰ ($n = 10$), with an average of −0.2‰ and robinsonite between −0.2‰ and −1.6‰ ($n = 10$), with an average of −0.74‰ (Table 1). Tao et al. (2011) [26] obtained $\delta^{34}\text{S}$ values of sphalerite and robinsonite that range from −0.4‰ to +2.4‰ (average 0.9‰) and −1.6‰ to +2.6‰ (average 0.4‰). In general, the $\delta^{34}\text{S}$ values of sulfides from the Lanuoma deposit are within the ranges of −1.4‰ to +2.6‰, averaging at −0.1‰. These results are narrowly distributed around 0‰, which is consistent with the isotopic compositions of sulfur of mantle origin ($\delta^{34}\text{S} = -2\text{‰} \sim 2\text{‰}$) [33].

5.3. Lead Isotopes

The lead isotopic compositions of seven sphalerite samples are uniform, with $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ranging from 19.041–19.079 (average 19.058), 15.653–15.699 (average 15.674) and 39.033–39.181 (average 39.102), respectively. Seven robinsonite samples have large variations of lead isotopic compositions. Their $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values are between 19.070 and 19.156 (averaging at 19.114), 15.686 and 15.796 (averaging at 15.742), 39.145 and 39.526 (averaging at 39.343) (Table 1).

Noticeably, sphalerite and robinsonite show positive relationship with robinsonite characterized by higher contents of radioactive lead.

Table 1. Zinc, lead and sulfur lead isotopic compositions in samples from the Lanuoma deposits.

Sample No.	Description	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\delta^{66}\text{Zn}_{\text{JMC}}$	$\delta^{67}\text{Zn}_{\text{JMC}}$	$\delta^{68}\text{Zn}_{\text{JMC}}$	$\delta^{34}\text{S}_{\text{V-CDT}}$
Pt11-1	Schist of precambrian metamorphic basement				0.12	0.18	0.25	
Pt11-3					0.23	0.34	0.46	
Pt11-4					0.18	0.26	0.36	
Pt11-6					0.15	0.22	0.29	
Pt11-8					0.42	0.62	0.83	
LNM11-3	Limestone of Upper Triassic Bolila Foramtion				−0.11	−0.17	−0.22	
LNM11-21					0.03	0.04	0.05	
LNM11-16					0.09	0.15	0.17	
LNM-12	Sphalerite	19.061	15.673	39.098	−0.31	−0.46	−0.55	−0.2
LNM-104		19.041	15.653	39.033	−0.23	−0.36	−0.46	−0.1
LNM-118		19.042	15.660	39.051	−0.13	−0.27	−0.32	−0.5
LNM-123		19.053	15.668	39.083	−0.20	−0.23	−0.30	−0.6
LNM-125		19.056	15.670	39.097	−0.12	−0.23	−0.33	−0.5
LNM-2	Robinsonite	19.156	15.796	39.526	0.13	0.16	0.24	−0.9
LNM-3		19.137	15.773	39.454	0.44	0.65	0.87	−0.2
LNM-118		19.080	15.698	39.183	0.08	0.12	0.15	−1.2
LNM-123		19.070	15.686	39.145	−0.22	−0.34	−0.45	−0.3
LNM-125		19.074	15.691	39.160	−0.13	−0.18	−0.16	−0.9
LNM-13	Sphalerite							0.6
LNM-14								0.5
LNM-26								−0.4
LNM-116								−0.5
LNM-124								−0.7
LNM-9	Robinsonite							−0.6
LNM-26								−0.3
LNM-27								−0.4
LNM-117								−1.6
LNM-124								−1.0

6. Discussion

6.1. Interpretation and Implications of Zn Isotopic Data

6.1.1. Mechanisms of Zn Isotope Variations

Previous studies have demonstrated that, in hydrothermal deposits, variations in $\delta^{66}\text{Zn}$ are mainly controlled by four factors: (1) temperature effects, (2) mixing of different Zn sources, (3) Zn isotopic fractionation between co-existing mineral pairs, and (4) kinetic Rayleigh fractionation [34,35]. Previous fluid inclusion data indicates that sphalerite at the Lanuoma deposit formed at temperatures between $\sim 153^\circ\text{C}$ and 250°C (average $\sim 189^\circ\text{C}$) [14]. These temperatures are within the low to moderate temperature range ($60\text{--}250^\circ\text{C}$) of natural hydrothermal systems where Zn isotope fractionation has been shown to be largely independent of temperature [36,37]. Therefore, the $\delta^{66}\text{Zn}$ variations in Lanuoma sphalerite are unlikely to be controlled by temperature. Rayleigh distillation process can produce significant Zn isotope fractionation in sphalerite within a single deposit (up to 0.84‰), and the process will result in progressively higher $\delta^{66}\text{Zn}$ values in later-formed sphalerite, as lighter Zn isotopes (^{64}Zn) are preferentially incorporated into earlier precipitates, leaving the fluid enriched in $\delta^{66}\text{Zn}$ [38,39]. In the Lanuoma deposit, sphalerite samples have a narrow range of Zn isotopic compositions, with $\delta^{66}\text{Zn}$ values ranging from -0.31‰ to -0.12‰ (Figure 6). This limited range does not support a Rayleigh fractionation-dominated mechanism for Zn isotope variation. Such homogeneous Zn isotopic compositions have also been reported in other Pb–Zn deposits, including the Navan Pb–Zn deposit (sample D2, D5; $\delta^{66}\text{Zn} = 0.14\text{‰}$ to $+0.20\text{‰}$) in Ireland, the Alexandrinka VHMS-type deposit ($\delta^{66}\text{Zn} = -0.027\text{‰}$ to $+0.231\text{‰}$) in the Urals, Russia, the MVT-type Maozu deposit ($\delta^{66}\text{Zn} = -0.06\text{‰}$ to $+0.23\text{‰}$) and the magmatic-hydrothermal Zhaxikang deposit ($\delta^{66}\text{Zn} = 0.03\text{‰}$ to $+0.28\text{‰}$) in southwestern China [40–43]. The

Zn isotope fractionation mechanisms in these deposits likewise do not favor Rayleigh-type processes.

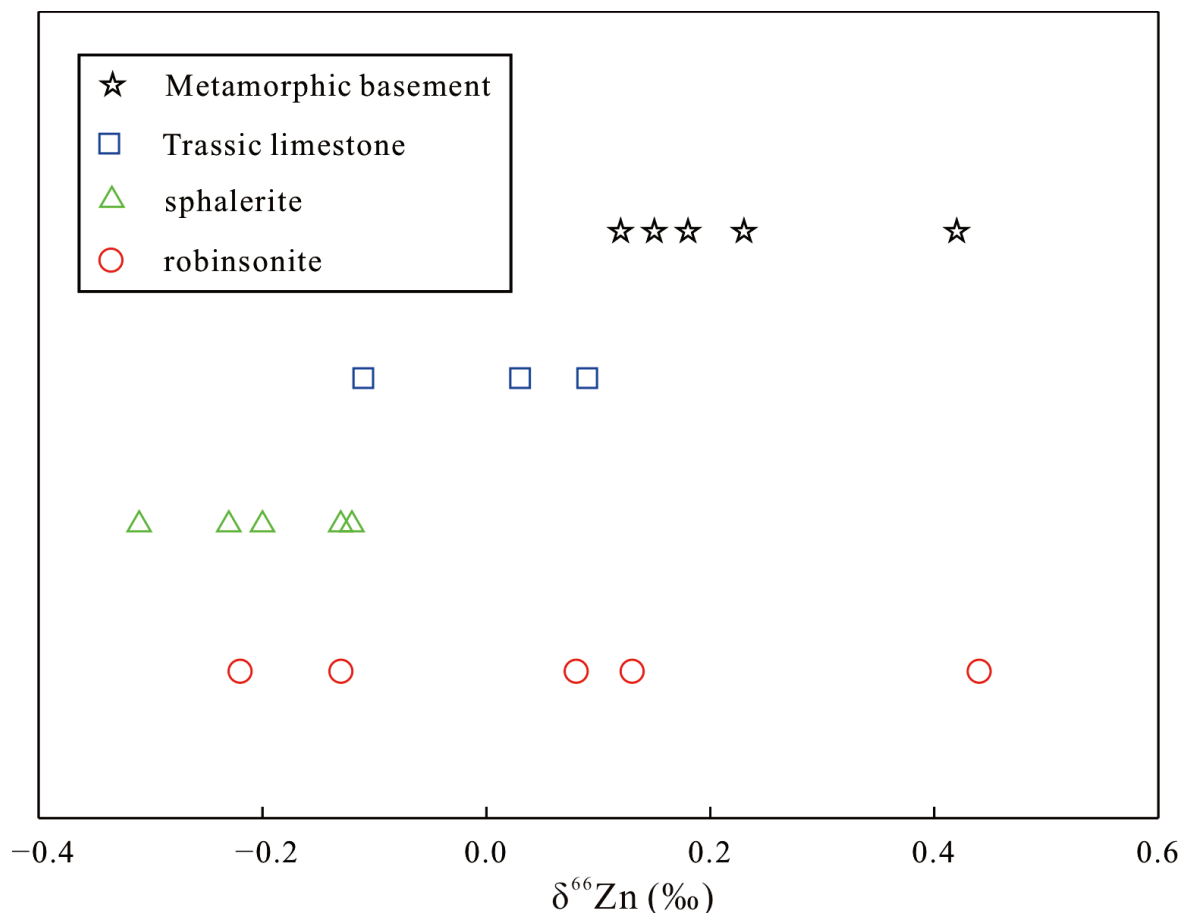


Figure 6. The $\delta^{66}\text{Zn}$ values of sphalerite and robinsonite samples from the Lanuoma deposit, as well as the ore-hosting strata and metamorphic basement.

The homogeneity of Zn isotopes in sphalerite from the Lanuoma deposit is attributed to near-equilibrium isotope partitioning between sphalerite and the hydrothermal fluid during precipitation under relatively closed and stable physicochemical conditions, which allowed extensive mineral-fluid isotopic exchange [17,42]. Fluid inclusion and ore texture studies indicate that sphalerite precipitation was triggered by isothermal mixing of different fluids, resulting in a relatively slow temperature decrease. Consequently, sphalerite grew slowly, forming coarse euhedral to subhedral crystals (Figure 4b) and lacking colloform, framboidal, brecciated, and fragmented textures typically associated with rapid or non-equilibrium precipitation [41,43]. These features support the conclusion that Zn isotope fractionation between the ore-forming fluid and sphalerite approached isotopic equilibrium. This mechanism is consistent with that of the Zhaxikang Pb–Zn deposit, where a stable fractionation relative to the Zn source is maintained [42].

Petrographic observations indicate that although robinsonite commonly coexists with sphalerite, it locally replaces sphalerite, suggesting that robinsonite formed later (Figure 4b). The coexisting robinsonite exhibits relatively large Zn isotope fractionation, with $\delta^{66}\text{Zn}$ values ranging from -0.22‰ to $+0.44\text{‰}$ (mean = $+0.06\text{‰}$), substantially higher than those of sphalerite (-0.31‰ to -0.12‰ , mean = -0.20‰), indicating isotopic fractionation between these coexisting sulfide phases (Table 1 and Figure 6). The overall pattern appears consistent with a Rayleigh fractionation model, in which later-formed minerals are expected to have heavier $\delta^{66}\text{Zn}$ values. However, the occurrence of both heavier and lighter $\delta^{66}\text{Zn}$

values in robinsonite and some robinsonite samples having $\delta^{66}\text{Zn}$ values even lighter than the associated sphalerite, indicate that isotopic equilibrium was not consistently maintained during its formation. The high variability in robinsonite is best explained by a combination of processes, including partial Rayleigh fractionation, kinetic effects linked to rapid or localized precipitation, and mixing of Zn from sources with distinct isotopic compositions [40,41].

6.1.2. Sources of Zn

To trace the source of Zn in sphalerite, it is essential to reconstruct the original Zn isotopic composition of the ore-forming fluid for comparison with potential Zn sources [20,36,42,44–46]. As discussed above, the Zn isotope partitioning between sphalerite and the hydrothermal fluid in the Lanuoma deposit reflects near-equilibrium processes. Therefore, we apply a +0.2‰ equilibrium fractionation factor [17] to the measured $\delta^{66}\text{Zn}$ values of sphalerite to estimate the $\delta^{66}\text{Zn}$ of the original hydrothermal fluid and thereby trace the Zn source more accurately. The inferred $\delta^{66}\text{Zn}$ values of the ore-forming fluid range from −0.11‰ to +0.08‰, with a mean close to ~0.00‰. These values closely match the $\delta^{66}\text{Zn}$ composition of the Triassic limestone (−0.11‰ to +0.09‰, mean = +0.00‰), but differ from metamorphic rocks (0.12‰~0.42‰, mean = +0.22‰), suggesting that Zn in sphalerite was predominantly sourced from the Triassic limestone through fluid–rock interaction. In contrast, robinsonite exhibits a much broader $\delta^{66}\text{Zn}$ range from −0.22‰ to +0.44‰ (mean $\approx$ +0.06‰), overlapping not only with sphalerite but also with both the Triassic limestone and the Precambrian schist ($\delta^{66}\text{Zn}$ = 0.12‰~0.42‰, mean $\approx$ +0.22‰) (Figure 6). This wide isotopic distribution indicates that robinsonite did not simply inherit the Zn isotope signature of a single, uniform source, but a mixture of the Triassic limestone and the Precambrian schist.

6.2. Sources of Pb

The Pb isotopic compositions of ore-hosting sedimentary strata from different sedimentary basins in the SMB were well constrained (see references in Figure 7 caption). Lead isotopes from the Yushu Basin in the north, the Changdu Basin in the central region, and the Lanping Basin in the south of the SMB exhibit some Pb isotope variation but partially overlap with each other (Figure 7). This indicates that regional heterogeneity of Pb isotopic compositions exists within the ore-hosting sedimentary strata of the SMB. The Pb isotopes of sphalerites overlap with the ore-hosting sedimentary strata in the Changdu Basin, suggesting a common source. Robinsonite, however, has large variations of Pb isotopic composition characterized by two end-members, one with low- and the other with high-radiogenic Pb content. The low-radiogenic Pb composition suggests a similar source as the sedimentary rocks in the region, whereas high-radiogenic Pb composition displays no affinity with any known sedimentary Pb reservoirs, indicating incorporation of an additional external Pb source (Figure 7).

In a plot of $^{206}\text{Pb}/^{204}\text{Pb}$ - $\delta^{66}\text{Zn}$ (Figure 8), a linear relation exists between the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio and $\delta^{66}\text{Zn}$ values of sphalerite and robinsonite ($R^2 = 0.66$). This indicates Pb and Zn have the same source. Both $\delta^{66}\text{Zn}$ and Pb isotope compositions of sphalerite indicate that Zn and Pb originated from sedimentary rocks, whereas the $\delta^{66}\text{Zn}$ of robinsonite shows the source of Zn is a mixture of sedimentary rocks and metamorphic basement. Thus, Pb in robinsonite is also derived from mixture of sedimentary rocks and metamorphic basement. The area in Figure 7 where robinsonites with high-radiogenic lead composition plot indicate metamorphic basement origin. This perspective is further supported by Hg isotopes from the Lanuoma deposit (Figure 9), where the Hg in sphalerite

indicates sourcing from sedimentary rocks and the Hg in robinsonites has a stronger input from the metamorphic basement (Figure 9).

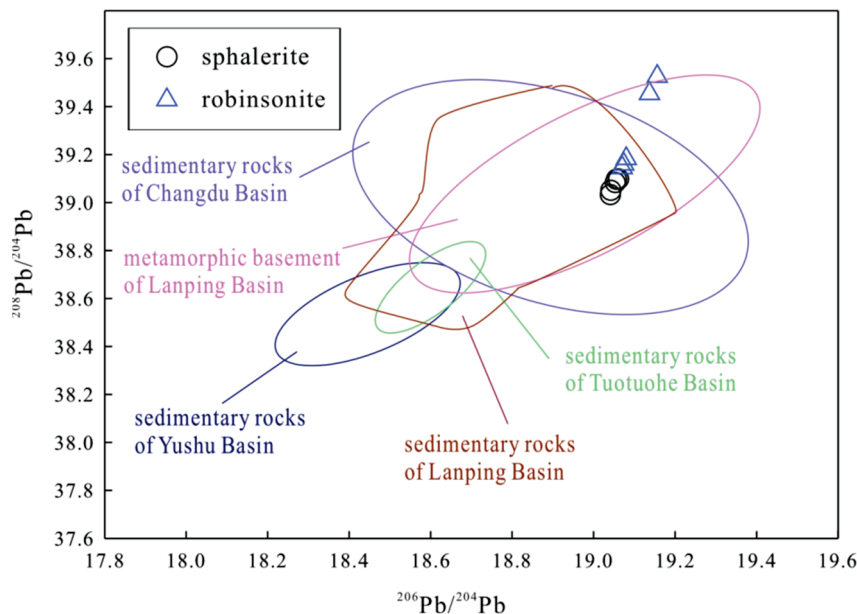


Figure 7. Plot of $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ of sphalerite and robinsonite samples from the Lanuoma deposit. Data of the bulk rock Pb isotopic compositions of the sedimentary rocks in the Yushan Basin and Tuotuohe Basin are from [47,48], in Changdu Basin are from [49,50]. Data of the bulk rock Pb isotopic compositions of the sedimentary rocks and metamorphic basement of Lanping Basin are from [51–54].

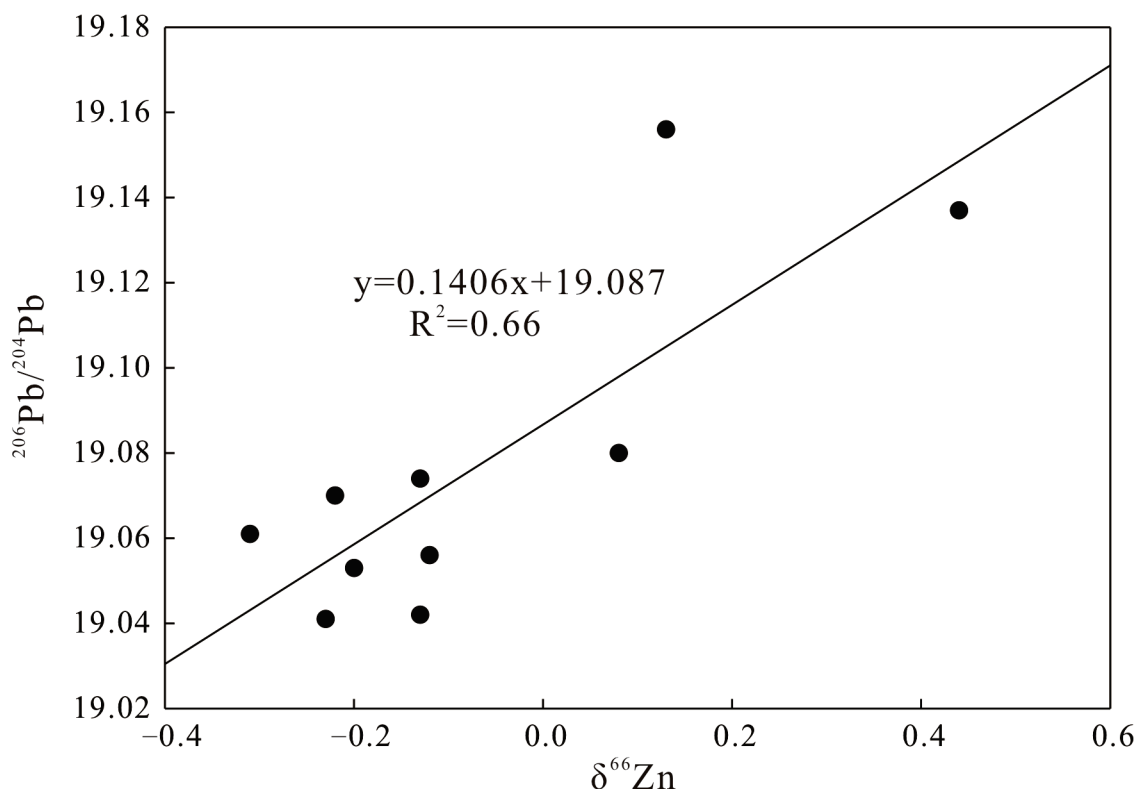


Figure 8. Plots of $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $\delta^{66}\text{Zn}$ in sphalerite and robinsonite samples from the Lanuoma deposit.

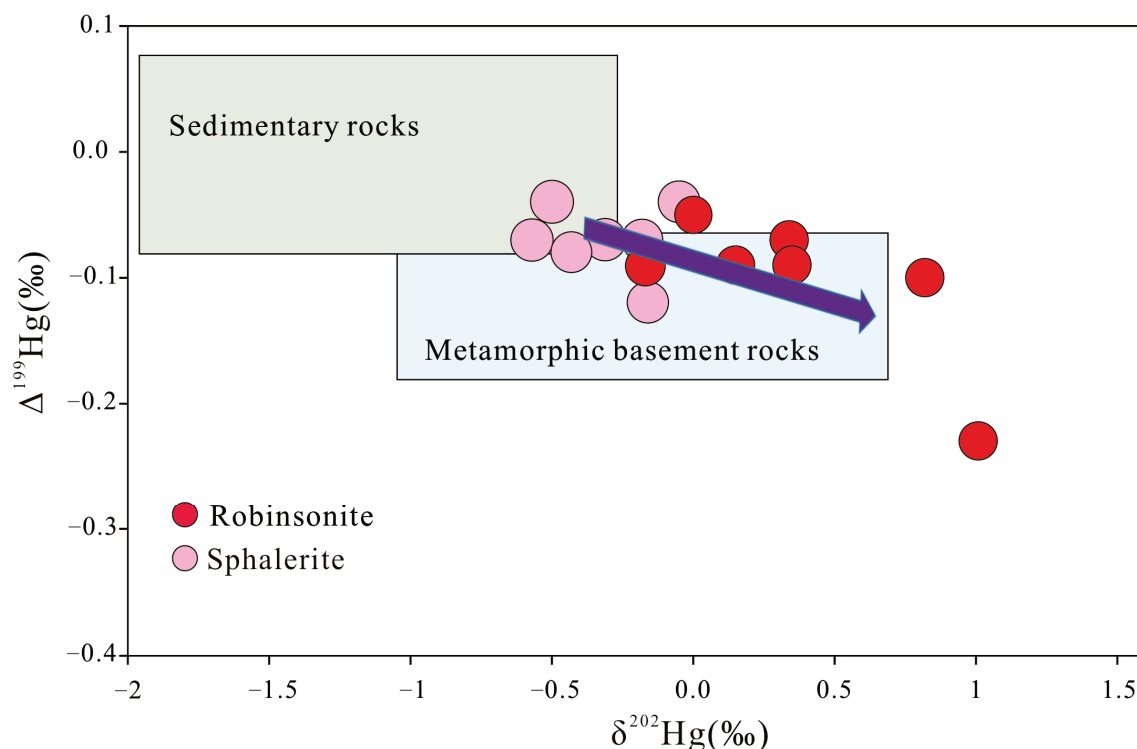


Figure 9. Plots of $\Delta^{199}\text{Hg}$ vs. $\delta^{202}\text{Hg}$ for sphalerite and robinsonite samples from the Lanuoma deposit (Modified after [17]). The purple arrow indicates a mixing trend from a sedimentary rock source toward a stronger contribution from the metamorphic basement.

6.3. Distinct Source of S

Sulfur in hydrothermal deposits is derived from three sources: (1) deep source, either from mantle or compositionally homogeneous deep crust with sulfur isotope compositions consistent with meteorite ($\delta^{34}\text{S}_{\Sigma\text{S}} -2\text{‰} \sim 2\text{‰}$); (2) sea water or marine evaporites, $\delta^{34}\text{S}_{\Sigma\text{S}}$ higher than 15‰; (3) biogenic sulfur, showing non-equilibrium sulfur isotope effect with the $\delta^{34}\text{S}_{\Sigma\text{S}}$ values varying significantly due to intensity of biological effect and open or closed system of SO_4^{2-} , H_2S [55,56].

To trace sulfur sources in hydrothermal deposits, $\delta^{34}\text{S}_{\Sigma\text{S-fluid}}$ needs to be calculated to determine the sulfur origin. The values of $\delta^{34}\text{S}_{\Sigma\text{S-fluid}}$ depend on the $f\text{O}_2$, pH, temperature, types of sulfur-bearing species and ionic strength of the solution [55,56]. The mineral assemblage in the Lanuoma deposit is sphalerite, robinsonite, orpiment and galena. No sulfate mineral coexists with these sulfides indicating a low oxygen fugacity and low pH environment. In addition, thermometry of fluid inclusions in sphalerite shows ore-forming temperature is $\sim 190^\circ\text{C}$ [14]. Based on the Ohmoto model, the $\delta^{34}\text{S}$ values of the sulfides are therefore representative of the sulfur isotope compositions of the hydrothermal fluid ($\delta^{34}\text{S}_{\Sigma\text{S-fluid}}$) [33,56].

The $\delta^{34}\text{S}$ values of sphalerite and robinsonite are fairly homogenous ($-1.4 \sim 2.6$, average -0.1‰), clustering around 0‰ and exhibiting a relatively normal distribution (Figure 10). Therefore, we can consider the $\delta^{34}\text{S}_{\Sigma\text{S-fluid}}$ value to be $\sim 0\text{‰}$, reflecting that the sulfur in the hydrothermal fluid originated from a deep-seated magmatic fluid. Xu et al. (2025) [14] conducted fluid inclusion, rare earth element, and C–O–Sr–Nd isotope studies on the Lanuoma deposit. Their results indicate that the Pb–Zn mineralization was formed through the isothermal mixing of two distinct sources of ore-forming fluids: a low-salinity magmatic fluid and a high-salinity brine [14]. The former carried reducing sulfur, whereas the latter was enriched in metals. The validity of the conclusion that sulfur and Zn–Pb

have different sources can be further assessed by examining the interrelationship among Zn, Pb, and S isotopes [21,38,41,45,57].

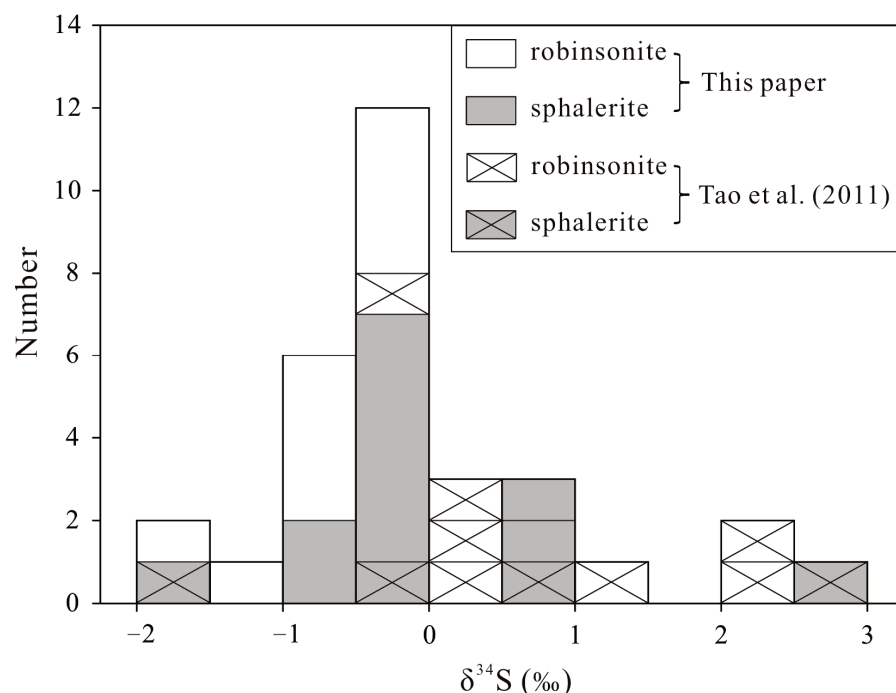


Figure 10. Histogram of $\delta^{34}\text{S}$ values of sulfides from the Lanuoma deposit. Data from this study are compared with reference data from Tao et al. (2011) [26].

Previous studies have shown that a positive correlation between $\delta^{66}\text{Zn}$ and $\delta^{34}\text{S}$ can reflect a common source. Both $\delta^{66}\text{Zn}$ and $\delta^{34}\text{S}$ values increase due to kinetic Rayleigh fractionation during long-distance migration of ore-forming fluids or long-periods of ore precipitation [21,45]. A negative correlation between $\delta^{66}\text{Zn}$ and $\delta^{34}\text{S}$ is attributed to preferential precipitation of ^{34}S in the early stages at the bottom of the hydrothermal system, where Zn and S share a common source [39]. In contrast, the absence of a linear relationship between $\delta^{66}\text{Zn}$ and $\delta^{34}\text{S}$ may reflect either mixing of zinc derived from two distinct sources in which sulfur and zinc underwent different fractionation processes [57], or the mixing of Pb- and S-bearing fluids with different origins, resulting in decoupled $\delta^{66}\text{Zn}$ and $\delta^{34}\text{S}$ values [37,38,43]. A lack of a linear relationship between $^{206}\text{Pb}/^{204}\text{Pb}$ and $\delta^{34}\text{S}$ also suggests mixing of Zn- and S-bearing fluids [21].

In the Lanuoma deposit, both $\delta^{66}\text{Zn}$ vs. $\delta^{34}\text{S}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $\delta^{34}\text{S}$ from the Lanuoma deposit show no significant correlation, with R^2 values of 0.05 (Figure 11a) and 0.07 (Figure 11b), respectively. Since the Zn and Pb isotope data indicate a common metal source, while fluid inclusions, trace element compositions, and C–O–Sr–Nd isotopic data collectively point toward the involvement of two types of mineralizing fluids [14], it is proposed that the Lanuoma deposit formed through the mixing of a magmatic fluid carrying reducing sulfur with metal-rich brines.

The occurrence of robinsonite ($\text{Pb}_4\text{Sb}_6\text{S}_{13}$), a rare Pb–Sb sulfosalt, provides an additional mineralogical constraint on the redox state and fluid evolution at Lanuoma. Robinsonite commonly occurs intergrown with, or locally replacing, sphalerite, which indicates that it formed during a relatively late phase of the main mineralization stage under more reduced and Sb-enriched conditions than those prevailing during early sphalerite deposition. On this basis, we infer that Sb enrichment represents a superimposed component in the ore-forming system. However, the present dataset does not allow determination of the Sb reservoir. The antimony could have been supplied by variable contributions from the

metal-bearing basinal brines, interaction with deeper lithologies along the fluid pathway, and/or episodic input of Sb-bearing fluids during structural reactivation. In addition, the characteristic mineral assemblage of sphalerite + robinsonite with late orpiment–realgar is consistent with reduced, sulfur-rich conditions at low to moderate temperatures, supporting a fluid-mixing scenario rather than purely sedimentary diagenesis. These mineralogical observations link the isotopic decoupling between metals (Zn–Pb) and sulfur ($\delta^{34}\text{S}$) to evolving physicochemical conditions during mineralization, and they provide a mineral-based framework for the metallogenic process and mineralization model discussed below.

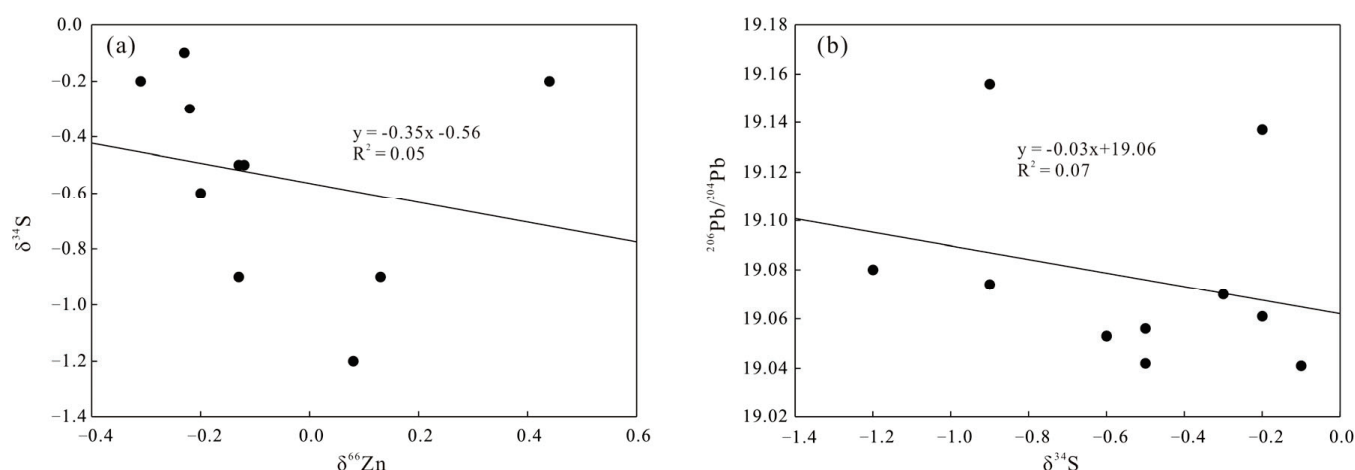


Figure 11. Plots of $\delta^{66}\text{Zn}$ vs. $\delta^{34}\text{S}$ (a) and $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $\delta^{34}\text{S}$ (b) in sphalerite and robinsonite samples from the Lanuoma deposit.

6.4. Metallogenic Process and Mineralization Model of the Lanuoma Deposit

During Cenozoic tectonic compression and basin evolution, basinal brines circulated through the Triassic carbonate strata and underlying metamorphic basement, leaching Pb and Zn from these lithologies. These metal-bearing brines migrated along fault zones and fracture networks within the Bolila Formation.

Concurrently, deep-seated magmatic fluids ascended along regional structures and supplied reduced sulfur, as indicated by the homogeneous $\delta^{34}\text{S}$ values of sulfides clustering around 0‰. The lack of correlation between sulfur and metal isotopic systems suggests that sulfur and metals were derived from distinct reservoirs. Isothermal mixing between metal-rich basinal brines and sulfur-rich magmatic fluids, within structurally prepared sites, triggered sulfide precipitation through sulfidation reactions. This led to the formation of sphalerite, galena, and robinsonite during the main mineralization stage.

Mineralization at Lanuoma is characterized predominantly by open-space filling, with minor replacement of host limestone, and is structurally controlled by faults and breccia zones. This mineralization mode reflects a hybrid system involving basin-derived metals and deep-sourced sulfur, representing a transitional type between classic MVT deposits and sediment-hosted systems influenced by deep-sourced fluids within the Sanjiang metallogenic belt.

From a genetic and classification perspective, the Lanuoma Pb–Zn–Sb mineralization exhibits features that are transitional between sediment-hosted Pb–Zn systems and Pb–Sb sulfosalt-bearing deposits. The occurrence of robinsonite as a late-stage mineral, together with its close association with sphalerite and evidence for highly reduced, Sb-enriched fluids, indicates that antimony was introduced during a superimposed mineralization stage rather than forming a primary Sb vein-type system. According to the evolutionary models and classification schemes of Sb and Pb–Sb mineralization proposed by Dill (1998), Dill et al. (2008), and Dill and Berner (2014) [58–60], such deposits are best interpreted as

structurally controlled, sediment-hosted base-metal systems with late-stage Sb enrichment, commonly related to fluid mixing and tectonic reactivation [61]. Within broader genetic classification frameworks of economic geology, the Lanuoma deposit is therefore classified as a sediment-hosted Pb–Zn deposit with superimposed Sb mineralization, rather than a typical primary Sb-dominated deposit.

7. Conclusions

(1) The ore-forming fluid that precipitated sphalerite has $\delta^{66}\text{Zn}$ values that correspond closely to the Triassic limestone, suggesting that Zn was mainly leached from sedimentary rocks. The $\delta^{66}\text{Zn}$ values of robinsonite imply Zn contributions from both sedimentary and metamorphic sources.

(2) Homogeneous Pb isotopic compositions in sphalerite are indicative of a sedimentary source, indicating Pb source from these rocks. In contrast, robinsonite displays variable Pb isotopes forming a mixing trend between low-radiogenic and high-radiogenic end-members, reflecting mixed inputs from sedimentary strata and metamorphic basement.

(3) The $\delta^{34}\text{S}$ values of sphalerite and robinsonite are narrowly distributed around 0‰, signifying that sulfur in the ore-forming fluids originated predominantly from magmatic fluids carrying reduced sulfur. The lack of correlation between $\delta^{34}\text{S}$ and $\delta^{66}\text{Zn}$ or $^{206}\text{Pb}/^{204}\text{Pb}$ suggests distinct sources for metals and reducing sulfur, further indicating mixing of magmatic sulfur-bearing fluids with metal-rich sedimentary brines. Such fluid mixing accounts for Pb–Zn deposition and the multi-source isotopic signatures.

(4) Integrated isotopic, mineralogical, and geological evidence indicates that Pb–Zn mineralization at the Lanuoma deposit was controlled by structurally focused mixing between metal-rich basinal brines and sulfur-rich magmatic fluids. Sulfide precipitation occurred predominantly through open-space filling, with subordinate replacement of the carbonate host rocks. This mineralization style represents a hybrid system involving basin-derived metals and deep-sourced sulfur, providing a genetic link between sediment-hosted Pb–Zn deposits and magmatic–hydrothermal processes in the Sanjiang metallogenic belt.

Author Contributions: Conceptualization, C.X. and J.P.; methodology, C.X. and J.G.; software, C.X. and J.G.; validation, C.X., J.G. and C.T.; formal analysis, C.X. and J.P.; investigation, C.X., J.G., C.T., Z.Y.; resources, C.X. and J.P.; data curation, C.X. and Z.Y.; writing—original draft preparation, C.X. and J.P.; writing—review and editing, C.X., J.P. and C.H.; supervision, J.P.; project administration, C.X. and J.P.; funding acquisition, C.X., J.P. and J.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key Basic Research Program of China (2015CB452603), the Natural Science Foundation of Jiangxi Province (20224BAB203043), and the National Natural Science Foundation of China (42162025).

Data Availability Statement: All the research data related to this paper have been listed in the manuscript.

Acknowledgments: We gratefully acknowledge Heng Chen from Columbia University for his assistance with Zn isotopic analyses. Ryan Sharpe from the University of Manitoba and Zhiqian Li from Lakehead University are greatly appreciated for their valuable suggestions and language polishing. Special thanks to two anonymous reviewers for their constructive comments and significant help in improving the manuscript.

Conflicts of Interest: The author declares no conflicts of interest.

References

- Deng, J.; Wang, Q.F.; Li, G.J.; Santosh, M. Cenozoic tectono-magmatic and metallogenic processes in the Sanjiang region, southwestern China. *Earth-Sci. Rev.* **2014**, *138*, 268–299. [CrossRef]
- Song, Y.C.; Liu, Y.C.; Hou, Z.Q.; Fard, M.; Zhang, H.R.; Zhuang, L.L. Sediment-hosted Pb–Zn deposits in the Tethyan domain from China to Iran: Characteristics, tectonic setting, and ore controls. *Gondwana Res.* **2019**, *75*, 249–281. [CrossRef]
- Bi, X.W.; Tang, Y.Y.; Tao, Y.; Wang, C.M.; Xu, L.L.; Qi, H.W.; Lan, Q.; Mu, L. Composite metallogenesis of sediment-hosted Pb–Zn–Ag–Cu base metal deposits in the Sanjiang collisional orogen, SW China, and its deep driving mechanisms. *Acta Petrol. Sin.* **2019**, *35*, 1341–1371.
- Tang, J.X.; Zhong, K.H.; Liu, Z.C.; Li, Z.J.; Dong, S.Y.; Zhang, L. Intracontinent orogen and metallogenesis in Himalayan epoch, Changdu large composite basin, Eastern Tibet. *Acta Geol. Sin.* **2006**, *80*, 1364–1376.
- Liu, Y.C.; Yang, Z.M.; Tian, S.H.; Song, Y.C.; Zhang, H.R. Fluid origin of fluorite-rich carbonate-hosted Pb–Zn mineralization of the Himalayan–Zagros collisional orogenic system: A case study of the Mohailaheng deposit, Tibetan Plateau, China. *Ore Geol. Rev.* **2015**, *70*, 546–561. [CrossRef]
- Tang, Y.Y.; Bi, X.W.; Mostafa, F.; Stuart, F.M.; Wu, L.Y.; Jiang, G.H.; Xu, L.L.; Liang, F. Genesis of the Jinding Zn–Pb deposit, northwest Yunnan Province, China: Constraints from rare earth elements and noble gas isotopes. *Ore Geol. Rev.* **2017**, *90*, 970–986. [CrossRef]
- Liu, Y.F.; Qi, H.W.; Bi, X.W.; Hu, R.Z.; Qi, L.K.; Yin, R.S.; Tang, Y.Y. Mercury and sulfur isotopic composition of sulfides from sediment-hosted lead-zinc deposits in Lanping basin, southwestern China. *Chem. Geol.* **2021**, *559*, 119910. [CrossRef]
- Jia, W.B.; Li, Y.S.; Yan, G.S.; Lv, Z.C.; Yu, X.F. Ore genesis of the Duocaima Pb–Zn deposit, Tuotuohe area, Qinghai Province, China: Evidences from in situ S and Pb isotopes. *Acta Petrol. Sin.* **2018**, *34*, 1285–1298.
- Zhang, H.S.; Ji, W.H.; Yang, X.Y.; Zhou, J.X.; Sun, C.; Jia, Z.Y.; Hong, J.; Lv, P.R.; Zhao, Z.; Hou, Q. The origin of the Quemocuo carbonate-hosted Pb–Zn deposit in the Sanjiang Tethyan Belt, SW China: Constrained by Sm–Nd isochronic age and Sr–S–Pb isotope compositions. *Resour. Geol.* **2020**, *117*, 103264. [CrossRef]
- Tang, Y.Y.; Bi, X.W.; Fayek, M.; Hu, R.Z.; Wu, L.Y.; Zou, Z.C.; Feng, C.X.; Wang, X.S. Microscale sulfur isotopic compositions of sulfide minerals from the Jinding Zn–Pb deposit, Yunnan Province, Southwest China. *Gondwana Res.* **2014**, *26*, 594–607. [CrossRef]
- Xue, C.J.; Zeng, R.; Liu, S.W.; Chi, G.X.; Qing, H.R.; Chen, Y.C.; Yang, J.M.; Wang, D.H. Geologic, fluid inclusion and isotopic characteristics of the Jinding Zn–Pb deposit, western Yunnan, South China: A review. *Ore Geol. Rev.* **2007**, *31*, 337–359. [CrossRef]
- Sheng, X.Y.; Bi, X.W.; Hu, R.Z.; Tang, Y.Y.; Lan, Q.; Xia, J.F.; Tao, Y.; Huang, M.L.; Peng, J.T.; Xu, L.L. The mineralization process of the Lanuoma Pb–Zn–Sb deposit in the Sanjiang Tethys region: Constraints from in situ sulfur isotopes and trace element compositions. *Ore Geol. Rev.* **2019**, *111*, 10294. [CrossRef]
- Liu, Y.C.; Kendrick, M.A.; Hou, Z.Q.; Yang, Z.S.; Tian, S.H.; Song, Y.C.; Honda, M. Hydrothermal fluid origins of carbonate-hosted Pb–Zn deposits of the Sanjiang thrust belt, Tibet: Indications from noble gases and halogens. *Econ. Geol.* **2017**, *112*, 1247–1268. [CrossRef]
- Xu, C.X.; Peng, J.T.; Hu, S.M.; Gan, J.J.; Huang, C. Characterization of ore-forming fluids in the Lanuoma Sediment-Hosted Pb–Zn deposit, Sanjiang Tethys Region, Southwestern China: Evidences from fluid inclusions, rare earth elements, and C–O–Sr–Nd isotopes. *Resour. Geol.* **2025**, *75*, e70013. [CrossRef]
- Xu, C.X.; Yin, R.S.; Peng, J.T.; Hurley, J.P.; Lepak, R.F.; Gao, J.F.; Feng, X.B.; Hu, R.Z.; Bi, X.W. Mercury isotope constraints on the source for sediment-hosted lead-zinc deposits in the Changdu area, southwestern China. *Miner. Depos.* **2018**, *53*, 339–352.
- Wilkinson, J.J. The potential of Zn isotopes in the science and exploration of ore deposits. In *Isotopes in Economic Geology, Metallogenesis and Exploration*; Huston, D., Gutzmer, J., Eds.; Springer International Publishing: Reston, VA, USA, 2023; pp. 451–463.
- Fujii, T.; Moynier, F.; Pons, M.L.; Albarède, F. The origin of Zn isotope fractionation in sulfides. *Geochim. Cosmochim. Acta* **2011**, *75*, 7632–7643. [CrossRef]
- Duan, J.L.; Tang, J.X.; Lin, B. Zinc and lead isotope signatures of the Zhaxikang Pb–Zn deposit, South Tibet: Implications for the source of the ore-forming metals. *Ore Geol. Rev.* **2016**, *78*, 58–68. [CrossRef]
- Qi, Y.Q.; Hu, R.Z.; Fan, H.F.; Zhao, J.H. Zn isotopic variations in ore-related granite and ore minerals in a magmatic-hydrothermal deposit. *Geochim. Cosmochim. Acta* **2025**, *408*, 258–268. [CrossRef]
- Zhu, C.W.; Wang, J.; Zhang, J.W.; Chen, X.C.; Fan, H.F.; Zhang, Y.X.; Yang, T.; Wen, H.J. Isotope geochemistry of Zn, Pb and S in the Ediacaran strata hosted Zn–Pb deposits in Southwest China. *Ore Geol. Rev.* **2020**, *117*, 103274. [CrossRef]
- Xu, C.; Zhong, H.; Hu, R.Z.; Wen, H.J.; Zhu, W.G.; Bai, Z.J.; Zhu, W.G.; Fan, H.F.; Li, F.F.; Zhou, T. Sources and ore-forming fluid pathways of carbonate-hosted Pb–Zn deposits in Southwest China: Implications of Pb–Zn–S–Cd isotopic compositions. *Miner. Depos.* **2020**, *55*, 491–513. [CrossRef]
- Song, Y.C.; Hou, Z.Q.; Liu, Y.C.; Zhuang, L.L.; Hu, G. Mississippi Valley-type Zn–Pb deposits in orogenic thrust belts: Ore formation in response to synorogenic crustal transpression or extension. *Miner. Depos.* **2023**, *58*, 1333–1350. [CrossRef]

23. Liu, C.; Su, J.B. Mississippi valley-type Pb–Zn deposits formed by episodic fluid migration in the fold-and-thrust belts of the Tibetan Plateau. *Ore Geol. Rev.* **2025**, *181*, 106597. [CrossRef]
24. Peng, Y.M.; Wang, M.J.; Chen, M. The Qamdo–Riwoqe Triassic cratonic basin in eastern Xizang, sequence stratigraphy and correlation. *Sedim. Geol. Tethyan Geol.* **2020**, *20*, 62–67.
25. Tao, Y.; Bi, X.W.; Li, C.S.; Hu, R.Z.; Li, Y.B.; Liao, M.Y. Geochronology, petrogenesis and tectonic significance of the Jitang granitic pluton in eastern Tibet, SW China. *Lithos* **2014**, *184*, 314–323. [CrossRef]
26. Tao, Y.; Bi, X.W.; Xin, Z.L.; Zhu, F.L.; Liao, M.Y.; Li, Y.B. Geology, geochemistry and origin of Lanuoma Pb–Zn–Sn deposit in Changdu area, Tibet. *Miner. Depos.* **2011**, *30*, 599–615.
27. Moynier, F.; Albarède, F.; Herzog, G.F. Isotopic composition of zinc, copper, and iron in lunar samples. *Geochim. Cosmochim. Acta* **2006**, *70*, 6103–6117. [CrossRef]
28. Chen, H.; Savage, P.S.; Teng, F.Z.; Helz, R.T.; Moynier, F. Zinc isotope fractionation during magmatic differentiation and the isotopic composition of the bulk Earth. *Earth Planet. Sci. Lett.* **2013**, *369–370*, 34–42. [CrossRef]
29. Paniello, R.C.; Moynier, F.; Beck, P.; Barrat, J.A.; Podosek, F.A.; Pichat, S. Zinc isotopes in HEDs: Clues to the formation of 4–Vesta, and the unique composition of Pecora Escarpment 82502. *Geochim. Cosmochim. Acta* **2012**, *86*, 76–87. [CrossRef]
30. Ueda, A.; Sakai, H. Sulfur isotope study of Quaternary volcanic rocks from the Japanese Islands Arc. *Geochim. Cosmochim. Acta* **1984**, *48*, 1837–1848. [CrossRef]
31. Ni, Z.Y.; Chen, Y.J.; Li, N.; Zhang, H. Pb–Sr–Nd isotope constraints on the fluid source of the Dahu Au–Mo deposit in Qinling Orogen, central China, and implication for Triassic tectonic setting. *Ore Geol. Rev.* **2012**, *46*, 60–67. [CrossRef]
32. Todt, W.; Cliff, R.A.; Hanser, A.; Hofmann, A.W. Evaluation of a ^{205}Pb – ^{202}Pb double spike for high-precision lead isotopic analysis. In *Earth Processes: Reading the Isotopic Code*; Basu, A., Hart, S.R., Eds.; American Geophysical Union: Washington, DC, USA, 1996; pp. 429–437.
33. Seal, R.R. Sulfur isotope geochemistry of sulfide minerals. *Rev. Miner. Geochem.* **2006**, *61*, 633–677. [CrossRef]
34. Zhang, H.; Zhou, J.X.; Zhou, M.F.; Yue, Z.P.; He, Y. Zinc isotopes revealed the role of ore-hosting carbonate rocks in the formation of MVT deposits: A case study of the Huize Pb–Zn deposit, SW China. *J. Geochem. Explor.* **2024**, *258*, 107396. [CrossRef]
35. Ma, H.C.; Wang, D.; Mathur, R.; Wang, G.T.; Bai, F. Zinc and cadmium isotope signatures: Insights into ore genesis and exploration strategies at the Xiaohongshilazi Pb–Zn–(Ag) deposit, northeast China. *Geosci. Front.* **2025**, *16*, 102054. [CrossRef]
36. Maréchal, C.; Albarède, F. Ion-exchange fractionation of copper and zinc isotopes. *Geochim. Cosmochim. Acta* **2002**, *66*, 1499–1509. [CrossRef]
37. Wilkinson, J.J.; Weiss, D.J.; Mason, T.F.D.; Coles, B.J. Zinc isotope variation in hydrothermal systems: Preliminary evidence from the Irish Midlands ore field. *Econ. Geol.* **2005**, *100*, 583–590. [CrossRef]
38. Kelley, K.D.; Wilkinson, J.J.; Chapman, J.B.; Crowther, H.L.; Weiss, D.J. Zinc isotopes in sphalerite from base metal deposits in the red dog district, northern Alaska. *Econ. Geol.* **2009**, *104*, 767–773. [CrossRef]
39. Zhou, J.X.; Huang, Z.L.; Zhou, M.F.; Zhu, X.K.; Muchez, P. Zinc, sulfur and lead isotopic variations in carbonate-hosted Pb–Zn sulfide deposits, southwest China. *Ore Geol. Rev.* **2014**, *58*, 41–54. [CrossRef]
40. Mason, T.F.D.; Weiss, D.J.; Chapman, J.B.; Wilkinson, J.J.; Tessalina, S.G.; Spiro, B.; Matthew, S.A.; Spratt, J.; Coles, B.J. Zn and Cu isotopic variability in the Alexandrinka volcanic-hosted massive sulphide (VHMS) ore deposit, Urals, Russia. *Chem. Geol.* **2005**, *221*, 170–187. [CrossRef]
41. Gagnevin, D.; Boyce, A.J.; Barrie, C.D.; Menuge, J.F.; Blakeman, R.J. Zn, Fe and S isotope fractionation in a large hydrothermal system. *Geochim. Cosmochim. Acta* **2012**, *88*, 183–198. [CrossRef]
42. Deng, J.; Wang, C.M.; Bagas, L.; Selvaraja, V.; Jeon, H.; Wu, B.; Yang, L.F. Insights into ore genesis of the Jinding Zn–Pb deposit, Yunnan Province, China: Evidence from Zn and in-situ S isotopes. *Ore Geol. Rev.* **2017**, *90*, 943–957. [CrossRef]
43. Zhang, H.J.; Xiao, C.Y.; Wen, H.J.; Zhu, X.K.; Ye, L.; Huang, Z.L.; Zhou, J.X.; Fan, H.F. Homogeneous Zn isotopic compositions in the Maozu Zn–Pb ore deposit in Yunnan Province, southwestern China. *Ore Geol. Rev.* **2019**, *109*, 1–10. [CrossRef]
44. Gao, Z.F.; Zhu, X.K.; Sun, J.; Luo, Z.H.; Bao, C.; Tang, C.; Ma, J.X. Spatial evolution of Zn–Fe–Pb isotopes of sphalerite within a single ore body: A case study from the Dongshengmiao ore deposit, Inner Mongolia, China. *Miner. Depos.* **2018**, *53*, 55–65. [CrossRef]
45. Zhu, C.W.; Liao, S.L.; Wang, W.; Zhang, Y.X.; Yang, T.; Fan, H.F.; Wen, H.J. Variations in Zn and S isotope chemistry of sedimentary sphalerite, Wusihe Zn–Pb deposit, Sichuan Province, China. *Ore Geol. Rev.* **2018**, *95*, 639–648. [CrossRef]
46. Chen, J.; Zhao, Y.; Xue, C.J.; Brzozowski, M.J.; Jing, G. Zinc isotopes trace the metal source and fluid flow pathways of the large Caixiashan Pb–Zn deposit, China. *Ore Geol. Rev.* **2025**, *176*, 106389. [CrossRef]
47. Tian, S.H.; Yang, Z.S.; Hou, Z.Q.; Liu, Y.C.; Song, Y.C.; Wang, F.C.; Xue, W.W. Sulfur, lead, strontium and neodymium isotope compositions of the Dongmohazhua lead-zinc ore deposit in the Yushu area, southern Qinghai: Implications for the sources of ore-forming material in the deposit. *Acta Petrol. Sin.* **2011**, *27*, 2173–2183.
48. Liu, Y.C. Characteristics and Metallogenic Genesis of the Carbonate-Hosted Lead-Zinc Deposits in the Middle Part of Sanjiang Area, Tibetan Plateau. Ph.D. Thesis, Chinese Academy of Geological Sciences, Beijing, China, 2012.

49. Liu, Y.C.; Hou, Z.Q.; Yu, Y.S.; Tian, S.H.; Li, Y.L.; Yang, Z.S. Characteristics and genesis of Lalongla MVT-like deposit in Changdu region, Tibet. *Acta Petrol. Sin.* **2013**, *29*, 1407–1426.
50. Liu, X.P.; Zhou, L.S.; You, J.; Li, S.Y.; Liu, R. Genesis of the Waliaoge Pb-Ag deposit in Qamdo City, Tibet, China: Constraints from ore deposit geology, fluid inclusions, and isotope geochemistry. *Acta Miner. Sin.* **2020**, *40*, 223–236.
51. Zhao, X. Stable isotope geochemistry of the Jinding lead-zinc ore deposit, Yunnan. *Earth Sci.* **1989**, *14*, 495–502.
52. Luo, J.L.; Yang, Y.H.; Zhao, Z.; Chen, J.S.; Yang, J.Z. *Evolution of the Tethys in Western Yunnan and Mineralization for Main Metal Deposits*; Geological Publishing Press: Beijing, China, 1994; pp. 157–215.
53. Zhang, Q.; Liu, J.J.; Shao, S.X.; Liu, Z.H. An estimate of the lead isotopic compositions of upper mantle and upper crust and implications for the source of lead in the Jinding Pb-Zn deposit in Western Yunnan, China. *Geochem. J.* **2002**, *36*, 271–287. [CrossRef]
54. Wang, G.H. A Genetic Study on the Jinman-Liancheng Vein Cu Deposits in the Northwestern Yunnan. Master's Thesis, Kunming University of Science and Technology, Kunming, China, 2010.
55. Ohmoto, H. Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. *Econ. Geol.* **1972**, *67*, 551–578. [CrossRef]
56. Ohmoto, H.; Rye, R.O. Isotopes of sulfur and carbon. In *Geochemistry of Hydrothermal Ore Deposits*, 2nd ed.; Barnes, H.L., Ed.; Wiley: New York, NY, USA, 1979; pp. 509–567.
57. Pašava, J.; Tornos, F.; Chrastný, V. Zinc and sulfur isotope variation in sphalerite from carbonate-hosted zinc deposits, Cantabria, Spain. *Miner. Depos.* **2014**, *49*, 797–807. [CrossRef]
58. Dill, H.G.; Melcher, F.; Botz, R. Meso- to epithermal W-bearing Sb vein-type deposits in calcareous rocks in western Thailand; with special reference to their metallogenetic position in SE Asia. *Ore Geol. Rev.* **2008**, *34*, 242–262. [CrossRef]
59. Dill, H.G. Evolution of Sb mineralisation in modern fold belts: A comparison of the Sb mineralisation in the Central Andes (Bolivia) and the Western Carpathians (Slovakia). *Miner. Depos.* **1998**, *33*, 359–378. [CrossRef]
60. Dill, H.G.; Berner, Z.A. Sedimentological and structural processes operative along a metalliferous catena from sandstone-hosted to unconformity-related Pb-Cu-Zn deposits in an epicontinental basin, SE Germany. *Ore Geol. Rev.* **2014**, *63*, 91–114. [CrossRef]
61. Li, Y.; Song, Y.; Tang, J.X.; Chen, W.; Sun, H. Distribution, types and metallogenic regularity of antimony deposits in Tibet. *Geol. China* **2024**, *51*, 1570–1600.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

In Situ Geochemical and Sulfur Isotopic Composition of Pyrites from the Jiepailing Tin–Beryllium Polymetallic Deposit, Southern Hunan Province, China: Implications for Ore-Forming Processes

Gao-Feng Du ^{1,2,3}, Xiang-Ying Ling ⁴, Dan Wang ^{1,2,3,*}, Wei-Jian Zhou ^{1,2,3,*}, Liu Yang ^{1,2,3}, You-Yue Lu ^{5,6} and Zun-Zun Zhang ^{5,6}

¹ Department of Natural Resources, Hunan Vocational College of Engineering, Changsha 410151, China; hbwhtgf2@ustc.edu.cn (G.-F.D.); xuqunhang2000@126.com (L.Y.)

² Hunan Mine Carbon Sequestration and Sink Enhancement Engineering Technology Research Center, Changsha 410151, China

³ Changsha Mining Wasteland Regeneration Technology Innovation Center, Changsha 410151, China

⁴ Geological Exploration Institute of the Seventh Geological Brigade of Jiangxi Geological Bureau, Ganzhou 341000, China; m18296150319@163.com

⁵ Wuhan Center, China Geological Survey (Geosciences Innovation Center of Central South China), Wuhan 430205, China; luyouyue@mail.ustc.edu.cn (Y.-Y.L.)

⁶ Research Center for Petrogenesis and Mineralization of Granitoid Rocks, China Geological Survey, Wuhan 430205, China

* Correspondence: 13875868886@163.com (D.W.); wjzhou2023@163.com (W.-J.Z.)

Abstract: The Jiepailing deposit in southern Hunan is a typical large to super-large polymetallic tin deposit enriched in beryllium and other rare metals. To enhance the understanding of the mineralization processes of the Jiepailing deposit, detailed mineralogical, in situ geochemical, and sulfur isotopic analyses were conducted on pyrite closely associated with tin–polymetallic mineralization. Five types of pyrite have been identified in the deposit: (1) euhedral to subhedral medium- to coarse-grained pyrite (PyI) in tungsten–tin ore; anhedral fine-grained pyrite (PyII) in tin polymetallic–fluorite ore; anhedral fine-grained or aggregate pyrite (PyIII) in lead–zinc ore; euhedral to subhedral coarse-grained pyrite (PyIV) in beryllium–fluorite mineralization; and subhedral to anhedral fine-grained pyrite (PyV) in carbonate veinlets developed in the wall rock. Backscattered electron imaging indicates consistent structural features across the five types of pyrite. In situ trace element analysis reveals differences in trace element concentrations among the pyrite types. PyI is relatively enriched in Sn, Cu, and Co. In contrast, PyIII is enriched in Pb, Zn, Sn, and Ti, while PyIV and PyV are enriched in Ag and Sb. PyI has a Co/Ni ratio more than 1, while the Co/Ni ratios in the other four types of pyrite are less than 1. LA-MC-ICP-MS in situ sulfur isotope analysis shows $\delta^{34}\text{S}$ values ranging from 2.5‰ to 5.8‰ (average 4.3‰, PyI), 2.5‰ to 5.8‰ (average 4.3‰, PyII), −7.6‰ to 9.5‰ (average 3.9‰, PyIII), −3.7‰ to 10.6‰ (average 3.6‰, PyIV), and 6.8‰ to 14.1‰ (average 9.2‰, PyV). Based on previous studies, regional geological background, deposit characteristics, and the in situ trace element and sulfur isotope compositions of pyrite, it is inferred that the various ore bodies in the Jiepailing deposit are products of Late Cretaceous magmatic–hydrothermal activity. The early ore-forming fluid originated from magmatic sources and during the migration into the wall rock and shallow formations, mixed with fluids primarily derived from atmospheric precipitation. Temperature, pressure, and composition changed of the ore-forming fluid which carried a large amount of substances, leading to tungsten–tin, tin polymetallic–fluorite, lead–zinc, and beryllium–fluorite mineralization, followed by carbonation during the late-stage mineralization.

Keywords: Jiepailing tin polymetallic deposit; pyrite; LA-ICP-MS; in situ trace elements; metallogenic process

1. Introduction

The Xiangnan region, part of the Nanling tungsten–tin metallogenic belt, is a significant area for rare metal exploration in Hunan Province [1–6]. There are a series of large to super-large nonferrous metal deposits developed in the area, including Shizhuyuan, Xianghualing, Furong, Huangshaping, Baoshan, Shuikoushan, Yaogangxian, etc. [7–10]. The Jiepailing tin polymetallic deposit, a typical rare element-rich deposit in this area, not only has a large amount of tin, copper, lead, zinc, fluorite mineralization, but also a large-scale beryllium mineralization with a reserve of about 1.027 million tons [11,12], belonging to a super-large deposit. This makes it an ideal subject for discussing the metallogenic mechanisms of metals in the Nanling belt and advancing the understanding of mineral exploration in the region.

Previous studies have extensively examined the geology, petrology, mineralogy, geochronology, and geochemistry of the Jiepailing deposit [13–16]. The mineralization is characterized by four distinct ore types: tungsten–tin ore bodies within fault zones in deep carbonate rocks; quasi-layered tin polymetallic–fluorite ore bodies in the external contact zone of deep granitic porphyry; lead–zinc ore bodies in the contact zone between granitic porphyry and surrounding rocks; and beryllium–fluorite ore bodies within interlayered fractured zones in shallow wall rocks [16]. Beryllium minerals, primarily hydroxyl–hercynite, chrysoberyl, and phenakite, are widespread in the shallow beryllium–fluorite ore bodies and altered host rocks and are typically found along the margins of beryllium-rich muscovite–fluorite veins [13,15]. The granitic porphyry in the district was identified by some researchers as the parent rock for the Jiepailing tin polymetallic mineralization [17,18]. There are 19 granitic porphyry outcrops as dikes in the mining area for observation. Granitic porphyry is light grayish-gray, porphyritic structure, with the phenocryst scales about 0.5–1.5 cm, mainly quartz, potassium feldspar, and plagioclase, and the content of phenocrysts about 30%–55%. The matrix is mainly quartz, feldspar, biotite, etc., and the content is about 45%–70% [17]. Furthermore, the 19 granitic porphyry dikes exposed in the mining area were subcategorized into three phases of magmatic activities according to petrology and interspersed relationship: a giant phenocryst granitic porphyry with intense cryptocrystalline brecciation, a medium-grained granitic porphyry with minor cryptocrystalline breccia, and a plagioclase-rich medium- to fine-grained granitic porphyry. All three phases are enriched in W, Sn, Be, and volatiles such as F and Li, with higher total rare earth elements than other typical granitic intrusions [17,18].

The zircon U–Pb ages of ore-bearing granitic porphyry are 92 ± 1.0 Ma (MSWD = 1.5) and 92 ± 1.6 Ma (MSWD = 1.05) [14,19], while the ^{40}Ar – ^{39}Ar plateau age of biotite in tungsten–tin ore bodies shows that the tin mineralization age is $\sim 91.1 \pm 1.1$ Ma [20], and muscovite ^{40}Ar – ^{39}Ar plateau ages from greisen indicate 92.1 ± 0.7 Ma [11], suggesting that mineralization slightly postdates rock formation. In situ trace element analyses of fluorite show similar Y/Ho ratios across different phases, indicating a consistent source of the mineralizing fluids [18]. Sulfur isotopes of sulfide minerals in shallow beryllium–fluorite ore are within the $\delta^{34}\text{S}$ range of the granitic porphyry, and lead isotopes also resemble those in feldspar from the granitic porphyry, suggesting that the ore-forming materials likely originated from the granitic porphyry [21]. However, the Nb–Ta mineral U–Pb concordant age from deep greisen-type ore is 89 ± 2 Ma, and the similarities between cassiterite, Nb–Ta minerals, and the deep concealed iron–lithium muscovite granite in

terms of microstructure and trace element content suggest a closer genetic relationship between deep tin polymetallic mineralization and the iron–lithium muscovite granite [12]. Therefore, integrating the spatial–temporal and material associations between shallow granitic porphyry and fluorite mineralization implies that the Jiepailing tin polymetallic mineralization is likely a multi-type, multi-stage magmatic–hydrothermal event.

Previous studies show that the element partition of pyrite and other sulfides is affected by different physicochemical conditions and fluid components, which could provide key information of metallogenic process, e.g., source of the ore-forming fluid, fluid evolution, and physicochemical conditions [22–28]. Pyrite is one of the common metal sulfides in the Jiepailing deposit, which is widely distributed in the tungsten–tin, tin polymetallic–fluorite, lead–zinc and beryllium–fluorite ore bodies and even in the carbonate wall rock. Therefore, these types of pyrites provide an ideal research target to probe into the source and evolution of the ore-forming fluids. In the present study, detailed mineralogical and in situ trace element and sulfur isotope analyses were conducted, aiming to provide some insights into the ore-forming conditions, source of ore-forming fluids, and ore-forming process of the Jiepailing deposit.

2. Regional Geological Setting

The Nanling tungsten–tin metallogenic belt, located in the interior of the South China Block, is the most crucial tungsten–tin metallogenic belt both in China and globally, as well as a vital source of rare metals in China [28,29]. The Xiangnan region, situated in the midsection of the Nanling belt within the Caledonian–Indosinian fold zone of the South China Fold System in the South China Block, experiences intense tectonic–magmatic activities and has undergone multiple tectonic evolution stages [8,20]. The region is characterized by the development of nearly a hundred Caledonian to Yanshanian period plutons, providing favorable metallogenic conditions. Concentrated large to super-large tungsten–tin polymetallic deposits, such as Yaogangxian, Xianghualing, Shizhuyuan, and Huashaping, are found in the area, featuring granite-type, greisen-type, skarn-type, cassiterite–sulfide-type, and quartz vein-type mineralization, commonly accompanied by rare metals, dispersed metals, or rare earth metals [11]. For instance, Shizhuyuan is associated with Bi, Nb, and Ta mineralization, Xianghualing with Be mineralization, and Yaogangxian with Bi mineralization. The Jiepailing deposit, a representative of tin polymetallic mineralization in this region, is also the earliest discovered beryllium-rich tin polymetallic deposit in the Nanling metallogenic belt, located in Yizhang County in southwestern Xiangnan, within the southwestern segment of the Chaling–Linwu fault zone in the Chenzhou section [29] (Figure 1).

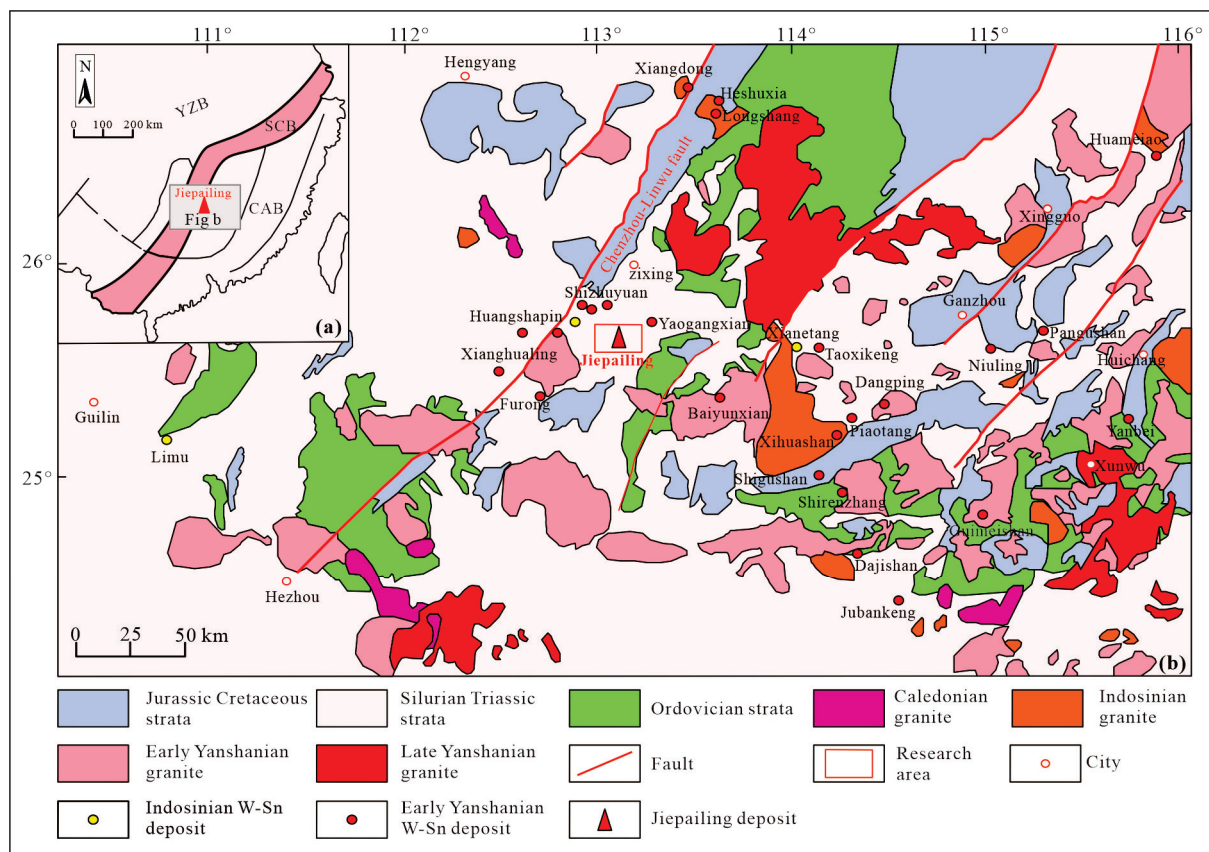


Figure 1. (a) Sketch map showing some tectonic units of China (modified after [29].) TB—Tarim Basin, NCB—North China Block, YZB—Yangtze Block, CAB—Cathaysian Block, SCB—South China Block that is composed of the YZB and CAB; (b) Simplified geological map of main tungsten–tin deposits in the Nanling metallogenic belt (modified after [18]).

3. Deposit Geology

3.1. Geology of the Jiepailing Area

The exposed strata in the Jiepailing mining area mainly consist of the Carboniferous System, with minor scattered distributions of Cretaceous System. The former is composed of the Shidengzi, Ceshu, Zimenqiao Formation, and Hutian Groups, with the Lower Carboniferous Shidengzi Formation being the primary host for mineralization [13]. The Shidengzi Formation is prominently exposed in the central and southern parts of the mining area, with its lithology divided into upper and lower sections: the upper section comprises approximately 300 m of muddy limestone, while the lower section consists of around 100 m of bioclastic limestone interbedded with muddy dolomite and dolomitic limestone [16]. The Ceshui Formation, about 120 m thick, mainly features siltstone, shale, and carbonaceous slate, predominantly distributed in the central–eastern part of the mining area [16,17]. The Zimenqiao Formation, a shallow marine carbonate rock, is approximately 50 m thick, primarily composed of medium-thick bedded limestone in the lower section and dolomite in the upper section [11]. The Middle–Upper Carboniferous Hutian Group also consists of shallow marine carbonate rocks, with a total thickness of about 420–450 m, distinguished from the Zimenqiao Formation carbonates by lighter colors, with limited distribution within the mining area [11,17].

The Jiepailing mining area lies in a secondary complex anticline at the southwestern edge of the NE–SW trending Xinhua–Xiaoxiang tectonic belt and the southern end of the Leiyang–Linwu longitudinal tectonic belt. The anticline axis trends NE 23–25°, dipping NNE with an inclination of approximately 5–8° [13,14,18]. The area features well-developed

fault structures, forming a chessboard pattern divided into NE-trending compressive shear reverse faults, NW-trending extensional normal faults, and nearly EW-trending translational shear normal faults (Figure 2). The NNE-trending faults primarily control the distribution, exposure, and extension of granitic porphyry, tin–polymetallic and beryllium–fluorite ore bodies [13,16,17]. Additionally, widespread cleavage in the Carboniferous strata, oriented approximately 15° with steep dips approaching 90° , is commonly filled with later hydrothermal minerals, forming beryllium-rich muscovite–fluorite veins [15,17,18].

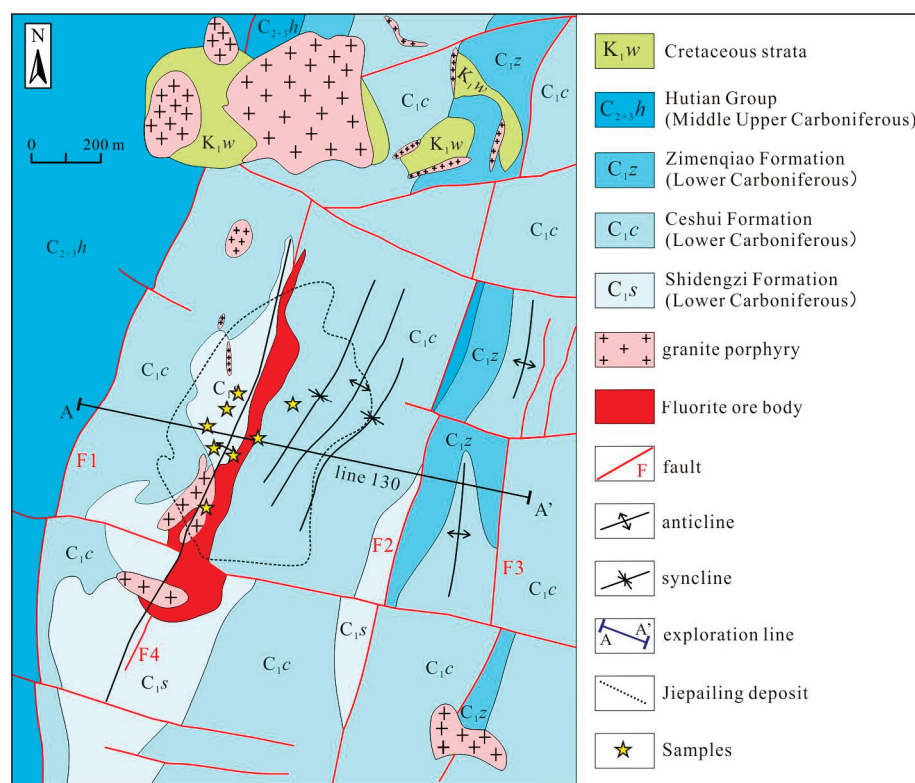


Figure 2. Geological map of Jiepailing deposit (modified after [11]).

Granitic porphyry dikes are exposed along the anticline axis, intruding to the surface with a discontinuous distribution and aligning with major structural features [14]. Early exploration suggested that these dikes might converge at a certain depth. The granitic porphyry exhibits intense alteration, often appearing light grey to greyish-white, with some parts showing a bluish-grey color, displaying a porphyritic texture and massive structure. Phenocrysts in the porphyry are primarily composed of potassium feldspar and quartz, constituting about 30%–55%, while the matrix consists of quartz, potassium feldspar, and muscovite, making up about 45%–70% [11,15]. The granitic porphyry is characterized by high silicon, alkali-rich, and low calcium content, with W, Sn, Cu, Pb, Be, and volatile elements like F, B, and Li with concentrations higher than the corresponding Clarke values, indicating a Late Cretaceous magmatic activity product [14].

3.2. Orefield Characteristics

In the Jiepailing deposit, nearly 50 ore bodies have been identified, which can be classified into four major categories: tungsten–tin ore bodies, tin polymetallic–fluorite ore bodies, lead–zinc ore bodies, and beryllium–fluorite ore bodies (Figure 3). These tungsten–tin ore bodies are primarily distributed in the Lower Carboniferous Shidengzi Formation, occurring as gently inclined sheeted and vein-type deposits, with retained tin metal reserves of 96,000 tons [11,13,18]. These ore bodies are controlled by secondary fault zones related to the F4 fault, trending approximately NNE and dipping towards SE [13].

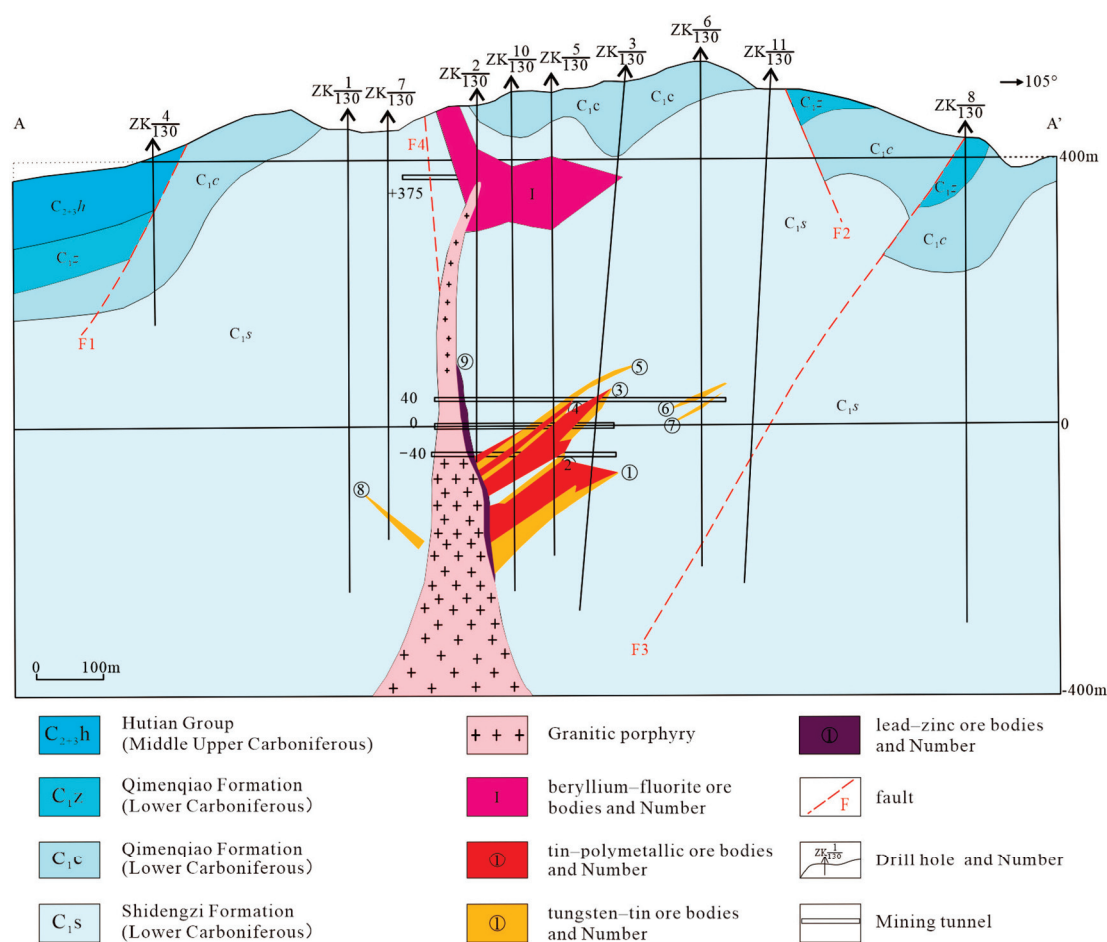


Figure 3. Geological cross section with mining tunnels (modified after [13]).

The tin polymetallic–fluorite ore bodies are vein-like or stockwork, occurring in the outer contact zone of the granitic porphyry and the fracture zones of the Shidengzi Formation, controlled mainly by stratigraphic and fault structures, with an average thickness of 15.99 m [13,16].

The lead–zinc ore bodies are jointly controlled by contact zones and faults, developing along the outer contact zone between porphyritic granite and the surrounding rocks. They strike NNW and dip SW, with a strike length of approximately 130 m and a dip extension of about 50 m. The ore body thickness ranges from 3.94 to 4.63 m, averaging 4.36 m [13].

The beryllium–fluorite ore bodies are found in fracture zones within near-surface strata, with the largest being the No. 1 beryllium-rich muscovite–fluorite ore body, which accounts for over 95% of the total Sn-Be-F resources in the area [13]. This ore body exhibits a massive stratiform structure, trending NE (20–25°), extending approximately 700 m, dipping SE (14–55°), with a depth extension of 160–350 m, an average thickness of 16.5 m, and an average width of 250 m [13,16]. In the beryllium–fluorite ore body, beryllium minerals typically form mineral associations with fluorite and muscovite, often developing at the edges of beryllium-rich muscovite–fluorite veins, resulting in significant beryllium mineralization [13]. Based on the total number of drill holes in the Jiepailing deposit, the average thickness of the fluorite ore bodies is 48.72 m, with Zk1305 being the largest diameter drill hole (with a thickness of 120.06 m) and Zk1343 the smallest (with a thickness of 2.0 m) [16]. The average grade of CaF₂ is 37.50%, and the average grade of BeO is 0.26% [11].

3.3. Alternation and Mineralization

The Jiepailing mining area has undergone multiple cycles of tectonic–magmatic–hydrothermal activity, resulting in widespread hydrothermal alteration. The alteration types are diverse, including albitization, fluoritization, polymetallic pyritization, chloritization, silicification, muscovitization, and carbonation [16]. These alternations exhibit a close genetic relationship with various metallogenic types and demonstrate pronounced vertical zoning from deep to shallow.

Greisenization can be divided into early and late stages based on alteration intensity. The early stage is characterized by the replacement of potassium feldspar phenocrysts in the granitic porphyry by ore minerals, such as quartz and muscovite. Simultaneously, in the fracture systems of the surrounding rocks, a significant amount of metallic minerals, including ferberite, cassiterite, and chalcopyrite, occur, coexisting with non-metallic minerals like fluorite, potassium feldspar, quartz, and muscovite.

The late-stage alteration cause to tin polymetallic–fluorite mineralization is primarily composed of metallic minerals such as cassiterite, chalcopyrite, stannite, pyrite, and orpiment, along with alteration minerals like fluorite, sericite, tourmaline, corundum, chlorite, quartz, and calcite (Figure 4a,d,e).

Topazization and fluoritization are dominated by extensive fluorite deposition, particularly in the exocontact zone of intermediate granitic porphyry where dense stockwork-veinlet fluorite networks develop. Local occurrences of brecciated fluorite are observable. Fluorite phenocrysts display spherical morphology with coarse-grained to pegmatitic textures, constituting distinct topaz–fluorite ore bodies (Figure 3). Chloritization and silicification predominantly occur in both endo- and exocontact zones of granitic porphyry intrusions. The exocontact zones host abundant metallic sulfides (pyrite, chalcopyrite, sphalerite, galena) forming lead–zinc ore bodies (Figures 3 and 4b,g).

Minor cassiterite and helvite are contemporaneously developed, with the latter exclusively occurring as disseminated grains in quartz vein interstices within the endocontact zone. Sericitization combined with fluoritization are predominantly developed in shallow distal areas from the intrusion. Fluorite associates with muscovite and sericite in interlayer fracture zones near the surface, forming the largest beryllium–fluorite ore bodies in the Jiepailing deposit through stockwork-veinlet systems (Figures 3 and 4c). Subordinate pyrite aggregates and sporadic cassiterite occur as nodular masses within muscovite–fluorite veins (Figure 4h).

Carbonatization features extensive calcite veinlets in shallow wall rocks containing carbonate minerals (calcite, dolomite) with minor pyritization, muscovitization, and fluoritization. Similar carbonatization is observed in fractures of deep-seated granitic porphyry. Notably, magnetite veinlets fill pyrite fractures during carbonatization, accompanied by fine-grained cassiterite–pyrite intergrowths (Figure 4i). This phenomenon is interpreted to result from secondary mineralization events driven by concealed deep-seated intrusions [15].

Pyrite is a common metallic sulfide in the Jiepailing deposit, occurring in tungsten–tin ore bodies, tin polymetallic–fluorite ore bodies, lead–zinc ore bodies, beryllium–fluorite ore bodies, and carbonate wall rock. It typically occurs as subhedral to anhedral grains, ranging from 100 to 500 μm in size, with a pale brass color. Pyrite is disseminated or occurs in aggregates within greisen gangue (Figure 4a,b,f), or as irregular fine veins filling muscovite–fluorite veins, along with sphalerite, galena, and chalcopyrite (Figure 4g). Some pyrite grains exhibit euhedral crystal forms and coarse-fractured textures (Figure 4e,h,i). It commonly associates with chalcopyrite (Figure 4f,g,h), sphalerite (Figure 4f,g,h), galena (Figure 4f,g), magnetite (Figure 4h,i), and cassiterite (Figure 4e,h,i), distributed within fine-grained fluorite, muscovite, and feldspar. Backscattered electron imaging and scanning

electron microscope energy spectrum analysis show that the different types of pyrite lack zoning structures, suggesting a uniform composition (Figure 4e,g–i).

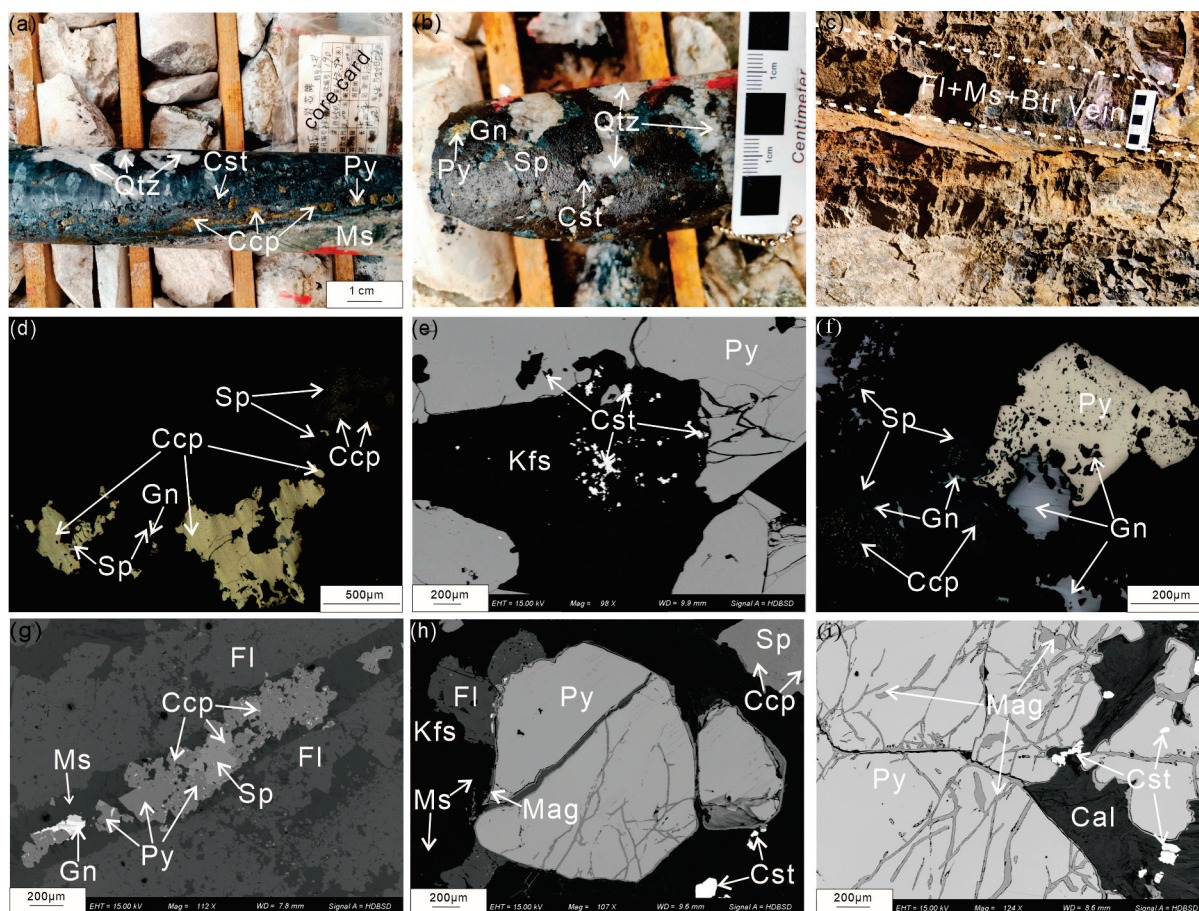


Figure 4. Ore characteristics of the Jiepailing deposit and photomicrographs and BSE images. (a) Tungsten–tin ore bodies; (b) Quartz vein-type lead–zinc ore bodies; (c) Beryllium–fluorite ore bodies, muscovite–fluorite vein; (d) Sphalerite coexisting with chalcopyrite and galena, with granular chalcopyrite within sphalerite; (e) Coarse-grained pyrite with cassiterite, encapsulating minor cassiterite (BSE); (f) Pyrite with sphalerite and galena assemblage, with minor chalcopyrite enclosed within pyrite and sphalerite interstices; (g) Pyrite with sphalerite and galena within muscovite–fluorite veins (BSE); (h) Euhedral pyrite with sphalerite, chalcopyrite, and cassiterite, with magnetite replacing pyrite edges or fractures (BSE); (i) Coarse-grained pyrite with magnetite and cassiterite, with magnetite filling pyrite interstices and minor cassiterite enclosed within pyrite (BSE). Py: Pyrite, Ccp: Chalcopyrite, Gn: Galena, Sp: Sphalerite, Mag: Magnetite, Cst: Cassiterite, Qtz: Quartz, Ms: Muscovite, Kfs: Potassium Feldspar, Fl: Fluorite, Cal: Calcite, Btr: Bertrandite.

Galena appears lead-gray, with grain sizes ranging from 2 to 100 μm , and often coexists with pyrite, sphalerite, and chalcopyrite. It is occasionally found as individual minerals or aggregates within gangue, and sometimes enclosed within pyrite and sphalerite (Figure 4d,f–g). Chalcopyrite, with its characteristic copper-yellow hue, typically exhibits anhedral grain structures, replacing or enveloping early-formed pyrite, sphalerite, and galena within their crystal lattices or interstices. Rarely, chalcopyrite occurs as single grains within gangue quartz (Figure 4d), but it frequently appears as bleb-like inclusions within sphalerite crystal lattices or fractures (Figure 4f–h). Sphalerite, mainly found in altered granitic porphyry and wall rocks, is black–brown, 0.01 to 0.5 mm in size, and anhedral. Besides partial replacement by pyrite (Figure 4f–g), sphalerite also occurs independently, developing as subhedral to anhedral grains (Figure 4d,h).

4. Samples and Analytical Methods

4.1. Samples

Samples were collected from various ore types at the Jiepailing deposit, including tungsten–tin ore bodies, tin polymetallic–fluorite ore bodies, lead–zinc ore bodies, beryllium–fluorite ore bodies, and carbonate wall rock. The samples underwent detailed hand-specimen and microscopic petrographic studies to analyze their mineralogical features. Based on the microstructural characteristics of pyrite particles, crystal forms, and associated mineral compositions, pyrite in different ores and wall rock were classified into five distinct types: PyI, PyII, PyIII, PyIV, and PyV.

PyI occurs in tungsten–tin ore bodies, where pyrite predominantly appears granular, coexisting with potassium feldspar and quartz. Typically displaying euhedral crystal structures, pyrite particles range in size from 2 μm to 200 μm and are often found as discrete minerals within quartz grains, with surface features showing small pores filled with potassium feldspar and fluorite (Figure 5b,c). Some pyrite samples exhibit uneven compositions under backscattered electron (BSE) imaging, showing band-like structures, while micro-fine to droplet chalcopyrite can be seen internally within sphalerite (Figure 5a). Pyrite particles with larger grain sizes often exhibit various-sized surface pores or cracks, commonly filled by later-formed chalcopyrite and other metallic minerals (Figure 5a); droplet chalcopyrite is distributed within sphalerite.

PyII is found in tin polymetallic–fluorite ore bodies, where pyrite is often associated with granular fluorite, occurring within fractured zones of the surrounding rocks. Pyrite crystals typically display semi-euhedral to euhedral structures, ranging in size from 50 μm to 500 μm . They are frequently observed as single particles or aggregates exposed within fluorite veins, often accompanied by occurrences of corundum, sphalerite, galena, chalcopyrite, and other sulfides within pyrite grains or fractures (Figure 5d–f).

PyIII is associated with lead–zinc ore bodies, where pyrite and sphalerite are primarily found intergrown with muscovite and fluorite, forming vein-like structures cutting through gravelly fluorite. Pyrite crystals mostly exhibit euhedral structures with grain sizes ranging from 200 μm to 1 mm, while sphalerite generally appears as euhedral crystals ranging from 50 μm to 200 μm , often occurring as banded or vein-like structures exposed within muscovite–fluorite veins (Figure 5g–i). Sphalerite, galena, and chalcopyrite typically replace pyrite along its edges or within fractures, with sphalerite showing internal droplet or granular chalcopyrite. Additionally, pyrite surfaces often exhibit small pores and fractures, with occasional inclusions of sphalerite, chalcopyrite, or galena (Figure 5g,h).

PyIV is found within beryllium–fluorite ore, characterized by coarse-grained pyrite particles ranging from 500 μm to 2 mm. Larger pyrite grains commonly exhibit fractured structures with inclusions of galena, chalcopyrite, and other metal sulfides (Figure 5j,k). Some pyrite samples also show abundant magnetite along pyrite fractures (Figure 5k).

PyV occurs within carbonate wall rocks, where pyrite particles typically appear semi-euhedral to euhedral with fine-grained structures (5 μm to 100 μm). These pyrite particles are often found individually or in aggregate forms within muscovite–calcite veins, with pyrite grains showing fractures and pores containing inclusions of calcite and other vein minerals (Figure 5l).

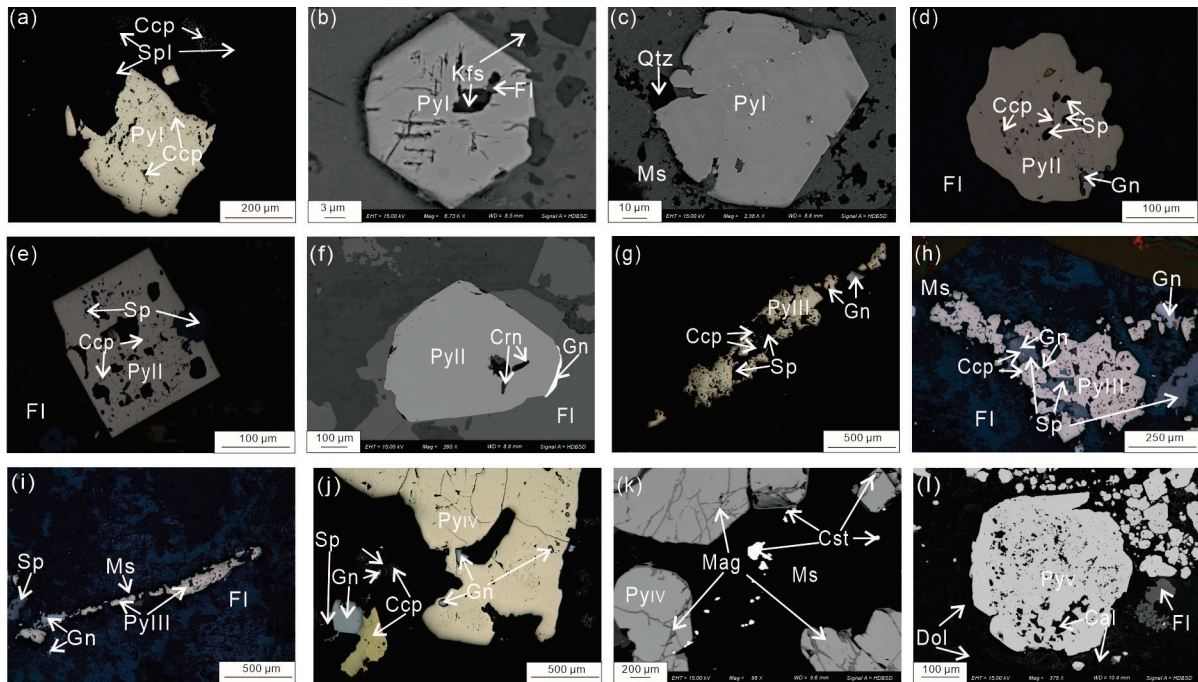


Figure 5. Microscopic structure and BSE image characteristics of different types of pyrite in the Jiepailing deposit. (a) Fine-grained pyrite in PyI containing minor chalcopyrite, associated with sphalerite and chalcopyrite; (b) Pentagonal dodecahedron pyrite in PyI with small pores or cracks, filled with potassium feldspar and fluorite (BSE); (c) Euhedral pyrite in PyI showing band-like structures (BSE); (d) Anhedral fine-grained pyrite in PyII with inclusions of sphalerite, chalcopyrite, and galena; (e) Euhedral crystal pyrite in PyII replacing sphalerite and chalcopyrite; (f) Semi-euhedral to euhedral granular pyrite in PyII associated with fluorite (BSE); (g) Striped pyrite in PyIII intergrown with sphalerite, galena, and chalcopyrite, exposed in muscovite–fluorite veins; (h) Euhedral pyrite in PyIII exposed in muscovite–fluorite veins as aggregates; (i) Vein-like euhedral pyrite in PyIII associated with sphalerite and galena; (j) Coarse-grained euhedral pyrite in PyIV associated with sphalerite (SpIV), galena, and chalcopyrite; (k) Coarse-grained pyrite in PyIV associated with magnetite and cassiterite (BSE); (l) Semi-euhedral to euhedral fine-grained pyrite in PyV (BSE); Kfs—potassium feldspar; Qtz—quartz; Ms—muscovite; Fl—fluorite; Cal—calcite; Dol—dolomite; Crn—corundum; Ccp—chalcopyrite; Gn—galena; Sp—sphalerite; Py—pyrite; Cst—cassiterite; Mag—magnetite.

4.2. Analytical Methods

Detailed petrographic observations of sample thin sections were conducted using a Leica DM2700P digital microscope at East China University of Technology. Representative pyrite grains from PyI, PyII, PyIII, PyIV, and PyV were selected for backscattered electron (BSE) imaging, in-situ trace element analysis, and sulfur isotope analysis.

Conducting micrometer-level observations on pre-analyzed pyrite samples by scanning electron microscopy (SEM) at the State Key Laboratory of Nuclear Resources and Environment in East China University of Technology allowed for the detection of microscopic inclusions or the assessment of the uniformity of sample components. Electron backscatter diffraction (BSE) images were captured, and energy-dispersive X-ray spectroscopy (EDS) was utilized for compositional analysis.

In Guangzhou Tuoyan Testing Technology Co., Ltd. (Guangzhou, China), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was employed to perform in situ trace element analysis on polished thick sections of pyrite. The laboratory utilized a New Wave Research 193 nm ArF excimer laser ablation system in conjunction with a Thermo Scientific iCap-RQ quadrupole ICP-MS. The excimer laser generated deep ultraviolet light focused on the sample surface through a homogenized optical path, with a laser beam spot diameter of 30 μm , operating at a frequency of 6 Hz and an energy density

of 3.0 J/cm². Helium was used as the carrier gas during laser ablation, with argon serving as the compensation gas to adjust sensitivity. The analysis covered a total of 36 elements, including S, Fe, Be, Ti, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Zr, Ag, Cd, In, Sn, Sb, Te, Au, Pb, Bi, Mo, V, Cr, Re, W, Sr, Th, U, Sc, Hf, Ta, Nb, and Tl. Glass standard materials NIST SRM 610, NIST SRM 612, and MASS-1 were used for external calibration with internal standards [30]. Proportionate standard materials BHVO-2G and BIR-1G were employed as control samples [31,32]. Each sample point was analyzed for 85 s, comprising 40 s of blank signal and 45 s of sample signal. Offline processing of analysis data, including selection of sample and blank signals and correction for instrument sensitivity drift, was carried out using the IOLITE V 1.4 software's 3D Trace Elements DRS mode [33]. Further details of the testing methods can be found in references [30,34].

Sulfide mineral sulfur isotopic analysis was performed using LA-MC-ICP-MS, conducted by Guangzhou Tuoyan Testing Technology Co., Ltd. The system included an ASI RESolution M50-LR 193 nm excimer laser ablation coupled with a Nu Plasma 1700 multi-collector ICP-MS. Helium was used as the carrier gas during the ablation process, with argon as the auxiliary gas. The experimental setup utilized a beam spot size ranging from 25 to 37 µm and operated at a frequency of 3 Hz, with a laser energy of 3.6 J/cm². Sulfur isotopes were analyzed using L4, Ax, and H5 Faraday cups for 32S, 33S, and 34S signals, respectively, at a resolution greater than 12,000 to minimize interference from other gas peaks. During testing, pyrite sample Py-4 ($\delta^{34}\text{S}_{\text{V-CDT}} = 1.7 \pm 0.3\text{‰}$, 2SD), sphalerite sample NBS123 ($\delta^{34}\text{S}_{\text{V-CDT}} = 17.8 \pm 0.2\text{‰}$, 2SD), chalcopyrite sample Cpy-1 ($\delta^{34}\text{S}_{\text{V-CDT}} = 4.2 \pm 0.3\text{‰}$, 2SD), and galena sample CBI-3 ($\delta^{34}\text{S}_{\text{V-CDT}} = 28.5 \pm 0.4\text{‰}$, 2SD) were used as standards. Laboratory internal standard materials such as chalcopyrite Cpy-1/GC, pyrite Py-4/PTST-2, and sphalerite NBS123/PTST-3 were added during each test of 8 points to improve the accuracy of monitoring data, utilizing the cross-test method (SSB) to correct the data. The $\delta^{34}\text{S}$ test achieved high precision of less than 0.1‰.

5. Results

5.1. Trace Element Compositions of Pyrite

The results of in situ LA-ICP-MS testing of different types of pyrite from the Jiepailing ore deposit are presented in Table 1. PyI consists of 18 points, PyII consists of 13 points, PyIII consists of 16 points, PyIV consists of 14 points, and PyV consists of 21 points. The analysis indicates varying ranges of chalcophile elements (Cu, Pb, Zn, Ag, Bi, As), siderophile elements (Sn, Co, Ni), as well as Mo, Tl, Mn, Cd, and Sb. Some elements such as Te, Ti, W, V, Cr, and Au are partially above the detection limits, with points showing notably high concentrations likely influenced by mineral inclusions. Elements including Sc, Ge, Re, Sr, Zr, Nb, Se, REE, Hf, Ta, W, Hg, Th, U, and Be are detected in very low amounts above detection limits, mostly below or near detection limits, with minimal variation among different types of pyrite, which is not discussed further in this paper.

Comparative analysis of average trace element content among different types of pyrite (Figure 6) shows similar spider diagrams, reflecting a common origin. PyI exhibits a higher Co-to-Ni ratio compared to other types of pyrite, relatively enriched in Cu, Sn, and other high-temperature elements. PyII is relatively enriched in Ni and Cd, while PyIII shows enrichment in Co, Pb, Zn, Bi, Ti, and Mn. PyIV is relatively enriched in As, Ag, and Sb, with similar ranges of Sn content among PyII, PyIII, and PyIV. In the PyV, apart from enrichment in elements such as As, Ag, and Sb, other ore-forming elements are lower compared to PyI, PyII, PyIII, and PyIV. The Mo content in all stages of pyrite is approximately consistent with a narrow distribution range (Figure 6).

Table 1. In situ trace elements (ppm) of pyrite by LA-(MC)-ICP-MS from the Jiepailing deposit.

Point	Co	Ni	Zn	As	Sn	Pb	Bi	Tl	Mn	Cu	Mo	Ag	Cd	Sb	Co/Ni
PyI@1	16.6	-	-	285	5.9	-	-	-	-	74.6	0.46	-	-	-	-
PyI@2	4.62	-	-	1038	-	3.48	0.42	-	-	-	0.32	0.05	-	-	-
PyI@3	8.68	0.9	-	1261	0.56	0.03	-	-	-	389	0.38	-	-	-	9.64
PyI@4	0.89	-	-	36.6	-	1.80	0.17	-	-	-	0.33	-	-	-	-
PyI@5	2.46	-	3.14	97.9	0.30	1.01	0.05	0.04	3.21	4.81	0.49	0.03	-	-	-
PyI@6	1.28	0.67	-	7.19	-	0.51	0.03	-	-	-	0.36	-	-	-	1.91
PyI@7	-	-	-	277	-	0.06	0.06	-	-	0.40	0.38	-	-	-	-
PyI@8	0.17	-	-	58.2	-	0.11	0.20	-	-	-	0.24	-	-	-	-
PyI@9	5.60	-	-	7.21	56.2	79.1	3.49	-	-	-	0.47	-	-	-	-
PyI@10	-	-	-	104	11.0	10.5	1.16	-	-	83.6	0.31	-	-	-	-
PyI@11	0.14	-	-	114	4.54	-	-	-	-	5937	-	-	-	-	-
PyI@12	19.4	-	6.34	79.3	1.86	31.2	3.73	0.01	-	889	0.56	0.68	-	0.17	-
PyI@13	2.05	-	-	4.50	-	0.89	0.01	-	-	3.88	0.36	-	-	-	-
PyI@14	1.01	0.76	-	25.9	-	0.03	-	-	-	3.86	-	-	-	-	1.33
PyI@15	1.20	-	-	1.13	-	0.26	0.02	-	-	23.5	0.31	-	-	-	-
PyI@16	7.80	5.47	-	12.0	-	0.68	-	0.004	-	2.99	-	-	-	-	1.43
PyI@17	20.6	2.29	-	505	-	2.27	0.42	0.008	-	-	0.42	-	-	-	9.00
PyI@18	8.35	1.88	-	268	-	-	-	-	-	-	0.17	-	-	-	4.44
Average	6.30	2.00	4.74	232	11.5	8.80	0.81	0.02	3.21	674	0.37	0.25	-	0.17	3.15
PyII@1	1.96	1.29	-	72.5	16.6	4.60	0.26	0.15	19.1	1.24	0.26	-	-	-	1.52
PyII@2	10.8	98.0	45.6	1509	-	39.4	4.21	0.01	-	4.92	0.41	-	-	0.08	0.11
PyII@3	8.70	35.0	6765	44.5	21.7	678	31.5	2.16	976	4.92	1.02	-	-	-	0.25
PyII@4	10.6	25.5	-	57.1	-	0.08	-	-	-	-	0.40	-	-	-	0.42
PyII@5	5.94	20.4	795	13.7	-	45.1	0.35	-	-	14.7	-	-	-	-	0.29
PyII@6	15.5	109	37.2	7.96	-	27.6	1.23	-	-	2.02	0.37	-	-	-	0.14
PyII@7	17.7	13.4	7.11	12.6	5.16	21.3	0.02	0.17	33.2	2.84	0.33	-	-	-	1.32
PyII@8	12.7	84.7	-	55.5	0.13	3.31	0.24	0.05	1.22	0.80	0.88	-	-	-	0.15
PyII@9	2.25	13.4	-	14.0	0.31	6.01	0.25	0.04	35.9	1.37	0.46	-	-	0.14	0.17
PyII@10	17.6	176	9798	79.0	16.4	2925	14.0	11.9	1.82	165	0.44	-	-	0.17	0.10
PyII@11	102	527	-	68.3	-	3.54	-	0.007	-	0.69	0.35	-	-	-	0.19
PyII@12	13.0	41.4	-	6146	-	-	-	-	-	0.49	0.25	1.00	-	0.96	0.31
PyII@13	11.1	139	3.54	7.20	0.23	18.5	-	0.07	-	7.65	0.90	-	-	0.08	0.08
Average	17.7	98.8	2493	622	8.65	314	5.78	1.62	178	17.2	0.51	1.00	-	0.29	0.18
PyIII@1	-	9.06	-	60	-	159	0.18	0.04	19.0	0.37	0.74	-	44	-	-
PyIII@2	0.71	30.8	-	2069	2.52	-	0.01	-	-	1.39	0.47	0.30	-	-	0.02
PyIII@3	1.08	214	-	287	0.15	19.1	0.20	0.20	41.4	2.79	0.55	0.91	0.35	-	0.01
PyIII@4	2.40	29.1	-	-	-	0.18	0.01	-	-	1.79	0.39	0.10	-	0.23	0.08
PyIII@5	2.00	69.6	-	1497	5.51	18.1	0.02	0.10	594	2.27	0.30	0.25	-	0.22	0.03
PyIII@6	1.33	48.2	-	3376	0.30	0.34	0.06	-	-	119	-	7.78	-	2.43	0.03
PyIII@7	0.85	23.6	-	52.1	-	0.54	0.06	-	-	8.13	0.32	0.37	-	0.15	0.04
PyIII@8	2.93	132	-	4.55	-	0.11	-	-	-	-	0.33	-	-	-	0.02
PyIII@9	1.29	171	-	11.3	0.14	2.86	-	0.02	3.59	7.75	0.30	1.64	-	0.84	0.01
PyIII@10	0.71	10.7	5.89	1045	-	214	0.33	0.2	31.3	2.39	0.30	-	0.47	-	0.07
PyIII@11	1.65	434	5.46	14,238	-	188	1.58	0.11	1.82	6.83	0.32	0.07	5.44	0.10	0.00
PyIII@12	10.2	396	216	1.10	-	1771	0.24	1.64	19.7	24.2	0.31	1.97	63.6	0.10	0.03
PyIII@13	1.57	72.0	-	15.8	-	13.6	0.03	0.13	2.99	7.38	0.77	0.14	-	0.12	0.02
PyIII@14	5.94	46.1	-	12.2	-	9.30	0.02	0.05	1.60	3.81	1.06	0.53	-	0.19	0.13
PyIII@15	4.52	31.9	-	12.8	-	31.4	0.03	0.19	27.8	-	2.25	-	-	-	0.14
PyIII@16	0.55	162	-	2.26	-	6.72	-	0.03	-	-	0.28	-	-	-	0.00
Average	2.52	118	75.8	1512	1.72	162	0.21	0.25	74.3	14.5	0.58	1.28	22.8	0.49	0.02
PyIV@1	2.00	5.36	-	645	-	0.81	0.03	0.01	0.50	0.58	0.32	20.8	-	0.20	0.37
PyIV@2	0.21	0.94	48.7	1.56	-	2.52	1.79	1.22	714	0.47	0.37	-	-	2.40	0.22
PyIV@3	0.19	6.79	121	-	-	3.00	3.77	-	-	0.67	-	6.52	0.67	-	0.03
PyIV@4	0.25	0.80	-	778	-	20.7	2.80	-	-	1.41	0.45	0.02	-	-	0.31

Table 1. Cont.

Point	Co	Ni	Zn	As	Sn	Pb	Bi	Tl	Mn	Cu	Mo	Ag	Cd	Sb	Co/Ni
PyIV@5	0.32	10.9	-	5.80	-	9.63	0.22	0.16	18.3	6.88	0.41	0.61	-	0.18	0.03
PyIV@6	2.22	2.58	130	16,618	-	976	0.31	0.20	21.0	0.68	0.32	-	1.18	1.32	0.86
PyIV@7	1.44	-	-	5849	-	3.32	-	0.03	-	-	0.62	0.04	-	0.34	-
PyIV@8	0.52	-	-	1019	-	0.08	-	-	-	3.55	0.54	0.04	-	0.07	-
PyIV@9	0.34	16.0	-	13.1	-	22.7	0.03	0.29	2.91	-	0.79	5.02	-	0.12	0.02
PyIV@10	-	3.97	-	5.97	-	10.4	-	0.01	-	-	0.53	28.0	-	65.7	-
PyIV@11	-	4.28	-	13.6	-	13.7	-	0.04	0.67	0.69	0.51	57.1	0.25	0.18	-
PyIV@12	1.57	16.6	-	4.24	-	26.5	-	0.32	-	3.54	0.37	0.82	0.45	-	0.09
PyIV@13	2.32	15.5	-	14.6	0.26	19.8	0.01	0.07	1.25	1.15	0.69	0.05	-	0.15	0.15
PyIV@14	0.36	1.42	-	7.70	-	12.9	0.01	0.06	5.04	-	0.30	0.86	-	-	0.25
Average	0.98	7.10	99.9	1921	0.26	80.2	1.00	0.22	95.5	1.96	0.48	9.99	0.64	7.07	0.14
PyV@1	1.04	1.07	-	886	-	0.11	0.01	0.001	-	-	0.29	0.07	-	1.89	0.97
PyV@2	-	-	-	865	-	0.24	0.06	-	-	0.68	0.47	3.37	-	-	-
PyV@3	-	-	-	5020	-	0.10	0.05	-	-	-	0.47	4.92	-	0.41	-
PyV@4	0.26	2.63	-	5.45	-	0.07	-	-	-	-	0.45	0.01	-	-	0.10
PyV@5	0.64	4.20	-	22.9	-	0.18	-	-	-	-	0.4	1.33	-	0.31	0.15
PyV@6	1.16	3.63	-	4571	-	0.05	-	-	-	-	0.38	0.08	-	-	0.32
PyV@7	-	-	-	2515	-	-	-	-	-	-	0.29	0.59	-	-	-
PyV@8	-	-	-	3379	-	0.03	0.03	-	-	0.46	-	0.05	-	-	-
PyV@9	-	-	-	11.5	-	1.18	0.04	0.00	-	0.52	0.42	0.12	-	0.08	-
PyV@10	-	-	-	1926	-	0.16	0.03	-	-	-	0.31	35.4	-	0.62	-
PyV@11	0.13	-	-	120	-	0.02	0.01	-	-	0.42	0.27	0.13	-	1.13	-
PyV@12	0.11	0.85	3.69	3558	-	12.5	1.37	0.08	-	4.7	0.44	-	-	15.9	0.13
PyV@13	2.67	-	9.61	137	-	0.25	0.23	-	-	1.93	0.58	-	-	0.50	-
PyV@14	-	-	-	714	-	-	-	0.00	-	0.56	0.34	0.01	-	0.08	-
PyV@15	0.19	-	-	122	-	-	0.01	-	-	-	0.29	0.17	-	0.26	-
PyV@16	0.21	-	-	9592	-	-	-	-	-	1.42	0.24	0.11	-	-	-
PyV@17	-	-	-	5.15	-	-	-	-	-	1.17	0.25	0.34	-	-	-
PyV@18	-	-	-	17.0	-	0.02	-	-	-	-	0.27	0.12	-	-	-
PyV@19	-	-	-	128	-	-	-	-	-	0.33	0.23	-	-	-	-
PyV@20	0.64	-	-	8.14	-	0.02	-	-	-	0.88	0.38	-	-	-	-
PyV@21	0.23	-	-	3.22	-	-	-	-	-	-	0.32	-	-	-	-
Average	0.66	2.48	6.65	1600	-	1.07	0.18	0.02	-	1.19	0.35	2.93	-	2.12	0.27

5.1.1. PyI

This type of pyrite exhibits relatively uniform contents of Bi, Tl, Mo, and Ag, with values ranging from 0.01 to 3.73 ppm (mean 0.81 ppm), 0.004 to 0.04 ppm (mean 0.02 ppm), 0.17 to 0.56 ppm (mean 0.37 ppm), and 0.03 to 0.68 ppm (mean 0.25 ppm), respectively. Other elements show relatively larger variations in content, with Co and Ni ranging from 0.14 to 20.6 ppm (mean 6.30 ppm) and 0.67 to 5.47 ppm (mean 2.00 ppm), respectively, resulting in a Co/Ni ratio ranging from 1.33 to 9.64 (mean 4.62). Chalcophile elements such as Cu, Pb, and As exhibit ranges of 0.40 to 5937 ppm (mean 674 ppm), 0.03 to 79.1 ppm (mean 8.80 ppm), and 1.13 to 1261 ppm (mean 232 ppm), respectively. PyI notably lacks in Pb, Zn, Mn, Tl, Ag, Cd, and Sb content (Figure 6).

5.1.2. PyII

This type of pyrite exhibits relatively uniform contents of Bi, Tl, Mo, and Sn, with values ranging from 0.005 to 1.58 ppm (mean 0.21 ppm), 0.02 to 1.64 ppm (mean 0.25 ppm), 0.28 to 2.25 ppm (mean 0.58 ppm), and 0.14 to 5.51 ppm (mean 1.72 ppm), respectively. Other elements show relatively larger variations in content. Co ranges from 0.55 to 10.2 ppm (mean 2.52 ppm), while Ni ranges from 9.06 to 434 ppm (mean 118 ppm), resulting in a

Co/Ni ratio ranging from 0.003 to 0.14 (mean 0.04). Chalcophile elements such as Cu, Pb, and As exhibit ranges of 0.37 to 119 ppm (mean 14.5 ppm), 0.11 to 1771 ppm (mean 162 ppm), and 1.10 to 14,238 ppm (mean 1512 ppm), respectively. Silver (Ag) and antimony (Sb), as copperophile elements, show ranges of 0.07 to 7.78 ppm (mean 1.28 ppm) and 0.10 to 2.43 ppm (mean 0.49 ppm), respectively, while tin (Sn) and bismuth (Bi) are notably depleted (Figure 6).

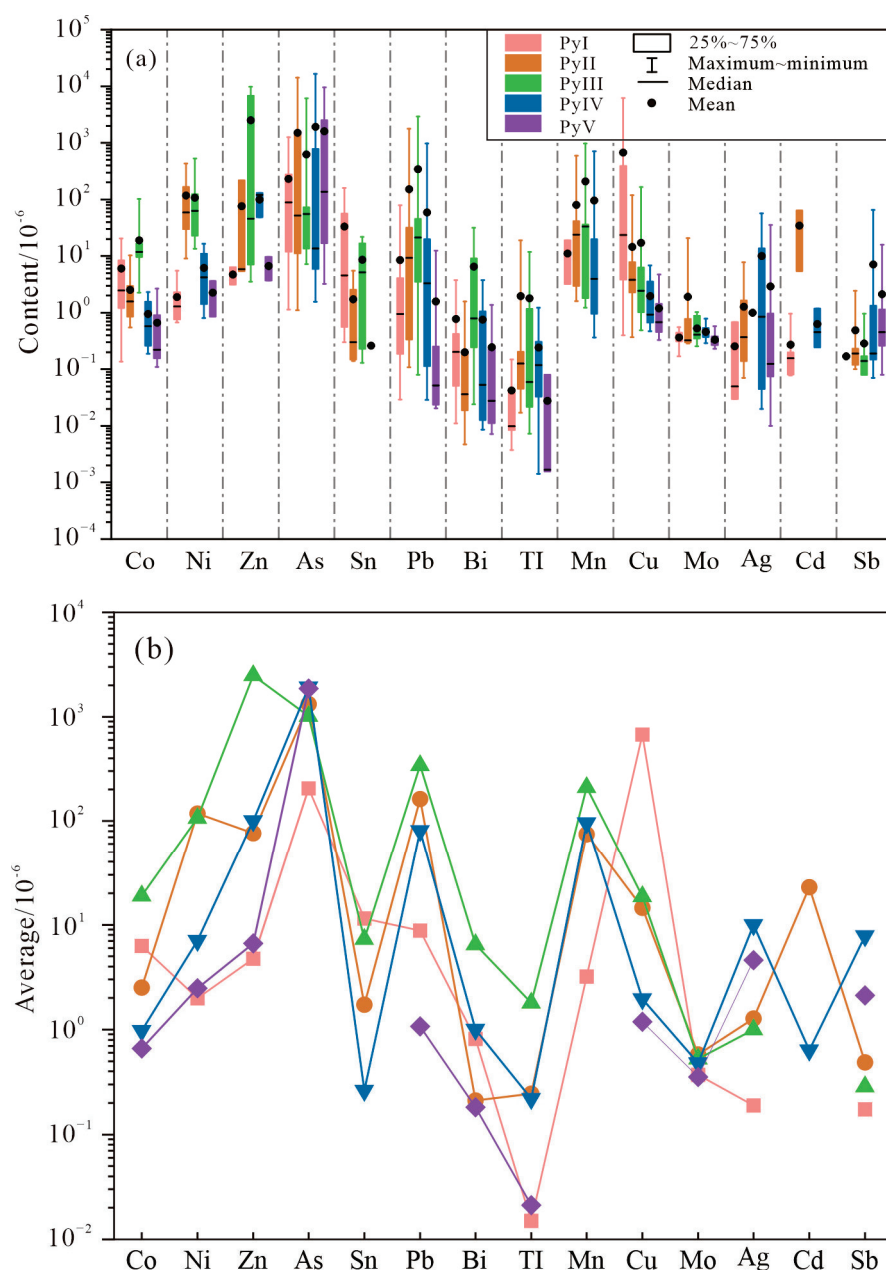


Figure 6. (a) Box diagram of trace element content of different types of pyrite in the Jiepailing deposit; (b) Plot diagram of trace element average content of different types of pyrite in the Jiepailing deposit.

5.1.3. PyIII

This type of pyrite exhibits relatively uniform contents of Bi, Tl, Mo, and Sn, with values ranging from 0.02 to 31.5 ppm (mean 5.78 ppm), 0.007 to 11.9 ppm (mean 1.62 ppm), 0.25 to 1.02 ppm (mean 0.51 ppm), and 0.13 to 21.7 ppm (mean 8.65 ppm), respectively. Other elements show relatively larger variations in content. Co ranges from 1.96 to 102 ppm (mean 17.7 ppm), while Ni ranges from 1.29 to 527 ppm (mean 98.8 ppm), resulting in

a Co/Ni ratio ranging from 0.08 to 1.52 (mean 0.39). Chalcophile elements such as Zn, Pb, and As exhibit ranges of 3.54 to 9798 ppm (mean 2493 ppm), 0.08 to 2925 ppm (mean 314 ppm), and 7.20 to 6146 ppm (mean 622 ppm), respectively, while silver (Ag), cadmium (Cd), and antimony (Sb) are notably depleted (Figure 6).

5.1.4. PyIV

This type of pyrite exhibits relatively uniform contents of Bi and Tl, with values ranging from 0.01 to 3.77 ppm (mean 1.00 ppm) and 0.01 to 1.22 ppm (mean 0.22 ppm), respectively. Mo content ranges from 0.30 to 0.79 ppm (mean 0.48 ppm). Co and Ni contents are lower, ranging from 0.19 to 2.32 ppm (mean 0.98 ppm) and 0.80 to 16.6 ppm (mean 7.10 ppm), respectively, resulting in a Co/Ni ratio ranging from 0.02 to 0.86 (mean 0.23). Cobalt (Co) and tin (Sn) are notably depleted (Figure 6).

5.1.5. PyV

This type of pyrite exhibits significantly lower trace element contents compared to other types of pyrite (Figure 6). Mo and chalcophile elements Bi, Cu, and Pb exhibit values ranging from 0.23 to 0.58 ppm (mean 0.35 ppm), 0.007 to 1.37 ppm (mean 0.18 ppm), 0.33 to 4.70 ppm (mean 1.19 ppm), and 0.02 to 12.5 ppm (mean 1.07 ppm), respectively. Co and Ni are detected slightly above detection limits, with contents ranging from 0.11 to 2.67 ppm (mean 0.66 ppm) and 0.85 to 4.20 ppm (mean 2.48 ppm), respectively, resulting in a Co/Ni ratio ranging from 0.10 to 0.97 (mean 0.33).

5.2. Sulfur Isotope Compositions

This research employed LA-MC-ICP-MS microanalysis to conduct in situ S isotope testing on metal sulfides from different ores of the Jiepailing deposit. These sulfides include: pyrite, sphalerite, and chalcopyrite in tungsten–tin ore bodies; pyrite, sphalerite, and galena in tin polymetallic–fluorite ore bodies; pyrite, sphalerite, and galena in lead–zinc ore bodies; pyrite, sphalerite, chalcopyrite, and galena in beryllium–fluorite ore bodies; and pyrite in carbonate wall rocks. A total of 52 analytical points were analyzed, with results presented in Table 2 (Figure 7). The $\delta^{34}\text{S}$ values for all sulfide analytical points ranged from -7.6‰ to 14.1‰ (mean 4.6‰), indicating significant variability in sulfur isotope composition across the Jiepailing deposit. For pyrite, $\delta^{34}\text{S}$ values ranged from -5.1‰ to 14.1‰ (mean 5.1‰) across twenty-seven points; for sphalerite, from 2.5‰ to 10.6‰ (mean 7.5‰) across twelve points; for chalcopyrite, from -2.8‰ to 9.2‰ (mean 3.2‰) across six points; and for galena, from -7.6‰ to 8.0‰ (mean -1.1‰) across seven points.

Table 2. In situ sulfur isotopic composition of different types of pyrite and other sulfide in the Jiepailing deposit.

Point	Mineral	$\delta^{34}\text{S}_{\text{V-CDT}}/\text{‰}$	2SE
PyI@01	Pyrite	3.3	0.2
PyI@02		5.4	0.2
PyI@03		4.7	0.2
PyI@04		2.8	0.2
PyI@05		3.7	0.2
PyI@06	Sphalerite	2.5	0.2
PyI@07		5.3	0.2
PyI@08	Chalcopyrite	5.5	0.3
PyI@09		5.8	0.3

Table 2. Cont.

Point	Mineral	$\delta^{34}\text{S}_{\text{V-CDT}}/\text{‰}$	2SE
PyII@01	Pyrite	6.9	0.2
PyII@02		−5.1	0.2
PyII@03		4.3	0.2
PyII@04		3.9	0.2
PyII@05		−1.9	0.2
PyII@06	Sphalerite	7.9	0.1
PyII@07		7.2	0.1
PyII@08	Galena	−3.8	0.2
PyII@09		−7.6	0.2
PyIII@01	Pyrite	6.2	0.2
PyIII@02		5.1	0.2
PyIII@03		5.8	0.2
PyIII@04		5.1	0.2
PyIII@05	Sphalerite	9.5	0.2
PyIII@06		7.3	0.1
PyIII@07		7	0.2
PyIII@08		8.8	0.2
PyIII@09	Galena	1.6	0.3
PyIII@10		8	0.2
PyIII@11		1.6	0.2
PyIV@01	Pyrite	9	0.2
PyIV@02		−2.1	0.2
PyIV@03		6.8	0.2
PyIV@04		3	0.2
PyIV@05		0.9	0.2
PyIV@06		4.4	0.2
PyIV@07	Sphalerite	10.6	0.1
PyIV@08		7.6	0.1
PyIV@09		8.1	0.2
PyIV@10		8.3	0.1
PyIV@11	Chalcopyrite	9.2	0.3
PyIV@12		−0.1	0.4
PyIV@13		−2.8	0.3
PyIV@14		1.6	0.3
PyIV@15	Galena	−3.7	0.2
PyIV@16		−3.5	0.2
PyV@01	Pyrite	6.8	0.2
PyV@02		7.2	0.2
PyV@03		7.2	0.2
PyV@04		14.1	0.2
PyV@05		10.2	0.2
PyV@06		10	0.2
PyV@07		9.3	0.2

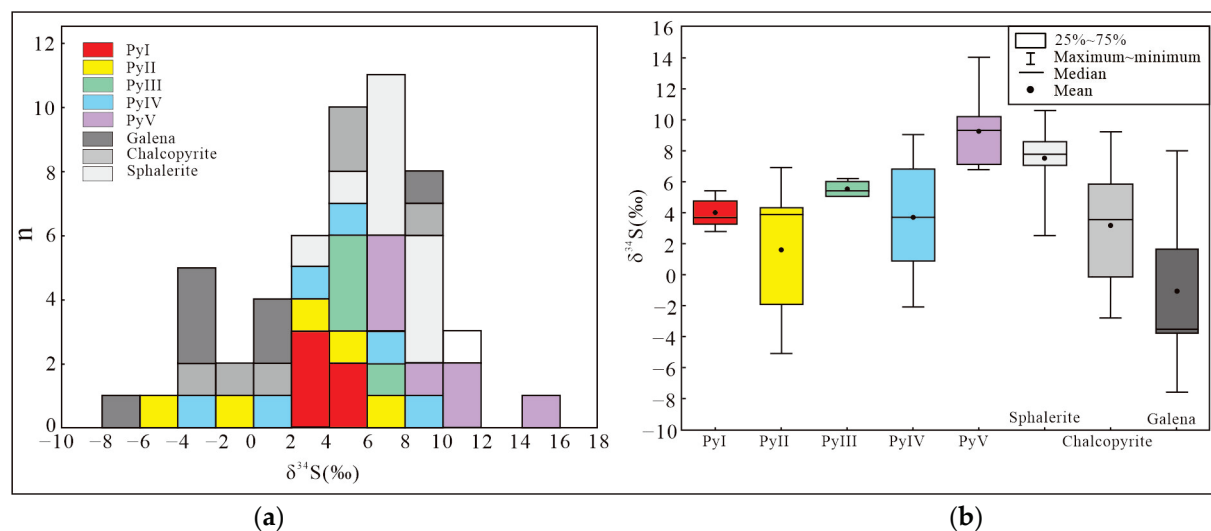


Figure 7. (a) Histogram diagram of $\delta^{34}\text{S}$ values of different types of pyrite and other sulfide in the Jiepailing deposit; (b) Box diagram of $\delta^{34}\text{S}$ values of different types of pyrite and other sulfide in the Jiepailing deposit.

In tungsten–tin ore bodies, pyrite (PyI) exhibited $\delta^{34}\text{S}$ values ranging from 2.8‰ to 5.4‰ (mean 4.0‰) at five analytical points, while sphalerite (SpI) showed $\delta^{34}\text{S}$ values ranging from 2.5‰ to 5.3‰ (mean 3.9‰) at two analytical points. In tin polymetallic–fluorite ore bodies, pyrite (PyIII) had $\delta^{34}\text{S}$ values ranging from −5.1‰ to 6.9‰ (mean 1.6‰) at five analytical points, and sphalerite (SpIII) showed $\delta^{34}\text{S}$ values ranging from 7.2‰ to 7.9‰ (mean 7.6‰) at two analytical points. In lead–zinc ore bodies, pyrite (PyII) exhibited $\delta^{34}\text{S}$ values ranging from 5.1‰ to 6.2‰ (mean 5.6‰) at four analytical points, while sphalerite (SpII) showed $\delta^{34}\text{S}$ values ranging from 7.0‰ to 9.5‰ (mean 8.1‰) at two analytical points. In beryllium–fluorite ore bodies, pyrite (PyIV) had $\delta^{34}\text{S}$ values ranging from −2.1‰ to 9.0‰ (mean 3.7‰) at six analytical points, and sphalerite (SpIV) showed $\delta^{34}\text{S}$ values ranging from 7.6‰ to 10.6‰ (mean 8.7‰) at four analytical points. Pyrite in carbonate wall rocks (PyV) exhibited $\delta^{34}\text{S}$ values ranging from 6.8‰ to 14.1‰ (mean 9.2‰) at seven analytical points.

The $\delta^{34}\text{S}$ values of metal sulfides varied significantly across different ores: in the tungsten–tin ore bodies (Py I), sulfides exhibited $\delta^{34}\text{S}$ values ranging from 2.5‰ to 5.8‰ (mean 4.3‰), with a relatively concentrated distribution. In the tin polymetallic–fluorite and lead–zinc ore bodies (PyII–III), sulfides exhibited $\delta^{34}\text{S}$ values ranging from −7.6‰ to 9.5‰ (mean 3.9‰), indicating the most dispersed distribution. In the beryllium–fluorite ore bodies (Py IV), sulfides exhibited $\delta^{34}\text{S}$ values ranging from −3.7‰ to 10.6‰ (mean 3.6‰), with a scattered distribution. In the carbonate wall rock (PyV), sulfides exhibited $\delta^{34}\text{S}$ values ranging from 6.8‰ to 14.1‰ (mean 9.2‰), showing a moderately dispersed distribution.

6. Discussion

6.1. Chemical Characteristics of Pyrite

Pyrite is widely distributed in various geological environments and can incorporate numerous trace elements (As, Co, Ni, Cu, Zn, Se, Ag, Sb, Au, Pb, Bi, Hg, and Tl) into its crystal through various mechanisms [10,24–26]. Previous studies have shown that the occurrence states of trace elements in pyrite are mainly of three types: (1) they are incorporated into the mineral lattice in the form of isomorphous substitution; (2) they are present in visible micron-sized mineral inclusions; (3) they are present as invisible nanoparticle inclusions [35,36]. Specifically, elements such as Co, Ni, As, Se, Mn, and Mo enter the pyrite lattice mainly in the form of isomorphism or nanoparticles, while elements

such as Cu, Pb, Zn, Bi, Ti, Tl, Te, Sn, Sb, Au, Ag, Th, U, Cr, V, and W mainly exist in the form of fine mineral daughter crystals [24,37–40].

When a certain element is distributed in pyrite in the form of isomorphism, the spectral line of the element time-resolved signal plots is flat, closely resembling that of Fe, with no significant fluctuation. When the elements occur in the form of fine mineral inclusions or nanoparticles, the spectral lines show obvious fluctuations on the element time-resolved signal plots [24–27,37,38]. Therefore, the micro-scale in situ analysis of pyrite can not only obtain the content of characteristic elements, but also determine the occurrence form of elements in pyrite through the changes of the element time-resolved signal, combined with other chemical behaviors [10,24,26,28].

In the element time-resolved signal plots of various types of pyrite, the spectral lines of Co and Ni rarely show significant fluctuations, indicating that they mainly exist in the pyrite in the form of solid solutions (Figure 8). In addition, the contents of Co and Ni are significantly increased in the PyIII type, which may be closely related to the development of pyrite in lead–zinc ore bodies, indicating that the rapid precipitation of pyrite may enhance the isomorphic substitution ability of Co and Ni.

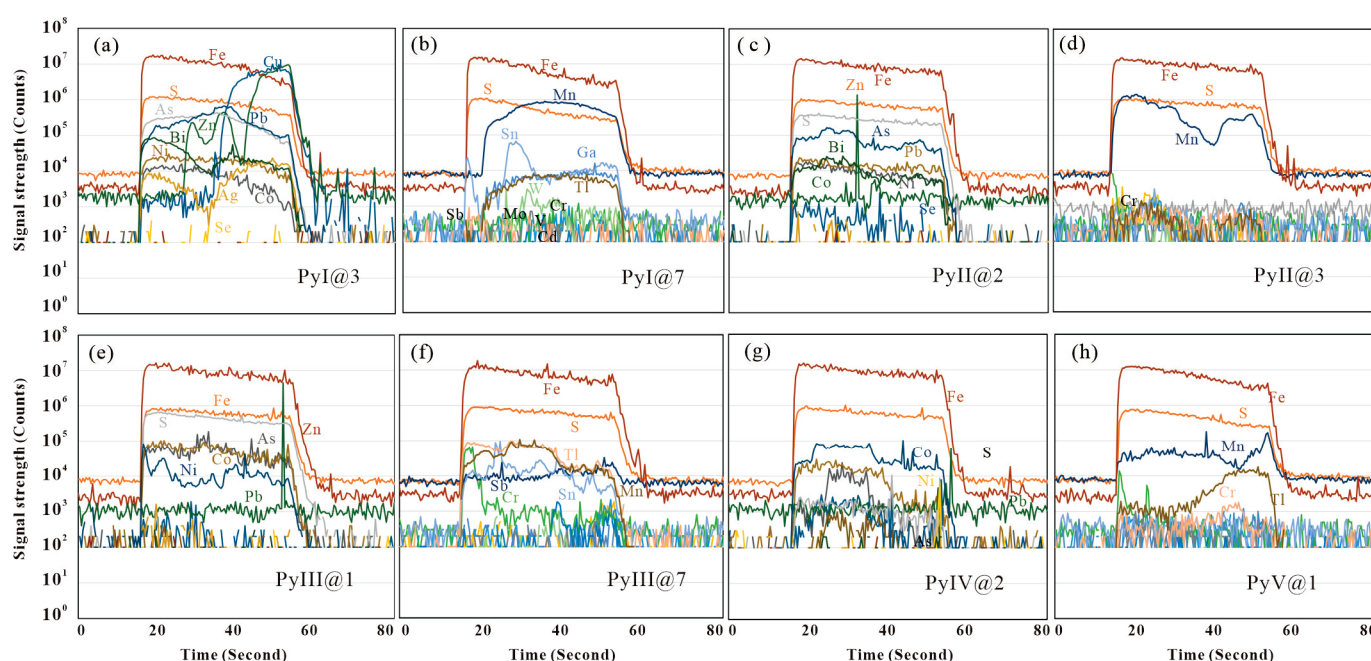


Figure 8. LA-ICP-MS trace element temporal resolution signal curve of different types of pyrite in the Jiepailing deposit. (a,b) PyI. (c,d) PyII. (e,f) PyIII. (g) PyIV. (h) PyV.

The signal of As in various pyrites in the mining area is relatively stable, which further indicates that As also replaces S in the form of isomorphism and enters the pyrite lattice. The As content in each generation of pyrite is relatively stable. Considering that tungsten–tin ore bodies, tin polymetallic–fluorite ore bodies, and lead–zinc ore bodies all develop arsenopyrite and tetrahedrite, it is speculated that their ore-forming fluids are similar and all of them are As-bearing fluids [24,26].

Mn is another element that exists in the PyV lattices by replacing S in the form of isomorphism, which is characterized by relatively stable spectral lines in the element time-resolved signal plots [26]. The content of Mn in PyI, PyII, and PyIII was close to each other and showed a gradual increase trend. The relationship between the solubility of Mn and temperature may reflect the gradual decrease in environmental temperature during the formation of PyI, PyII, and PyIII.

The ionic radius of lead is larger than that of Fe^{2+} , which limits the ability of lead to enter the lattice of pyrite in the form of isomorphism [10]. Therefore, lead mainly exists in pyrite in the form of micron- to nanoscale mineral inclusions. In each type of pyrite in Jiepailing, lead and zinc show strong peaks or protrusions on the element time-resolved signal plots, indicating that they mainly exist in pyrite in the form of mineral inclusions (Figure 8).

Studies also show that Bi, Ag, Cd, and Sb are typically incorporated into the galena lattice in solid solution form. In the five types of pyrite from the mining area, Ag, Bi, and Sb exhibit a positive correlation with lead (Figure 9), and their contents are relatively low, with irregular “concave–convex” peaks in the element time-resolved signal plots. Therefore, it is inferred that lead exists in pyrite as fine galena inclusions, while Ag, Bi, and Sb exist in solid solution within these galena inclusions [24,40].

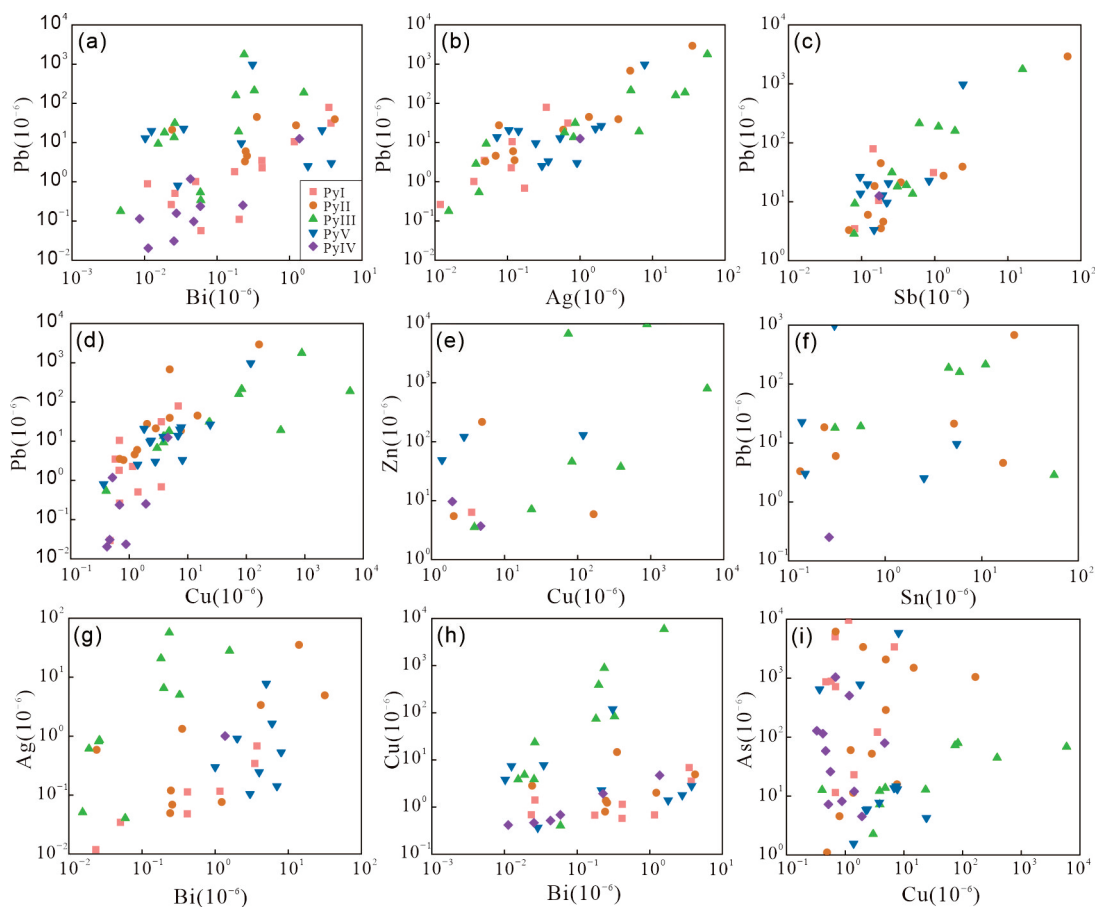


Figure 9. Trace element relationship diagram of pyrite in the Jiepailing deposit. (a) Pb vs. Bi. (b) Pb vs. Ag. (c) Pb vs. Sb. (d) Pb vs. Cu. (e) Zn vs. Cu. (f) Pb vs. Sn. (g) Ag vs. Bi. (h) Cu vs. Bi. (i) As vs. Cu.

Copper shows significant “spikes” and “valleys” on the element time-resolved signal plots, indicating that copper mainly exists in pyrite as mineral inclusions. In the Jiepailing mining area, chalcopyrite mainly develops in the tungsten–tin ore bodies, followed by the tin polymetallic–fluorite ore bodies and lead–zinc ore bodies. Correspondingly, copper content is higher in PyI, while it significantly decreases in PyII, PyIII, PyIV, and PyV, showing no correlation with Pb, Zn, Bi, or As (Figure 9). Usually, after copper is formed as an independent mineral in the ore-forming fluid, the copper content in the fluid will be greatly reduced [39,40].

During mineralization, mineral crystallization is typically influenced by the chemical composition, temperature, and pressure of the fluid. The content, distribution, and occur-

rence states of trace elements in minerals record changes in these environmental conditions. Based on the occurrence and variation characteristics of elements such as Co, Ni, As, Mn, Cu, and Pb in the Jiepailing mining area, as well as the mineral assemblages and spatial relationships of the ore bodies, it is inferred that the formation of the five types of pyrite may originate from the same hydrothermal system [41].

6.2. Sources of Ore-Forming Fluid

The sulfur isotope composition of sulfides serves as crucial geochemical evidence for determining the sources of ore-forming materials and exploring ore-forming mechanisms [41–46]. The widespread application of sulfur isotope geochemistry in studying ore deposit formation processes has become a central focus of current research in the field [41–48]. The in situ sulfur isotope information of sulfides allows for the reconstruction of mineral formation processes within fluids, thereby delving into key scientific questions concerning the sources and mechanisms of ore formation. Similar to micro-area in situ trace element analysis of sulfides, recent advancements in in situ sulfur isotope analysis techniques, including point analysis, have been widely applied in studying various types of ore deposit formation environments, sources of ore-forming materials, and mechanisms of ore formation such as those in rare metal deposits, magmatic–hydrothermal environments, and their evolution processes, enrichment, precipitation, and mineralization mechanisms [47–51].

Previous studies indicated that using the single mineral grain powder method, the $\delta^{34}\text{S}$ values of metal sulfides in the Jiepailing fluorite ores ranged from -1.0‰ to $+7.5\text{‰}$ [21]. In contrast, this study employing metal sulfide LA-MC-ICP-MS in situ testing revealed a wider range of $\delta^{34}\text{S}$ values from -7.6‰ to 14.1‰ (mean 4.6‰ ; range 21.7‰), demonstrating significantly greater variability in sulfur isotopes compared to the single mineral grain powder method. This approach ensures more accurate determination of sulfur isotopic values for individual sulfide minerals, distinguishing itself by preventing errors that may arise in other methods [47].

The sulfur isotope composition of sulfides in ore deposits serves as a tracer for determining the sources of ore-forming materials and fluid evolution mechanisms, helping to identify sulfur sources in ore-forming fluids and further exploring the formation processes of ore deposits [52–54]. Through comprehensive identification methods such as field surveys, hand specimens, optical microscopy, and scanning electron microscopy, the Jiepailing deposit is primarily characterized by metal sulfides such as pyrite as the main sulfur-bearing minerals. No evidence of sulfate minerals (e.g., anhydrite, gypsum) was found in the ore bodies or surrounding rocks, indicating that sulfur in the ore-forming fluids mainly exists in the form of HS^- and S^{2-} .

Therefore, the total sulfur isotope value ($\delta^{34}\text{S}_{\Sigma\text{S}}$) in ore-forming fluids is approximately equivalent to the sulfur isotope composition of metal sulfides [55–57]. The relationship between $\delta^{34}\text{S}$ values of metal sulfides in the Jiepailing deposit is $\delta^{34}\text{S}_{\text{sphalerite}} > \delta^{34}\text{S}_{\text{pyrite}} > \delta^{34}\text{S}_{\text{chalcopyrite}} > \delta^{34}\text{S}_{\text{galena}}$, which does not follow the thermodynamic equilibrium fractionation principle obtained experimentally for coexisting sulfides $\delta^{34}\text{S}$ values, namely $\delta^{34}\text{S}_{\text{pyrite}} > \delta^{34}\text{S}_{\text{sphalerite}} > \delta^{34}\text{S}_{\text{chalcopyrite}} > \delta^{34}\text{S}_{\text{galena}}$, indicating that sulfur isotopes of sulfides in the deposit are not in equilibrium fractionation [58,59]. Hence, $\delta^{34}\text{S}$ values of sulfides in this deposit generally do not represent $\delta^{34}\text{S}_{\Sigma\text{S}}$ values in ore-forming fluids but are noticeably lower. Therefore, the $\delta^{34}\text{S}_{\Sigma\text{S}}$ value of ore-forming fluids in the Jiepailing deposit should be higher than the average $\delta^{34}\text{S}$ value of sulfides [47,60].

Extensive studies on sulfur isotopes have identified five sources of sulfur in hydrothermal deposits: (1) mantle-derived sulfur, typically with $\delta^{34}\text{S}$ values near 0‰ and a range of $0 \pm 3\text{‰}$ [61]; (2) crustal-derived sulfur, with a wide range of $\delta^{34}\text{S}$ values [61,62];

(3) seawater-derived sulfur, characterized by modern seawater $\delta^{34}\text{S}$ values (approximately +20‰), which can represent sulfur isotopes of sulfates in marine evaporite rocks [62]; (4) biogenic sulfur, typically characterized by large negative $\delta^{34}\text{S}$ values [63,64]; and (5) mixed sulfur, characterized by mixed sulfur isotope values ranging from +5‰ to +15‰ [59,61].

The in situ sulfur isotope values of sulfide minerals measured in this study range from −7.6‰ to 14.1‰, with an average value of 4.59‰. This indicates that the $\delta^{34}\text{S}$ values of the mineralizing fluids in the study area exhibit a more complex range compared to the common sulfur sources typically found in hydrothermal deposits. Previous studies on hydrothermal deposits have shown that the sulfur isotope composition of sulfide minerals is not solely determined by the sulfur isotopes of the mineralizing material in the source region. It is also influenced by physicochemical conditions, such as oxygen fugacity, pH, and temperature, during the evolution of the mineralizing hydrothermal fluids [54–65].

As shown in Table 2 and Figure 7, the $\delta^{34}\text{S}$ values of different types of pyrite from the Jiepailing deposit range as follows: 2.5‰ to 5.8‰ (PyI), −7.6‰ to 7.9‰ (PyII), 1.6‰ to 9.5‰ (PyIII), −3.7‰ to 10.6‰ (PyIV), and 6.8‰ to 14.1‰ (PyV). According to extensive research, the factors leading to negative $\delta^{34}\text{S}_{\text{V-CDT}}$ values in mineralizing fluids are primarily related to several situations: (1) the initial stage of the mineralizing fluid is already enriched in light sulfur, closely linked to biogenic processes; (2) the mineralizing fluid undergoes water–rock reactions or fluid mixing during its evolution, resulting in negative $\delta^{34}\text{S}_{\text{V-CDT}}$ values with relatively small absolute values [66,67].

Based on the $\delta^{34}\text{S}$ value range of PyI, it is inferred that the mineralizing fluids associated with tungsten–tin mineralization should have higher $\delta^{34}\text{S}$ values, closer to the sulfur source range of granite (Figure 10). This is consistent with previous studies suggesting that the granitic porphyry or deep granite in the region is the parent rock for tungsten–tin mineralization. However, the $\delta^{34}\text{S}$ values of PyII, which developed in the tin polymetallic ore body, and PyIV, found in the shallow fluorite ore body, exhibit some negative values. This suggests that the fluids may have undergone water–rock reactions or fluid mixing.

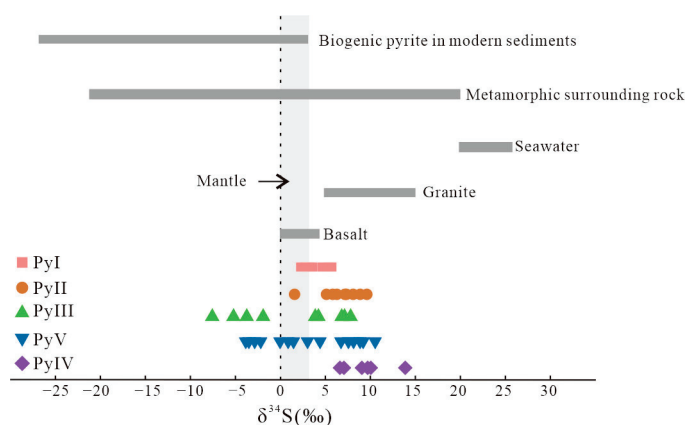


Figure 10. Diagram of in situ $\delta^{34}\text{S}$ values of sulfides at different ores of Jiepailing deposit (modified according to [62]).

Studies on quartz fluid inclusions in the tungsten–tin and tin polymetallic–fluorite ore bodies of the Jiepailing deposit show that the homogenization temperatures of fluid inclusions associated with tin mineralization range from 250 °C to 350 °C, indicating that the mineralizing fluids are of medium to high temperature [68]. The δD values (−42.3‰ to −85‰) and $\delta^{18}\text{O}$ values (4.64‰ to 9.08‰) of the mineralizing fluids calculated from the H–O isotopes of quartz fall within or close to the magmatic water range, with contributions from atmospheric precipitation [18]. Therefore, the variation in $\delta^{34}\text{S}$ values of sulfides

within the tin polymetallic–fluorite, lead–zinc, and beryllium–fluorite ore bodies suggests that the mineralizing fluids in the Jiepailing deposit may have undergone fluid mixing.

Therefore, based on the variation characteristics of $\delta^{34}\text{S}$ values in different types of pyrite, the tungsten–tin mineralizing fluids in the high-temperature stage exhibit relatively high positive $\delta^{34}\text{S}$ values, reflecting that the early mineralizing fluids originated from a magmatic system associated with granite. In contrast, the $\delta^{34}\text{S}$ value range of PyII and PyIV, which developed in the shallow fluorite ore body, reflects that after the fluids extensively infiltrated the fracture system within the surrounding rocks, they mixed with other fluids, including atmospheric precipitation, resulting in a broader $\delta^{34}\text{S}$ value range for the mineralizing fluids [69].

6.3. Fluid Evolution of Multi-Stage Ore-Forming

The trace element composition of minerals indirectly reflects rich ore-forming information and processes such as temperature and redox changes in ore-forming fluids [70,71]. Specifically for metal sulfides, which are often associated with magmatic–hydrothermal systems, variations in trace element content or ratios in minerals can to some extent reflect the physical and chemical conditions of the ore-forming fluids during crystallization, and can be used to infer the sources of ore-forming fluids [70], thereby aiding in exploration for ore deposits [64]. Pyrite is the most common mineral in the Jiepailing ore district, developed throughout various polymetallic mineralizations including the early-stage tungsten–tin mineralization to tin polymetallic–fluorite mineralization, and the late-stage lead–zinc and beryllium–fluorite mineralization, and even in the carbonate wall rock. Therefore, conducting in situ trace element analysis of pyrite from different ores in the district can elucidate the sources of ore-forming materials and fluid evolution.

Previous studies indicate significant differences in Co/Ni ratios in pyrite crystals of different genetic origins, and within different mineralization stages of the same type of deposit [63]. Researchers suggested that Co, compared to Ni, is more sensitive to temperature changes: as the temperature of the ore-forming fluid increases, Co is more likely to enter the pyrite lattice in a solid solution form, typically resulting in a higher Co/Ni ratio in pyrite, indicating higher fluid temperatures; conversely, lower temperatures result in lower Co/Ni ratios [72]. On the other hand, studies show that sedimentary or sedimentary-reformed pyrite typically has lower Co and Ni contents, with Co/Ni ratios usually <1. In hydrothermal (vein-type) deposits, the Co and Ni contents and Co/Ni ratios of pyrite vary widely, with Co/Ni ratios ranging from 1.17 to 5.00. In porphyry, skarn, and volcanic vent sulfide deposits, pyrite Co and Ni contents and Co/Ni ratios vary greatly, with Co/Ni ratios ranging from 1.1 to 4.6, 3 to 23.5, and 5 to 50, respectively [10,63,73]. Based on these characteristics, previous researchers have used a Co–Ni binary plot of pyrite to classify different genetic types of deposits.

The Co/Ni ratio of pyrite in the Jiepailing deposit ranges from 0.003 to 9.63 (mean 0.76), indicating significant differences in ore-forming fluids between different ores. Pyrite with a Co/Ni ratio greater than 1 reflects ore-forming fluids with higher environmental temperatures, closely related to magmatic–hydrothermal processes. Pyrite with a Co/Ni ratio less than 1 reflects lower crystallization temperatures, suggesting an origin closer to sedimentary or reformed environments, with a significant contribution from non-magmatic sources [43]. Pyrite samples from different ores in the Jiepailing deposit were plotted for Co and Ni content on a Co–Ni genetic plot [24,68] (Figure 11). PyI-type pyrite is predominantly located in the lower left quadrant of the hydrothermal genesis area, indicating that the ore-forming fluids for this type of pyrite were influenced by magmatic–hydrothermal processes.

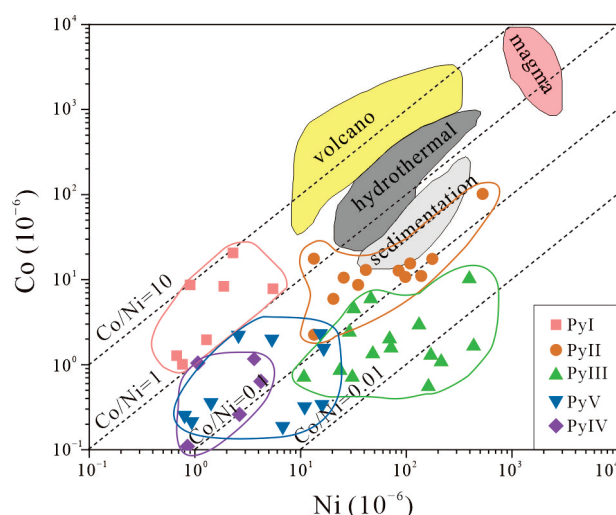


Figure 11. Co-Ni genesis of pyrite in the Jiepailing deposit (the fields are modified after [63]).

Overall, PyI-type pyrite is enriched in high-temperature elements such as Sn and Cu, while depleted in As, Mn, Ag, and Sb, consistent with the geochemical characteristics of high-temperature hydrothermal pyrite. In contrast, PyII, PyIII, PyIV, and PyV-type pyrite have Co/Ni ratios primarily located below the sedimentary genesis area, with higher concentrations of Pb, Zn, Tl, Mn, Ag, Cd, and Sb, indicating influences from metamorphic hydrothermal or atmospheric precipitation during magmatic–hydrothermal processes, leading to the enrichment of ore-forming elements in late-stage pyrite. Additionally, the gradual decrease in Co/Ni ratios in late-stage ore-forming fluids reflects a gradual decrease in temperature during the formation of PyII, PyIII, PyIV, and PyV-type pyrite. In summary, within the Jiepailing deposit, the decrease in Co/Ni ratios and Co + Ni contents in pyrite throughout multiple stages of mineralization indicates a continuous decrease in ore-forming fluid temperature. Early-stage ore-forming materials primarily originated from magmatic–hydrothermal processes, whereas the influx of significant non-magmatic materials during intermediate to late stages resulted in pyrite formations with sedimentary characteristics [63].

In the Jiepailing deposit, quartz inclusion thermometry reveals homogeneous temperatures in the tungsten–tin ore bodies ranging between 250 and 350 °C [68], in the lead–zinc ore bodies between 170 and 260 °C [74], and in the carbonate wall rock, quartz inclusion temperatures are primarily within 110–190 °C [74]. This reflects higher temperatures in the early stages of mineralization, with relatively minor temperature variations during the carbonate wall rock and lead–zinc mineralization, consistent with the characteristics indicated by trace elements in pyrite. Furthermore, H–O isotope studies on quartz indicate that δD values (−42.3‰ to −85‰) and $\delta^{18}O$ values (4.64‰ to 9.08‰) of the ore-forming fluids are consistent with magmatic water ranges [74].

In summary, it is believed that the tin–polymetallic ore-forming fluids in the Jiepailing originate from deep-seated magmas. During the evolution of ore-forming fluids, they were influenced by mixing with atmospheric precipitation, leading to changes in fluid composition and physicochemical conditions. This resulted in the coexistence of different types of pyrite during the rare metal element mineralization process.

Previous studies suggest that elements such as W, Cu, Pb, and Zn typically undergo mineralization in medium- to low-temperature fluids ranging from 200 to 400 °C, whereas Sn can mineralize over a broader temperature range [75–77]. Additionally, early high-temperature fluids to some extent increased the solubility and activity of rare metal elements in ore-forming fluids, promoting complexation with halide elements (F-, Cl-) and rare metal

elements. Subsequently, significant temperature decreases led to extensive precipitation and mineralization of rare metal elements [77–82].

Considering the regional geological background, geological characteristics of the deposit, and the evolution mechanism of ore-forming fluids in the Jiepailing area, it is inferred that during the late Yanshan period and multiple tectonic stages, granitic magma carrying abundant ore-forming elements such as W, Sn, Pb, Zn, Be, Cu, and F intruded into carbonate formations. Ore-forming fluids formed through magma cooling and degassing ascended along fault structures in the core of the Jiepailing anticline, causing greisenization, topalization, and fluoritization to occur near concealed plutons, forming tin–copper and topaz–fluorite ores. Thus, PyI-type pyrite formed during this stage is enriched in Cu, Sn, and other elements, with lower concentrations of As, Tl, Ag, Cd, Sb, Cr, V, Mn, and Ga, and a Co/Ni ratio mostly >1, indicating higher early-stage ore-forming fluid temperatures. Pyrite of PyII type in the tin polymetallic–fluorite exhibits lower Co/Ni ratios, reflecting a gradual decrease in fluid temperatures.

As ore-bearing fluids continued to ascend, they extensively entered interlayered fractured zones, mixing with pre-existing fluids in open systems through shallow structural fractures and fissures. This process progressively lowered fluid temperatures and pressures, resulting in substantial unloading of elements such as Pb, Zn, As, and Cd into mineralization. This led to the formation of PyIII-type pyrite in the upper part of the tungsten–tin ore bodies containing lead–zinc ore bodies. Subsequently, as fluid temperatures and pressures continued to decrease, PyIV-type pyrite formed in the beryllium–fluorite ore bodies, with some PyV-type pyrite forming in the surrounding carbonate wall rocks at shallow depths.

7. Conclusions

1. The Jiepailing Sn polymetallic deposit hosts five types of pyrite, developed in five types of ores: tungsten–tin ore bodies (PyI), tin polymetallic–fluorite ore bodies (PyII), lead–zinc ore bodies (PyIII), beryllium–fluorite ore bodies (PyIV), and carbonate wall rock (PyV).

2. PyI is enriched in high-temperature elements such as Cu and Sn, while PyII, PyIII, PyIV, and PyV are enriched in medium-temperature elements such as Pb and Zn, as well as medium- to low-temperature elements like As, Ag, and Mn, with most Co/Ni ratios formed early to late falling below those indicative of magmatic to sedimentary origins, reflecting a gradual decrease in temperature during the evolution of ore-forming fluids, possibly due to the influence of metamorphic or meteoric water.

3. Sulfur isotopic characteristics of sulfides indicate that ore-forming fluids result from mixing between mantle and metamorphic wall rock during the water–rock interaction progress.

4. Granitic magma carrying abundant ore-forming elements such as W, Sn, Pb, Zn, Be, Cu, and F intruded into carbonate formations. Ore-forming fluids formed through magma cooling and degassing ascended along fault structures, resulting in tungsten–tin and tin polymetallic–fluorite ore bodies forming. As ore-bearing fluids continued to ascend to shallow depths, they interacted extensively along host rock fractures, generating lead–zinc ore bodies. Subsequent temperature decreases in the system facilitated significant precipitation of Be and F elements, forming beryllium–fluorite ore bodies.

Author Contributions: Conceptualization, G.-F.D. and W.-J.Z.; methodology, G.-F.D. and D.W.; software, X.-Y.L.; validation, Y.-Y.L., L.Y. and Z.-Z.Z.; formal analysis, X.-Y.L.; investigation, G.-F.D., X.-Y.L., Y.-Y.L. and Z.-Z.Z.; resources, D.W. and W.-J.Z.; data curation, X.-Y.L.; writing—original draft preparation, G.-F.D.; writing—review and editing, D.W. and W.-J.Z.; supervision, L.Y.; project administration, D.W. and W.-J.Z.; funding acquisition, G.-F.D. and L.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Hunan Provincial Natural Science Foundation grant number (NO. 2024JJ8105, NO. 2023JJ60189), National Science and Technology Major Project of the Ministry of Science and Technology of China (NO. 2024ZD1001000), the Scientific Research Fund of Hunan Provincial Education Department grant number (NO. 22B0963) and Open Research Fund Program of Key Laboratory of Metallogenic Prediction of Nonferrous Metals and Geological Environment Monitoring (Central South University), Ministry of Education (2023YSJS13).

Data Availability Statement: All the research data related to this paper have been listed in the manuscript.

Acknowledgments: We sincerely appreciate the critical comments and constructive suggestions from the anonymous reviewers, which have played a significant role in improving this manuscript. We also thank the State Key Laboratory of Nuclear Resources and Environment at East China University of Science and Technology and Guangzhou Tuoyan Testing Technology Co., Ltd. for their support in experimental analysis.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wang, D.-H.; Chen, Y.-C.; Chen, Z.-H.; Liu, S.-B.; Xu, J.-X.; Zhang, J.-J.; Zeng, Z.-L.; Chen, F.-W.; Li, H.-Q.; Guo, C.-L. Assessment on Mineral Resource in Nanling Region and Suggestion for Further Prospecting. *Acta Geol. Sin.* **2007**, *7*, 82–890.
2. Chen, Y.-C.; Wang, D.-H.; Xu, Z.-G.; Huang, F. Outline of Regional Metallogeny of Ore Deposits Associated with the Mesozoic Magmatism in South China. *Geotecton. Metallog.* **2014**, *2*, 219–229.
3. Yuan, S.-D.; Williams-Jones, A.; Romer, R.; Zhao, P.-L.; Mao, J.-W. Protolith-Related Thermal Controls on the Decoupling of Sn and W in Sn-W Metallogenic Provinces: Insights from the Nanling Region, China. *Econ. Geol.* **2019**, *5*, 1005–1012. [CrossRef]
4. Wang, D.-H.; Huang, F.; Wang, Y.; He, H.-H.; Li, X.-M.; Liu, X.-X.; Sheng, J.-F.; Liang, T. Regional metallogeny of Tungsten-tin-polymetallic deposits in Nanling region, South China. *Ore Geol. Rev.* **2020**, *120*, 103305. [CrossRef]
5. Wu, F.-Y.; Guo, C.-L.; Hu, F.-Y.; Liu, X.-C.; Zhao, J.-X.; Li, X.-F.; Qin, K.-Z. Petrogenesis of the highly fractionated granites and their mineralizations in Nanling Range, South China. *Acta Petrol. Sin.* **2023**, *1*, 1–36. [CrossRef]
6. Hou, Z.-D.; Zhao, Z.; Liu, Z.-J.; Wang, J.-P. Metallogenetic regularity and prospecting direction of granite related Li-Be-Nb-Ta deposits in the Nanling region, South China. *Acta Petrol. Sin.* **2023**, *7*, 1950–1972. [CrossRef]
7. Mao, J.-W.; Li, H.-Y.; Guy, B.; Raimbault, L. Geology and Metallogeny of the Shizhuyuan Skarn-Greisen W-Sn-Mo-Bi Deposit, Hunan Province. *Miner. Depos.* **1996**, *1*, 1–15.
8. Mao, J.-W.; Li, X.-F.; Lehmann, B.; Chen, W.; Lan, X.-M.; Wei, S.-L. ⁴⁰Ar-³⁹Ar Dating of Tin Ores and Related Granite in Furong Tin Orefield, Hunan Province, and Its Geodynamic Significance. *Miner. Depos.* **2004**, *2*, 164–175.
9. Chen, Y.-X.; Li, H.; Sun, W.-D.; Ireland, T.; Tian, X.-F. Generation of Late Mesozoic Qianlishan A2-type granite in Nanling Range, South China: Implications for Shizhuyuan W-Sn mineralization and tectonic evolution. *Lithos* **2016**, *266–267*, 435–452. [CrossRef]
10. Gong, X.; Wei, X.-Y.; Zhao, Y.-Y.; Liu, C.-H.; Shui, X.-F.; Du, L.; Song, X.-J.; Gun, M.-S.; Tan, W. LA-ICP-MS Analysis of Pyrite from Hulalin Gold Deposit in the Upper Heilongjiang Basin and its Implication on Genesis of the Deposit. *Geotecton. Metallog.* **2021**, *4*, 745–760.
11. Yuan, S.-D.; Mao, J.-W.; Cook, N.-J.; Wang, X.-D.; Liu, X.-F.; Yuan, Y.-B. A Late Cretaceous tin metallogenic event in Nanling W-Sn metallogenic province: Constraints from U-Pb, Ar-Ar geochronology at the Jiepailing Sn-Be-F deposit, Hunan, China. *Ore Geol. Rev.* **2015**, *65*, 283–293. [CrossRef]
12. Xie, L.; Wang, R.-C.; Chen, X.-D.; Huang, F.-F.; Erdmann, S.; Zhang, W.-L. Tracking magmatic and hydrothermal Nb-Ta-W-Sn fractionation using mineral textures and composition: A case study from the late Cretaceous Jiepailing ore district in the Nanling Range in South China. *Ore Geol. Rev.* **2016**, *78*, 300–321. [CrossRef]
13. Lei, Z.-H.; Wang, X.-F.; Qiao, Y.-S.; Xu, Y.-M.; Liu, Y.-X. Geological Characteristic and Metallogeny of Jiepailing Tin Polymetallic Deposit in Yizhang, South Hunan Province. *South China Geol.* **2009**, *3*, 43–50.
14. Wang, Y.-L.; Peng, Q.-M.; Zhu, X.-Y.; Cheng, X.-Y.; Li, S.-T. Geochemical and Chronological Characteristics of the Granite Porphyry in the Jiepailing Tin-Polymetallic Deposit, Hunan Province and Mineralization Belt Division. *Geol. Explor.* **2014**, *3*, 475–485.
15. Lin, X.-Q.; Rao, C.; Qin, L.-Q.; Wu, R.-Q.; Wang, Q. Alteration processes and rare(earth) metal mineralization of jiepailing porphyry deposit, Hunan Province. *J. Nanjing Univ. (Nat. Sci.)* **2020**, *6*, 830–846.
16. Zhou, X.-T.; Qin, Y.-J. Geological characteristics and genesis of Jiepailing fluorite deposit in Yizhang County of Hunnan. *Miner. Resour. Geol.* **2020**, *1*, 33–40.
17. Tian, Y.; Zhu, X.-Y.; Zhang, Y.-J.; Jiao, S.-T.; Sun, Y.-L.; Liu, X.; Jiang, B.-B. Emplacement and metallogenic model of the Jiepailing tin polymetallic metals depsoit in Hunan. *Miner. Explor.* **2016**, *1*, 126–135.

18. Xu, R.-C.; Long, X.-R.; Liu, B.; Liu, Y.-G.; Wu, Q.-H.; Luo, X.-Y.; Jiang, H. LA-ICP-MS trace element analysis of fluorite and implications in Jiepailling tinpolymetallic deposit from South of Hunan Province. *Miner. Depos.* **2022**, *1*, 158–173.
19. Lu, Y.-Y.; Fu, J.-M.; Cheng, S.-B.; Ma, L.-Y.; Zhang, K. SHRIMP zircon U-Pb geochronology of the ore-bearing granite porphyry in the Jiepailling Tin polymetallic deposit, Southern Hunan province. *South China Geol.* **2013**, *3*, 199–206.
20. Mao, J.-W.; Xie, G.-Q.; Guo, C.-L.; Chen, Y.-C. Large-scale tungsten-tin mineralization in the Nanling region, South China: Metallogenic ages and corresponding geodynamic processes. *Acta Petrol. Sin.* **2007**, *10*, 2329–2338.
21. Yu, A.-N. Study on coal prospecting and remote sensing geologic interpretation in the periphery of Meitanba, Ningxiang. *Hunan Geol.* **1992**, *11*, 7–10.
22. Zhou, T.-F.; Zhang, L.-J.; Yuan, F.; Fan, Y.; Cooke, D. LA-ICP-MS in situ trace element analysis of pyrite from the Xinqiao Cu-Au-S Deposit in Tongling, Anhui, and its constraints on the ore genesis. *Earth Sci. Front.* **2010**, *2*, 306–319.
23. Tsang, H.; Cao, J.Y.; Yang, X.Y. Source of the Chaoyangzhai Gold Deposit, Southeast Guizhou: Constraints from LA-ICP-MS Zircon U-Pb Dating, Whole-rock Geochemistry and In Situ Sulfur Isotopes. *Minerals* **2019**, *9*, 235. [CrossRef]
24. Zhao, X.-Y.; Yang, Z.-S.; Zhang, X.; Pei, Y.-R. In Situ Trace Element Analysis of Pyrite from Bangbu Orogenic Gold Deposit and Its Metallogenic Significance. *Earth Sci.* **2019**, *6*, 2052–2062.
25. Cao, J.Y.; Yang, X.Y.; Zhang, D.X.; Yan, F.B. In situ trace elements and Sr isotopes in scheelite and S-Pb isotopes in sulfides from the Shiweidong W-Cu deposit, giant Dahutang ore field: Implications to the fluid evolution and ore genesis. *Ore Geol. Rev.* **2020**, *125*, 103696. [CrossRef]
26. Leng, C.-B. Genesis of Hongshan Cu polymetallic large deposit in the Zhongdian area, NW Yunnan: Constraints from LAICPMS trace elements of pyrite and pyrrhotite. *Earth Sci. Front.* **2017**, *6*, 162–175.
27. Lin, Z.-W.; Zhao, X.-F.; Xiong, L.; Zhu, Z.-X. In-situ Trace Element Analysis Characteristics of Pyrite in Sanshandao Gold Deposit in Jiaodong Peninsula: Implications for Ore Genesis. *Adv. Earth Sci.* **2019**, *4*, 399–413.
28. Cao, J.Y.; Lu, Y.Y.; Liu, L.; Fu, J.M.; Xu, G.F.; Wu, Q.H.; Yang, S.X.; Qiu, X.F.; Zhang, Z.Z. Insights into the Crustal Evolution and Tungsten Mineralization of the West Cathaysia Block: Constraints from the Inherited Zircons from the Mesozoic Dengfuxian and Paleozoic Tanghu Plutons, South China. *Minerals* **2023**, *13*, 550. [CrossRef]
29. Mao, J.-W.; Chen, M.-H.; Yuan, S.-D.; Guo, C.-L. Geological Characteristics of the Qinhang (or Shihang) Metallogenic Belt in South China and Spatial-Temporal Distribution Regularity of Mineral Deposits. *Acta Geol. Sin.* **2011**, *5*, 636–658.
30. Liu, Y.-S.; Hu, Z.-C.; Gao, S.; Gunther, D.; Xu, J.; Gao, C.-G.; Chen, H.-H. In situ analysis of major and trace elements of anhydrous minerals by LA-ICP-MS without applying an internal standard. *Chem. Geol.* **2008**, *1–2*, 34–43. [CrossRef]
31. Jochum, K.P.; Weis, U.; Stoll, B.; Kuzmin, D.; Yang, Q.-C.; Raczek, I.; Jacob, D.E.; Stracke, A.; Birbaum, K.; Frick, D.A.; et al. Determination of reference values for NIST SRM 610-617 glasses following ISO guidelines. *Geostand. Geoanal. Res.* **2011**, *4*, 397–429. [CrossRef]
32. Wu, S.-T.; Wörner, G.; Jochum, K.P.; Stoll, B.; Simon, K.; Kronz, A. The Preparation and Preliminary Characterisation of Three Synthetic Andesite Reference Glass Materials (ARM-1, ARM-2, ARM-3) for In Situ Microanalysis. *Geostand. Geoanal. Res.* **2019**, *4*, 567–584. [CrossRef]
33. Paton, C.; Hellstrom, J.; Paul, B.; Woodhead, J.; Hergt, J. Iolite: Freeware for the visualisation and processing of mass spectrometric data. *J. Anal. At. Spectrom.* **2011**, *12*, 2508–2518. [CrossRef]
34. Chu, G.-B.; Chen, H.-Y.; Zhang, S.-T.; Zhang, Y.-C.; Jia, M. Geochemistry and geochronology of multi-generation garnet: New insights on the genesis and fluid evolution of prograde skarn formation. *Geosci. Front.* **2023**, *1*, 101495. [CrossRef]
35. Reich, M.; Deditius, A.; Chrysosoulis, S.; Li, J.-W.; Ma, C.-Q.; Parada, M.A.; Barra, F.; Mittermayr, F. Pyrite as a record of hydrothermal fluid evolution in a porphyry copper system: A SIMS/EMPA trace element study. *Geochim. Cosmochim. Acta* **2013**, *3*, 42–62. [CrossRef]
36. Hu, X.-K.; Tang, L.; Zhang, S.-T.; Santosh, M.; Spencer, C.J.; Zhao, Y.; Cao, H.-W.; Pei, Q.-M. In situ trace element and sulfur isotope of pyrite constrain ore genesis in the Shapoling molybdenum deposit, East Qinling Orogen, China. *Ore Geol. Rev.* **2019**, *2*, 123–136. [CrossRef]
37. Bi, S.-J.; Li, Z.-K.; Tang, K.-F.; Gao, K. LA-ICP-MS In Situ Trace Element Analysis of Pyrite from Dongtongyu Gold Deposit and Its Metallogenic Significance, Xiaoqinling Gold District. *Earth Sci.* **2016**, *7*, 1121–1140.
38. Ma, J.; Lv, X.-B.; Dan, R.-F.; Zhu, D.-Y.; Lu, F.; Yuan, B.; Yin, X. Ore genesis of the Zuoqiazhuang gold deposit in the West Qinling Orogen: constraints from pyrite trace elements and multi-isotope analyses. *Earth Sci. Front.* **2019**, *5*, 146–162.
39. Large, R.R.; Danyushevsky, L.; Hollit, C. Gold and Trace Element Zonation in Pyrite Using a Laser Imaging Technique: Implications for the Timing of Gold in Orogenic and Carlin-Style Sediment-Hosted Deposits. *Econ. Geol.* **2009**, *5*, 635–668. [CrossRef]
40. Belousov, I.; Large, R.R.; Meffre, S.; Danyushevsky, L.V.; Steadman, J.; Beardsmore, T. Pyrite compositions from VHMS and orogenic Au deposits in the Yilgarn Craton, Western Australia: Implications for gold and copper exploration. *Ore Geol. Rev.* **2016**, *79*, 474–499. [CrossRef]

41. Fan, H.-R.; Li, X.-H.; Zuo, Y.-B.; Chen, L.; Liu, S.; Hu, F.-F.; Feng, K. In-situ LA-(MC)-ICPMS and (Nano) SIMS trace elements and sulfur isotope analyses on sulfides and application to confine metallogenic process of ore deposit. *Acta Petrol. Sin.* **2018**, *12*, 3479–3496.
42. Wang, M.-Y.; Li, J.; Song, M.-C.; Zhang, L.-P.; Tang, Z.-Y.; Ding, Z.-J. The metallogenic mechanism of the Dadengge gold polymetallic deposit in the Jiaodong Peninsula: Constraints from pyrite Rb-Sr dating, in situ S isotope and trace elements. *Acta Petrol. Sin.* **2023**, *5*, 1501–1515. [CrossRef]
43. Wu, T.; Huang, Z.-L.; Xiang, Z.-Z.; Ye, L.; Sui, Z.-H.; Hu, Y.-S.; Yan, Z.-F. In situ trace element study of pyrites from the Danaopo super-large Pb-Zn deposit in the western Hunan, China. *Acta Mineral. Sin.* **2020**, *4*, 430–440.
44. Luan, Y.; Wang, R.-T.; Qian, Z.-Z.; Sun, X.-H.; Zheng, C.-Y.; Zhang, T.-Y.; Ding, K. Genesis of Tongchang Copper-Iron Deposit in Mian-Lue-Ning Area: Constraints from Re-Os Isotopic Dating of Chalcopyrite and In-Situ Sulfur Isotope Compositions of Sulfides. *Earth Sci.* **2022**, *1*, 259–276.
45. Zhang, J.; Ding, Z.; Bo, J.; Ji, P.; Li, T.; Xin, W. In Situ Trace Element and S-Pb Isotope Study of Pyrite from the Denggezhuang Gold Deposit in the Jiaodong Peninsula—Insights into the Occurrence of Gold and the Source of Ore-Forming Materials. *Minerals* **2024**, *14*, 158. [CrossRef]
46. Suo, Q.-Y.; Li, C.-H.; Shen, P.; Zhao, J.-K.; Chu, X.-K. Superimposed mineralization of the Duobaoshan Cu (Mo) deposit in Heilongjiang Province: Indicated by the molybdenite Re-Os isotopic dating and sulfur isotope composition. *Acta Petrol. Sin.* **2023**, *11*, 3479–3490. [CrossRef]
47. Liu, B.; Chen, W.-F.; Fang, Q.-C.; Tang, X.-S.; Mao, Y.-F.; Sun, L.-Q.; Gao, S.; Yan, Y.-J.; Wei, X.; Ling, H.-F. Study on In-Situ Sulfur Isotope Compositions of Sulfides: Implication for the Source of Pb-Zn Mineralized Body of Niutoushan in the Xiangshan Area. *Earth Sci.* **2020**, *2*, 389–399.
48. Cai, G.-Y.; An, F.; Yuan, Y.; Liu, F.; Liu, W.; Zhang, J.-B. Ore-forming material source and metallogenic mechanism of NE-oriented pyrite-quartz veins in the Baguamiao gold deposit, Shaanxi Province: Evidence from in situ S isotope. *Acta Geol. Sin.* **2021**, *5*, 1561–1572.
49. Li, H.-L.; Li, G.-M.; Ding, J.; Zhang, Z.; Qin, C.-S.; Fu, J.-G.; Ling, C.; Liu, Y.-Q. Genesis of Zhaxikang Pb-Zn Polymetallic Deposit in Southern Tibet: Evidence from in Situ S Isotopes of Sulfides. *J. Jilin Univ. (Earth Sci. Ed.)* **2020**, *5*, 1289–1303.
50. Du, Z.-Z.; Yu, X.-F.; Sun, H.-R.; Du, Y.-L.; Kang, K. Genesis of the Huaniushan Pb-Zn-Ag deposit in Gansu: Constraints from in situ S, Pb isotopes and trace elements. *Acta Petrol. Sin.* **2021**, *6*, 1813–1842.
51. Li, H.-K.; Li, G.-M.; Zhang, Z.; Zhang, L.-K.; Dong, S.-L.; Qin, C.-S.; Li, Y.-X. Genesis of Jienagepu Gold Deposit in Zhaxikang Ore Concentration Area, Eastern Tethys Himalayas: Constraints from He-Ar and In-Situ S Isotope of Pyrite. *Earth Sci.* **2021**, *12*, 4291–4315.
52. Shang, Q.; Ren, F.; Yang, Q.; Wang, B. In Situ Compositional and Sulfur Isotopic Analysis of Sphalerite from the Erdaodianzi Gold Deposit in Southern Jilin Province, Northeast China. *Minerals* **2025**, *15*, 57. [CrossRef]
53. Ohmoto, H. Stable isotope geochemistry of ore deposits. *Rev. Mineral. Geochem.* **1986**, *1*, 491–559.
54. Chaussidon, M.; Lorand, J.P. Sulphur isotope composition of orogenic spinel lherzolite massifs from Ariège (North-Eastern Pyrenees, France): An ion microprobe study. *Geochim. Cosmochim. Acta* **1990**, *10*, 2835–2846. [CrossRef]
55. Ohmoto, H. Systematics of Sulfur and Carbon Isotopes in Hydrothermal Ore Deposits. *Econ. Geol.* **1972**, *5*, 551–578. [CrossRef]
56. Rye, R.O.; Ohmoto, H. Sulfur and Carbon Isotopes and Ore Genesis: A Review. *Econ. Geol.* **1974**, *6*, 826–842. [CrossRef]
57. Seal, R.R. Sulfur Isotope Geochemistry of Sulfide Minerals. *Rev. Mineral. Geochem.* **2006**, *1*, 633–677. [CrossRef]
58. Bachinski, D.J. Bond Strength and Sulfur Isotopic Fractionation in Coexisting Sulfides: A Reply. *Econ. Geol.* **1969**, *8*, 56–65. [CrossRef]
59. Zheng, Y.-F.; Xu, B.-L.; Zhou, G.-T. Geochemical studies of stable isotopes in minerals. *Earth Sci. Front.* **2000**, *2*, 299–320.
60. Zhang, G.-L.; Tian, T.; Wang, R.-T.; Gao, W.-H.; Chang, Z.-D. Pb isotopic composition of the Dongtangzi Pb–Zn deposit in the Fengtai ore concentration area of Shaanxi Province for tracing sources of ore-forming materials. *Geol. China* **2020**, *2*, 472–484.
61. Zhao, W.-C.; Zhu, X.-Y.; Wang, S.-L.; Jiang, B.-B.; Liu, Z.; Guan, Y.-C. Sulfur and lead isotopic compositions of ores from the Dengying Formation and their prospecting implications in the Huize Pb-Zn deposit, Yunnan Province. *Sediment. Geol. Tethyan Geol.* **2023**, *1*, 156–167.
62. Chen, M.-H.; Zhang, Z.-Q.; Santosh, M.; Dang, Y.; Zhang, W. The Carlin-type gold deposits of the “golden triangle” of SW China: Pb and S isotopic constraints for the ore genesis. *J. Asian Earth Sci.* **2015**, *1*, 115–128. [CrossRef]
63. Bralial, A.; Sabatini, G.; Troja, F. A Revaluation of the Co/Ni Ratio in Pyrite as Geochemical Tool in Ore Genesis Problems. *Miner. Depos.* **1979**, *3*, 353–374.
64. Deyell, C.L.; Hedenquist, J.W. Trace element geochemistry of enargite in the Mankayan district, Philippines. *Econ. Geol.* **2011**, *8*, 1465–1478. [CrossRef]
65. Chaussidon, M.; Albarède, F. Sheppard SMF. Sulphur isotope variations in the mantle from ion microprobe analyses of microsulphide inclusions. *Earth Planet. Sci. Lett.* **1989**, *2*, 144–156. [CrossRef]

66. Dai, J.-Z.; Gao, J.-S.; Qian, Z.-Z.; Zhang, L.-B.; Zhou, J.-L.; Li, P.; Gao, Y. Geological Characteristics and S Isotopic Compositions of Pyrite from Lianzigou Gold Deposit in Xiaoqinling Area, and Its Genetic Significance. *J. Jilin Univ. (Earth Sci. Ed.)* **2018**, *6*, 1669–1682.
67. Tao, L.-X.; Zhen, S.-M.; Bai, H.-J.; Wang, J.; Wang, D.-Z.; Zha, Z.-J. Pyrite Trace Element Composition and S-Pb Isotope Characters of the Dabaiyang Gold Deposit, Hebei Province. *J. Jilin Univ. (Earth Sci. Ed.)* **2020**, *5*, 1582–1598.
68. Liu, W.-H.; Li, H.-L.; Li, Y.; Dai, T.-G. Geological, geochemical characteristics of the Jiepailing tin deposit and its genetic type. *Miner. Resour. Geol.* **2006**, *20*, 327–333.
69. Xu, Y.-F.; He, W.-B.; An, F.; Cai, G.-Y. In situ S-Pb isotopes study of Baguamiao gold deposit, western Qinling: Constraints on its ore-forming material sources and metallogenic process. *Miner. Depos.* **2023**, *4*, 773–790.
70. Ye, L.; Gao, W.; Yang, Y.-L.; Liu, T.-G.; Peng, S.-S. Trace elements in sphalerite in Laochang Pb-Zn polymetallic deposit, Lancang, Yunnan Province. *Acta Petrol. Sin.* **2012**, *5*, 1362–1372.
71. Maslennikov, V.V.; Maslennikova, S.P.; Large, R.R.; Danyushevsky, L.V. Study of Trace Element Zonation in Vent Chimneys from the Silurian Yaman-Kasy Volcanic-Hosted Massive Sulfide Deposit (Southern Urals, Russia) Using Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS). *Econ. Geol.* **2009**, *8*, 1111–1141. [CrossRef]
72. Sheng, J.-F.; Li, Y.; Fan, S.-Y. A Study of minor elements in minerals from polymetallic deposits in the central part of the Da Hinggan mountains. *Miner. Depos.* **1999**, *2*, 57–64.
73. Bajwah, Z.U.; Seccombe, P.K.; Offler, R. Trace element distribution, Co:Ni ratios and genesis of the Big Cadia iron-copper deposit, New South Wales, Australia. *Miner. Depos.* **1987**, *22*, 292–303. [CrossRef]
74. Chen, W.-D. Geologic features of Jiepailing tin-polymetallic deposit, Yizhang county. *Hunan Geol.* **1989**, *2*, 35–40.
75. Tan, Y.-J. The ore-forming mechanism of Lianhuashan porphyry tungsten deposit. *Sci. Sin. (Chim.)* **1985**, *6*, 563–570.
76. Xie, Y.-H.; Zhao, R.; Li, R.-M.; Wang, Y.-L. Physical-chemical conditions and material sources for mineralization of the Yinyan porphyry tin deposit. *Miner. Depos.* **1988**, *3*, 42–49.
77. Liu, S.-X. Geological characteristics and mineralization mechanism of the Tashan porphyry tin deposit. *Geochimica* **1992**, *2*, 149–159.
78. Chen, Z.-L.; Zhou, X.-Q.; Yang, N.; Chen, X.-H. Modeling the migration and accumulation of ore-forming elements under high temperatures and pressures. *J. Geomech.* **1996**, *2*, 90–93.
79. Yang, Z.-M.; Hou, Z.-Q.; Song, Y.-C.; Li, Z.-Q.; Xia, D.-X.; Pan, F.Z. Qulong superlarge porphyry Cu deposit in Tibet: Geology, alteration and mineralization. *Miner. Depos.* **2008**, *3*, 279–318.
80. Li, D.-F.; Zhang, L.; Zheng, Y. Fluid inclusion study and ore genesis of the Talate Fe-Pb-Zn deposit in Altay, Xinjiang. *Acta Petrol. Sin.* **2013**, *1*, 178–190.
81. Zhang, D.; Fan, J.-J.; Liu, P.; Pan, A.-J.; Wang, Z.-H.; Zhang, F.; Jin, B.-Y.; Wang, B.; Chao, Y.-Y.; Zhao, J.; et al. Genetic study of porphyry-type deposit in Songkaersu Cu-Au ore district in eastern Junggar, Xinjiang. *Miner. Depos.* **2014**, *2*, 286–306.
82. Liu, S.-Y.; Liu, Y.-P.; Ye, L.; Su, G.-L. A Study on Metallogenic Temperature Field of The Dulong Sn-Zn Polymetallic Deposit. *Acta Mineral. Sin.* **2018**, *3*, 280–289.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Kinetics of Sulfide Dissolution Controlled by Sulfur Radical Diffusion: Implications for Sulfur Transport and Triggering of Volcanic Eruptions

Anastassia Borisova

Géosciences Environnement Toulouse, GET-UMR 5563-OMP-CNRS, 14 Avenue E. Belin, 31400 Toulouse, France; anastassia.borisova@get.omp.eu or anastassiafr@yahoo.fr

Abstract

Chemical mixing of different types of magma, such as basaltic magma and silica-rich, hydrous magma, often triggers volcanic eruptions. However, the kinetics, mechanisms, and rates of sulfide dissolution reactions in hydrous melts are currently unknown, despite the fact that these reactions can influence the sulfur budget in the crust and mantle. I experimentally model dissolution of pyrrhotite minerals in hydrous rhyolite melt at conditions corresponding to the sulfate–sulfide transition field at 1 GPa pressure. The reaction results in the production of FeO, SO_4^{2-} , H_2 , H_2S and di- and tri-sulfur radical ions, (S_2^- or S_3^-) in fluid/melt. The calculated sulfur diffusion coefficient implies extremely fast sulfur diffusion in the hydrous hybrid melt. The production of S-rich magma is controlled by the fastest-ever-recorded chemical diffusion of sulfur in the form of S_2^- or S_3^- in hybrid magma under sulfate-sulfide transition conditions. I demonstrate that such dissolution reactions can be responsible for triggering explosive volcanic eruptions (e.g., the 1991 Mount Pinatubo eruption) in volcanic arc settings. The sulfide dissolution reaction can also promote the production of chalcophile metal (sulfur-loving Au, Cu and Pt) ore deposits associated with the formation of volcanic arcs.

Keywords: sulfur; chemical diffusion; di- and tri-sulfur radical ions; hydrous melt; magma mixing; volcanic eruptions; 1991 Mount Pinatubo volcano eruption; porphyry ore deposits

1. Introduction

Chemical mixing or physical mingling of contrasting types of magmas are principal factors triggering volcanic eruptions [1]. The strongest volcanic eruptions with a VEI (Volcanic Explosivity Index) higher than four, as those produced by Mount Pinatubo in 1991 were (VEI = 5), are triggered by either mixing of hydrous felsic magma with intruding mantle-derived basaltic magma or basaltic underplating, where the basaltic magmas regularly contain Fe-rich sulfide minerals or globules [2–5]. For example, the 1991 Mount Pinatubo eruption liberated 15–19 Mt of sulfur in the form of SO_2 in the terrestrial stratosphere [6] and was associated with triggering by basaltic intrusion [4,7,8]. The release of SO_2 - H_2O -fluid, which may have caused oxidation of the dacitic magma, preceded the 1991 eruption of Mount Pinatubo [4,9]. The liberated sulfur was related to the mixing of basaltic magmas with the overlaying hydrous felsic magma in a shallow reservoir [4,8]. In addition, numerous deep-level mixing events preceding the 1991 eruption were also recorded [10], suggesting deep basaltic underplating or mixing events, possibly at the crust–mantle transition zone. In this study, I experimentally model the interaction of FeS

pyrrhotite as an important sulfur source hosted by mantle-derived basaltic magmas or by deep cumulates at the mantle–crust transition zone, or deep or lower crust with a hydrated silica-rich melt. Thermodynamic modeling of the fluid phase composition and the implication of the sulfur behavior are performed for the plumbing system preceding the 1991 Mount Pinatubo volcanic eruption.

2. Materials and Methods

2.1. Experimental Method

The experiments were performed at 0.5 to 1.0 GPa and 900 and 1000 °C using the “Max Voggenreiter” (Germany) end-loaded Boyd–England piston–cylinder apparatus at the Bavarian Research Institute of Experimental Geochemistry and Geophysics (BGI), Bayreuth, Germany, with conditions and apparatus similar to those used [11,12] (Table S1). The experimental design of the runs included a doubly polished cylinder of pure pyrrhotite mineral (BA-1881-59) [13] in the lower part, and the aluminosilicate powder in the upper part of the Au₈₀Pd₂₀ capsule. The doubly polished pyrrhotite Fe_(1-x)S (x = 0) cylinder was placed together with the powder of the glass or volcanic ash (Table S1). The distilled water^{MQ} was directly introduced into the powder of Macusanite rhyolite glass (sulfur-free) which was previously characterized [14], or into the volcanic ash by micro-syringe. Redox conditions were controlled by sulfate–sulfide transition (Table S1) approaching the NNO mineral buffer (nickel–nickel oxide mineral buffer) at the run temperatures and limited by the intrinsic oxygen fugacity (see below) to allow me to establish redox conditions close to and above the NNO mineral buffer. Talc cells of 3/4 inch diameter with Pyrex sleeves were used. A tapered graphite furnace was inserted into each cell. Alumina (Al₂O₃) spacers were used as the pressure-transmitting medium. The pressure was calibrated using several metamorphic reactions (quartz to coesite transformation and albite = jadeite + quartz [15]). The Au₈₀Pd₂₀ capsule loaded with starting materials was placed in the central part of the assembly. A 20% pressure correction was applied for the friction between the talc cell and pressure vessel [11]. A molybdenum disulfide (MoS₂) lubricant was introduced to minimize friction. The applied 3/4 inch assembly allowed me to obtain a ±0.05 GPa uncertainty. The temperature in the upper part of the capsules was controlled by a EURO THERM (2404) controller and either W₃Re₉₇/W₂₅Re₇₅ (type D) or Pt₆Rh₉₄/Pt₃₀Rh₇₀ (type B) thermocouples accurate to ±0.5 °C. The samples were compressed to 0.5 (or 1.0) GPa for 20 min and then heated up to the run temperature at a rate of 100 °C/min. The samples were maintained at the run conditions for the desired durations. The successful samples were maintained at run conditions (900 and 1000 °C and 1.0 GPa, Table S1) for 30 min. All capsules were quenched by switching off the electrical power. The samples were decompressed after the quenching, over periods ranging from 20 min to 3 h. The quench rate to room temperature was ~300 °C/min.

The intrinsic oxygen fugacity (f_{O_2}) during piston–cylinder runs generally varied between −0.5 and +3 log units, relative to the synthetic fayalite–magnetite–quartz oxygen buffer (i.e., QFM−0.5 to QFM+3) for a piston–cylinder apparatus up to 3 GPa and ~1000 °C [16]. The water-rich runs in this work were performed using a similar experimental technique and capsule material at 1.0 GPa and 1000 °C runs at NNO to NNO+2, based on XANES measurement of Fe²⁺/Fe³⁺ in the quenched glasses [11]. These redox conditions are favorable for the production of sulfur radical species, as S₂[−] and S₃[−] are known to be stable at high temperatures [17,18]. All numerical data are given in Tables S1–S5.

2.2. Micro-Raman and ATR-FTIR Spectroscopy

The background-normalized integrated intensities of SO₄^{2−} contents in the glasses at contact with the reacting pyrrhotite have been obtained with profiles of the experimental

reaction zone by Raman spectroscopy (Figure 1A, Table S2). The Raman spectra were recorded with a HORIBA Jobin Yvon LabRAM HR800 Vis Raman spectrometer (Taiwan) (grating 1800 lines/mm, focal length 800 mm, confocal pinhole 1000 μm , slit aperture 100 μm), equipped with a Synapse back-illuminated CCD detector (2048 $\times$ 512 pixels) and an Olympus BXFM microscope with a motorized XYZ sample stage in CEMES laboratory, Toulouse. The unpolarized spectra were acquired with backscattering geometry, using an Olympus SLMPlan N 20 $\times$ objective (Japan) with a working distance of 25 mm [18] and a COBOLT BluesTM DPSS laser (Sweden) (wavelength 473 nm, power stability).

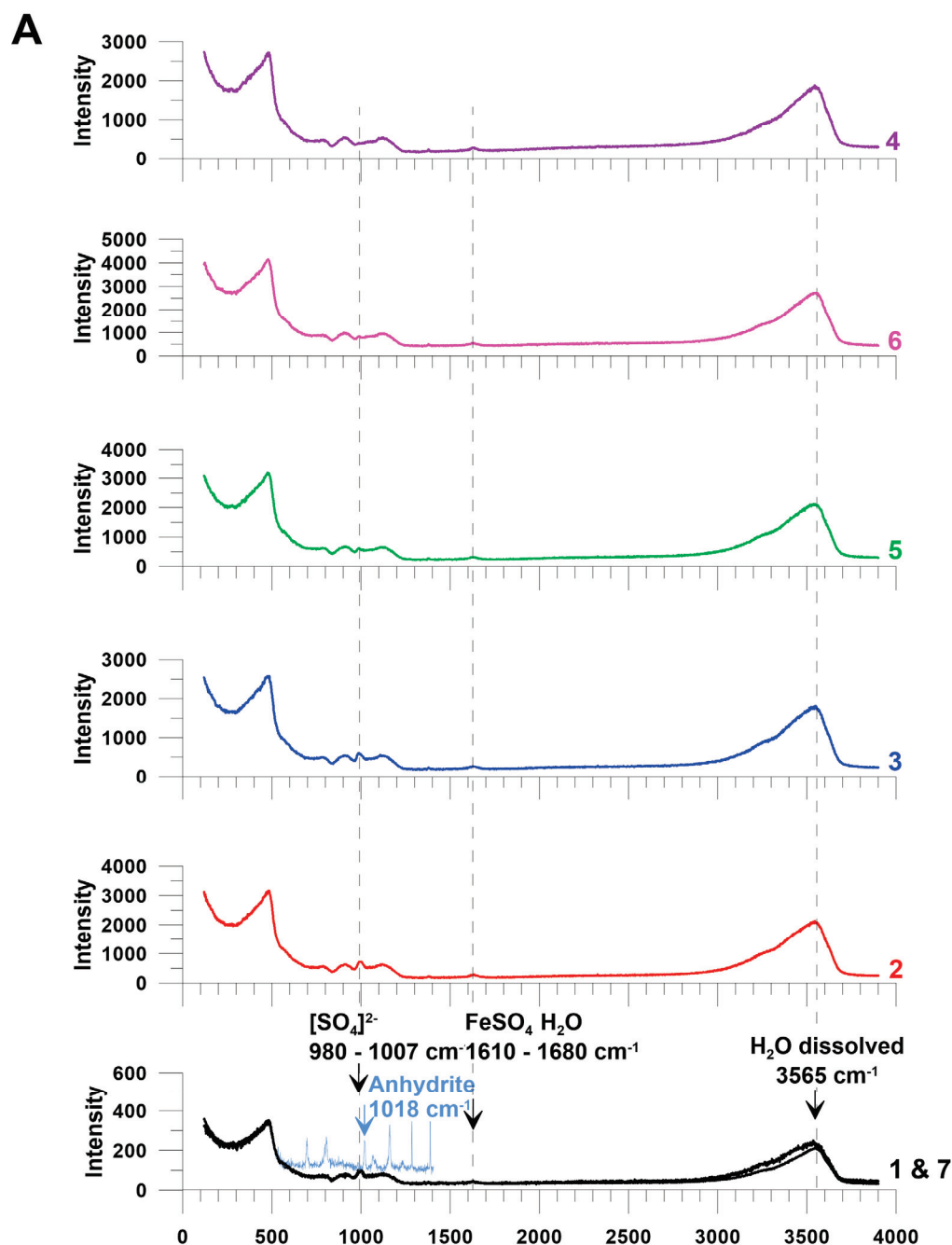


Figure 1. Cont.

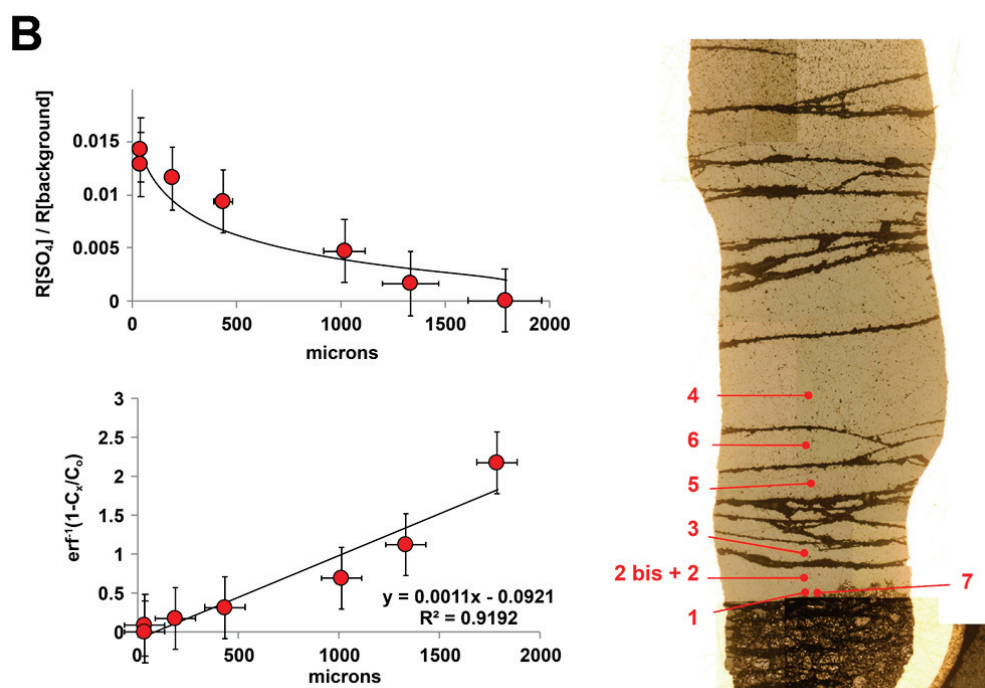


Figure 1. (A) Raman spectra with visible peaks of 980 to 1007 cm^{-1} , 1610 to 1680 cm^{-1} and 3565 cm^{-1} correspond to the dissolved $[\text{SO}_4^{2-}]$ and $[\text{FeSO}_4 \cdot \text{H}_2\text{O}]$ as well as dissolved H_2O in hydrous rhyolitic glass of the PS3 sample. Micro-Raman peak of anhydrite-bearing inclusion is afterwards [8]. (B) Background-normalized integrated Raman peak intensity of SO_4^{2-} and $\text{erf}^{-1}(1 - C_x/C_0)$, where C_x is micro-Raman intensity and C_0 is the intensity at the interface with pyrrhotite in the experimental sample, imaged using optical microscope. This allows extraction of diffusion coefficient of the bulk S species identified in hydrous rhyolitic glasses by micro-Raman spectroscopy. The diffusion coefficient extracted from the profile corresponds to $1.06 \times 10^{-10}\text{ m}^2/\text{s}$ at $900\text{ }^\circ\text{C}$, 1 GPa , and $\sim 9\text{ wt\% H}_2\text{O}$ in the rhyolitic melt. The data are summarized in the Tables S1–S3.

The Attenuated Total Reflectance (ATR) micro-FTIR technique by Thermo (Nicolet iN10) (Waltham, MA, USA) requires only a singly polished sample for quantitative results. The maximal absorbance on the peak of 3500 cm^{-1} peak was used for the H_2O quantification [19]. The H_2O contents were calibrated based on the background-subtracted absorbance on peaks of 3500 cm^{-1} using three reference glasses of rhyolitic composition (Macusanite) [13] with different water content (0.1 to $6\text{ wt\% H}_2\text{O}$). Because the same rhyolitic glasses were applied in the runs, no density correction was applied for the calibration. The calibration was extrapolated to $\sim 9\text{ wt\% H}_2\text{O}$, assuming the same trend of the water absorbance intensity versus the glass water contents. In addition, the high H_2O contents below the water fluid saturation obtained by micro-FTIR are in good agreement with the bulk water contents and the approximate estimations, based on the electron probe analysis (Tables S1 and S3).

2.3. Electron Probe Microanalysis

Microanalyses of major and minor element contents in the experimental minerals and glasses and the experimental sample imaging were performed at the Géosciences Environnement Toulouse (GET, Toulouse, France) laboratory (Table S3). The main experimental phases in the samples have been identified by using a scanning electron microscope (SEM) JEOL JSM-6360 LV microprobe technique (Japan) at GET (Toulouse, France) [11]. Major and minor element compositions of the crystals and glasses were analyzed using a CAMECA SX-Five microprobe (France) at the Centre de Microcaractérisation Raimond Castaing (Toulouse, France). An electron beam of 15 kV accelerating voltage and of 20 nA

current was defocused on the glass sample to give an analytical lateral resolution of $5\ \mu\text{m}^2$. The following synthetic and natural standards were used for calibration: albite (Na), corundum (Al), wollastonite (Si, Ca), sanidine (K), pyrophanite (Mn, Ti), hematite (Fe), periclase (Mg), tugtupite (Cl), and celestine-MAC10617 (S). Element and background counting times for most analyzed elements were 10 and 5 s, respectively, and 60 s for S and 30 s for the background. The detection limits for S and Cl in the felsic glasses were of about 200 ppm. The silicate reference materials such as NIST SRM-610 and other reference glasses [20,21], were analyzed as unknown samples to additionally monitor the analysis accuracy. The silicate reference material analysis allowed me to control precision for the major and minor (e.g., S, Cl in glasses) element analyses to be within the limit of the analytical uncertainty (related to the count statistics). The accuracy estimated for the reference glasses ranges from 0.5% to 3% (1σ RSD = relative standard deviation), depending on the element contents in the reference glasses.

2.4. Thermodynamic Modeling

To assess the sulfur content in the aqueous fluid produced by pyrrhotite dissolution, and thus, to estimate its potential role in the transport and fractionation of the elements in experimental systems, the thermodynamic equilibrium calculations in the FeS-to-FeO melt-fluid system (Equation (4)) were applied. The calculations were conducted at a temperature of up to 1000 °C, redox conditions of NNO and above NNO and pressure up to 1.0 GPa. Table S5 summarizes the predicted dissolved sulfur concentrations in the aqueous fluid phase, depending on the pH in the fluid and FeO in the melt. The calculations were performed using the current version 4.6 of HCh software package and the associated Unitherm database, allowing chemical equilibrium predictions in multicomponent fluid-mineral systems. This approach is based on the minimization of the Gibbs free energy of the system [22], while accounting for non-ideality of the species in aqueous solution by using the extended Debye-Hückel equation [23]. The thermodynamic properties of the end members of FeS and FeO phases were adopted from [24] (HP11 database) and the thermodynamic models [22,24] were used. In the absence of an appropriate thermodynamic model, using solid FeO instead of FeO in the melts ($\alpha_{\text{FeO}} < 1$) is currently the only way to calculate our large range of elements and temperature-pressure-composition conditions in the presence of an aqueous fluid. The uncertainties of such predictions are dependent on FeO content in the hybrid melt and the pH in the fluid (Table S5). Nevertheless, these uncertainties are much lower compared to the extremely large range of the predicted solubility for sulfur. Therefore, I am confident that my calculations provide a robust first-order estimate of concentrations and relative abundances in the aqueous fluids formed during FeS dissolution under the applied experimental conditions.

3. Results

Sulfide Dissolution Reactions and the Reaction Products

The performed experimental runs modeled the reaction of a pure pyrrhotite mineral with a hydrous melt and production of S-rich magma (Table S1). The first two preliminary runs at 0.5 GPa were initiated at run temperatures but were promptly terminated and quenched, due to the presence of a strong hydrogen sulfide (H_2S) odor in the liberated fluid. This was likely caused by leakage of the capsule and cooling of the sulfur-bearing fluid, which escaped from the capsule due to an excess of the fluid phase.



or



These two preliminary runs at 0.5 GPa record the H_2S liberation upon the reaction. Subsequently, I increased the pressure and performed the successful runs with the same starting materials at 1.0 GPa for 30 min (Table S1). The successful runs at 1.0 GPa (PS3, PS4) (Table S1) demonstrate the presence of pyrrhotite, quenched hydrous glass, and anhydrite crystals at the interface between the two in the PS4 run sample, whereas the PS3 sample contains only the glass and the pyrrhotite. The micro-size anhydrite crystals were identified by the scanning electron microscope (SEM) (JEOL, Japan) uniquely at the interface between the glass and the reacted pyrrhotite in the PS4 sample.

In the quenched hydrous glasses of these runs, I observed the Raman peaks of 980 to 1007 cm^{-1} corresponding to species of SO_4^{2-} (Figure 1A,B, Tables S1 and S2). The important point is that the large Raman SO_4^{2-} peaks in the rhyolitic glasses of the PS3 sample are different from the characteristic peak of anhydrite of 1018 cm^{-1} , suggesting that there was no contamination of the quenched glass with the anhydrite crystals. All analyzed hydrous glasses recorded the peaks (from 1610 to 1680 cm^{-1}) similar to the peak of 1648 cm^{-1} for the solid phase of $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ [25], which is interpreted as a solid species of $[\text{FeSO}_4 \text{H}_2\text{O}]$ as possible nanoscale Fe-S-(Au-Pd)-nuggets, related to the quenching effect. All spectra demonstrate the broad peak of the dissolved H_2O (around 3565 cm^{-1}), similar to the natural glasses hosted by quartz [8].

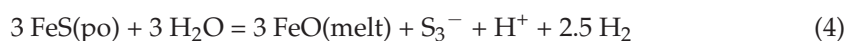
4. Discussion

Sulfur Diffusion and Speciation in Hybrid System

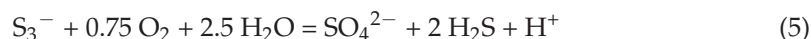
To calculate the sulfur diffusion coefficients at 900°C and 1.0 GPa and 8.9 wt% $\text{H}_2\text{O}_{\text{melt}}$, I have applied the diffusion extraction method based on the sulfur concentration profiles in the glasses, perpendicular to the interface between the pyrrhotite mineral and quenched glass [26,27]. Figures 1B and 2A demonstrate that the calculated diffusion rate of the sulfur species at 1.0 GPa and 900°C based on the Raman intensities of the SO_4^{2-} species ($1.1 \times 10^{-10} \text{ m}^2/\text{s}$) is similar to the SO_3 diffusion coefficient ($2.6 \times 10^{-10} \text{ m}^2/\text{s}$) extracted from the SO_3 wt% analysis by electron probe microanalysis (EPMA). This suggests extremely fast sulfur diffusion, as S-bearing species dissolved in the hydrous rhyolite melt. Importantly, high-pressure and high-temperature species of S_2^- and S_3^- were recorded in situ at the conditions of sulfate-to-sulfide transition during the high-temperature pressure experiment by diamond anvil cells [17,18] and specific oxygen fugacity of NNO and above the nickel-nickel oxide buffer, which is the case for this study of pyrrhotite dissolution experiments. The S_2^- and S_3^- species existing at high temperature were transformed to H_2S upon cooling, explaining the strong odor of H_2S in the two initial runs of the common configuration. In the performed experimental runs (Table S1), the recorded H_2S in the liberated fluid of the first runs (Equations (1) and (2)), as well as SO_4^{2-} identified here by micro-Raman spectroscopy in the hydrous glasses, suggest the following reactions:



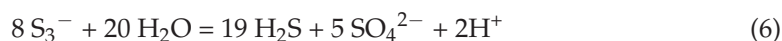
and



and



or

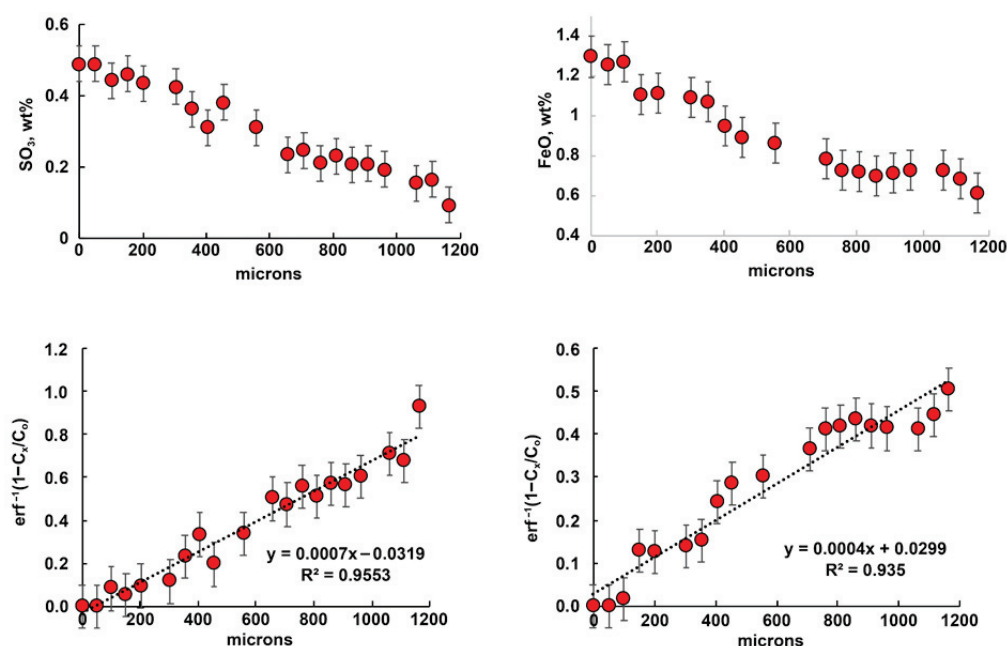


and



at 900–1000 °C and 1.0 GPa pressure, where FeS(po) is pyrrhotite, FeO(melt)—FeO and SO_4^{2-} and H_2S , and H_2 and S_2^- , S_3^- components of the hydrous felsic melt or fluid. H_2O is H_2O dissolved in the hydrous melt and can be the fluid phase at conditions of fluid saturation. These reactions are also confirmed by the similar behaviors of SO_3 (or SO_4^{2-}) and FeO contents in the interface glass measured by electron probe microanalysis, EPMA (Figure 2A).

A



B

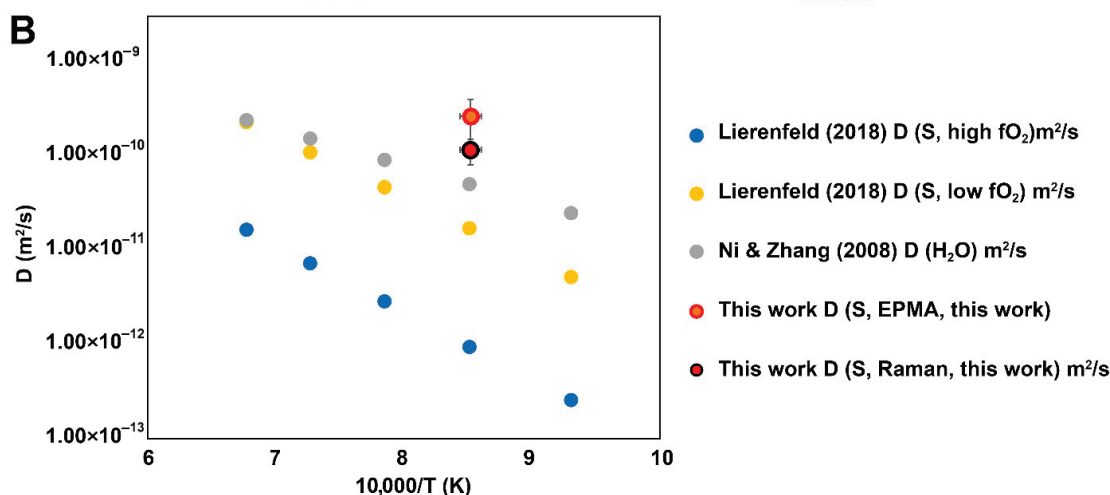


Figure 2. (A) Modeling of the bulk S and Fe diffusion in hydrous rhyolitic melt based on SO_3 and FeO (wt%) contents in the glasses measured by EPMA at the interface with pyrrhotite. SO_3 and FeO wt% contents and erf^{-1} function versus the distance from the interface (in μm) are plotted. The bulk sulfur diffusion coefficient extracted from the EPMA profile corresponds to $2.62 \times 10^{-10} \text{ m}^2/\text{s}$ at 900 °C, 1 GPa and 8.9 wt% H_2O in the rhyolitic melt. (B) Diffusion coefficients of sulfur and water (in m^2/s) versus $10^4/T$ (in K^{-1}), according to the available data on the coefficients at different temperature conditions and new data obtained in this work at 900 °C. The available diffusion data are from [28] (4.5 wt% H_2O) [29] (up to 7.0 wt% H_2O). All numerical data are summarized in Table S4.

The micro-Raman and EPMA data used to quantify the diffusion coefficients are given in Tables S2–S4. According to the slope of 0.004 on the plot of FeO profiles in the rhyolitic glasses at the interface with pyrrhotite and the erf^{-1} error function versus the distance from the interface (in μm) (Table S3), the FeO diffusion is $8.01 \times 10^{-10} \text{ m}^2/\text{s}$, which is slightly faster than the SO_4^{2-} and SO_3 diffusion coefficients (1.06×10^{-10} and $2.62 \times 10^{-10} \text{ m}^2/\text{s}$, respectively, Tables S1 and S4). Nevertheless, Figure 2B, plotted based on these diffusion data, demonstrates that the SO_4^{2-} and SO_3 diffusion coefficients obtained in this work are higher for oxidized and reduced sulfur species [28] and for water [29] in comparison to those of recent data. The sulfur diffusion coefficients for the hydrous melts obtained in this work are much higher than those for water, as well as for reduced and oxidized sulfur species, at 900 °C (equivalent to $10,000/T = 8.5$). These coefficients correspond to the redox conditions of NNO and above NNO at 1 GPa and 900 °C. This indicates the production of sulfur species that have not been investigated before.

Previous S diffusion studies [28] demonstrated that a direct comparison of S and H_2O diffusion reveals that S diffusion is slower than that of H_2O ($\text{H}_2\text{O} \leq 7 \text{ wt}\%$), whereas my new data imply that the oxidized sulfur species can diffuse in highly hydrated melt (9 wt% H_2O) faster than water. This fast S diffusion is controlled by the presence of highly volatile S_3^- and S_2^- radical species. My experiments demonstrate that Fe diffusion is decoupled from the S species diffusion, even in the Fe-rich sulfide dissolution system, suggesting that sulfur speciation is independent from that of Fe. The previous Fe-free experiment-based conclusion [30] states that alkalis are only available for sulfate complexation when they are present in excess, compared to the required amount to charge balance for the Si^{4+} to Al^{3+} substitution in the melt structure. In contrast, [31] hypothesized the presence of $(\text{Fe,Ca})\text{SO}_4 \cdot n\text{H}_2\text{O}$ or $(\text{Na,K})_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ at similar physical-chemical conditions and a similar hydrous system. In the experimental system studied here, the sulfur transport in the hydrous melt is decoupled from water, iron, and alkalis and is related to the sulfur radical species, which have very poor solubility and chemical bonding to the aluminosilicate melt [18], explaining the extremely rapid diffusion of these sulfur species in the hydrous melts.

5. Implications

5.1. Hybrid S-Rich Magma and Its Role in Explosive Eruptions

Hybrid mafic fragments from the 1991 Mount Pinatubo eruption contain Fe-rich sulfide globules [2,3,5]. However, the previously reported high oxidation state of the basaltic magma [32] suggests relatively high oxidation states (NNO+1.4 – NNO+2) of the 1991 Mount Pinatubo magmas. These conditions where sulfide was present and likely dissolved are similar to the experimental out of equilibrium conditions of the pyrrhotite dissolution runs performed here. Based on my experimental runs at 9 wt% $\text{H}_2\text{O}_{\text{melt}}$, the equilibrium S concentrations in the hybrid melt measured at the interface between pyrrhotite and hydrous felsic melt is of 2000 ppm S at 900 °C (Table 1). Similar high concentrations of 1300–2900 ppm S were recorded in the natural dacitic to rhyolitic melt inclusions in the 1991 Mount Pinatubo enclaves of basaltic composition [32], the hybrid andesite [33], and the groundmass glass near the partially dissolved sulfides [34], reflecting hybrid S-rich magma formation in direct relation to the sulfide dissolution and saturation with sulfur.

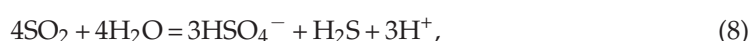
Table 1. Parameters of sulfide dissolution reaction applied to the 1991 Mount Pinatubo eruption.

Parameters	Dissolution Experiment and Thermodynamic Modeling Data		Parameters for the Explosive Eruption	1991 Mount Pinatubo Eruption	
S in FeS	37.7 wt%	377,000 ppm S	Mass of ash (literature) ****	13,000	Mt
SO ₃ melt at the interface	0.5 wt%	2000 ppm S	Mass of aqueous fluid (literature) ****	95	Mt
Fluid S _{thermodynamics}	7.0–20 wt%	70,000–300,000 ppm S			
Fluid SO ₃ *	25 wt%	-	Mass of erupted S	10–13	Mt
Fluid S *** experiment	10 wt%	100,126 ppm S			
K _D (fluid/sulfide) Estimate **		0.2–0.5	Mass of liberated SO ₂ (literature) ****	19–27	Mt
K _D (fluid/melt) ***		50–150			
Model calculations §					
1991 Mount Pinatubo eruption					
Mass of FeS in basalt			25–32		Mt
FeS in the hybrid magma			0.2–0.6		wt%

* Thermodynamically constrained S concentrations in the water fluid (Table S5). ** K_D (fluid/sulfide) estimate is performed based on the fluid/melt partitioning and the thermodynamic modeling (Table S5) constraints. *** K_D (fluid/melt) typical [18,35] for the conditions of the experiments (and the corresponding thermodynamic modeling). **** Literature data [7,36–38]. The maximal K_D (fluid/melt) of 150 is according to the sulfur solubility at NNO, 1 GPa and 950 °C [38]. § Mass balance calculations performed, suggesting that the total mass of the liberated sulfur-bearing fluid is derived from Fe-rich sulfides.

Equation (4) suggests that the equilibrium S content in the hybrid fluid produced by sulfide dissolution in the hydrous aluminosilicate melt is a strong function of the FeO contents in the hybrid melt and pH of the fluid (Table S5). For example, 3 to 5 wt% FeO in the hybrid melt will result in 7 to 20 wt% S in the aqueous fluid (Tables 1 and S5), similar to 3 wt% SO₂ in the 1991 Mount Pinatubo pre-eruptive fluid. Thermodynamic calculations (Table S5) of modeled fluid composition give the fluid sulfur concentrations of 70,000 ppm S, which is similar to the reported in experiments on sulfate–sulfide transition [18] and highly hydrated systems [31]. The maximal sulfur concentrations in the fluid of 300,000 ppm S for the S₂[−] and S₃[−]—bearing systems are estimated here based on high fluid-melt partitioning (K_D) of 50 to 150, which is typical for the sulfate–sulfide transition [18,38]. Indeed, the modeled mass of S in the pre-eruptive fluid is similar to the measured masses of the liberated S in form of SO₂ of the Mount Pinatubo pre-eruptive fluid (Table 1). If the pre-eruptive sulfur is uniquely derived from the dissolution of the Fe-rich sulfides [34], the 1991 Mount Pinatubo eruption related to the magma mixing events [8] could be triggered by such S-rich fluid (Equation (4)). The bulk mass of sulfur in the S-bearing fluid phase produced due to sulfide decomposition may be considerable, provided that all sulfur is derived from the basaltic source (e.g., sulfides). The required percentage of Fe-rich sulfides in the parental basaltic magma is 0.2–0.6 wt% (Table 1). Such sulfide concentrations are in agreement with typical S contents of 900 to 2500 ppm recorded in the primitive arc basalts [38].

In fact, two main stages of the mixing event could happen in the 1991 Mount Pinatubo plumbing system. (1) Previous studies of the 1991 Mount Pinatubo hybrid andesitic and basaltic quartz-hosted fluid inclusions suggest that the following reaction occurred at shallow levels, corresponding to the pressure of 0.3 GPa:



where the reaction yields sulfate, sulfide, and an increase in fluid acidity. The reaction shifts to the right with decreasing temperature. The fact that SO_4^{2-} ion is systematically present in the (pseudo-)secondary $\text{H}_2\text{O}-\text{CO}_2-\text{S}$ fluid inclusions [8] is consistent with the transformation of the supercritical S-rich fluid upon cooling, rather than with post-entrapment modifications within the fluid inclusions.

(2) In addition, an important source of deep sulfur-fluxing periods [10,32] due to dissolution of deep-settled sulfides (e.g., Fe-rich sulfides) could happen as described by reactions (Equations (3)–(7)). Indeed, hybrid S-rich magma was recorded by high S contents (up to 2900 ppm, respectively) into the felsic melt inclusions entrapped in amphiboles of the 1991 Mount Pinatubo basalt [32]. This magma could be formed due to sulfide decomposition during deep mixing events, which could occur at depths of up to 45 km (1.5 GPa), based on the Al_2O_3 content recorded in the quenched melts and those of the host amphiboles [39]. This scenario of deep sulfide dissolution is compatible with the presence of sulfide accumulation layers formed in the lower crust and the mantle–crust transition zone [40,41].

This scenario implies that these S-rich magma-forming reactions, in addition to the previously assumed Equation (8) for the shallow levels, could be related to multiple mixing events with hydrous felsic magmas. The percolating hydrous felsic magma could react to the deep sulfide layers upon its transport through the lower crustal cumulates and the mantle–crust transition zone. Thus, if the sulfide-enriched layer reacted with the felsic magma percolating from the subducting slab [39], hybrid S-rich magma would form. These facts and estimations indicate that if the reactions (Equations (3)–(7)) triggered by dissolution of the pyrrhotite or other Fe-rich sulfides proceeded upon the magma mixing, the fastest sulfur diffusion mechanism ever observed for sulfur species in hydrous hybrid magma would occur.

The results of experiments and thermodynamic modeling summarized in Tables 1 and S5 show that the interaction of hydrous felsic magmas with the Fe-rich sulfides through magma transport to shallower magma reservoirs is a viable mechanism for the effective transport of S. The reactions established here (Equations (3)–(7)) imply that such dissolution of sulfides in hydrous magmas can happen in the arc geodynamic settings at different levels and can result in the extremely efficient enrichment of sulfur. The dissolution reactions, if controlled by NNO to NNO+2 redox conditions, imply that sulfides can react with hydrous felsic magma, as shown in Figure 3. This reaction of sulfide dissolution is extremely rapid at shallow and deep levels and can promote the production of S-rich magma. It can also increase the pressure of the pre-eruptive hybrid fluid associated with the release and diffusion of S-radical species at shallow and deep levels. Thus, the accumulation of the hybrid S-rich fluid can trigger explosive eruptions of hybrid magmas. Future numerical modeling of hybrid, fluid-saturated systems can benefit from the sulfur radical diffusion data obtained here. These data can be used to create numerical models of explosive eruptions, paying particular attention to the role of sulfide dissolution reactions.

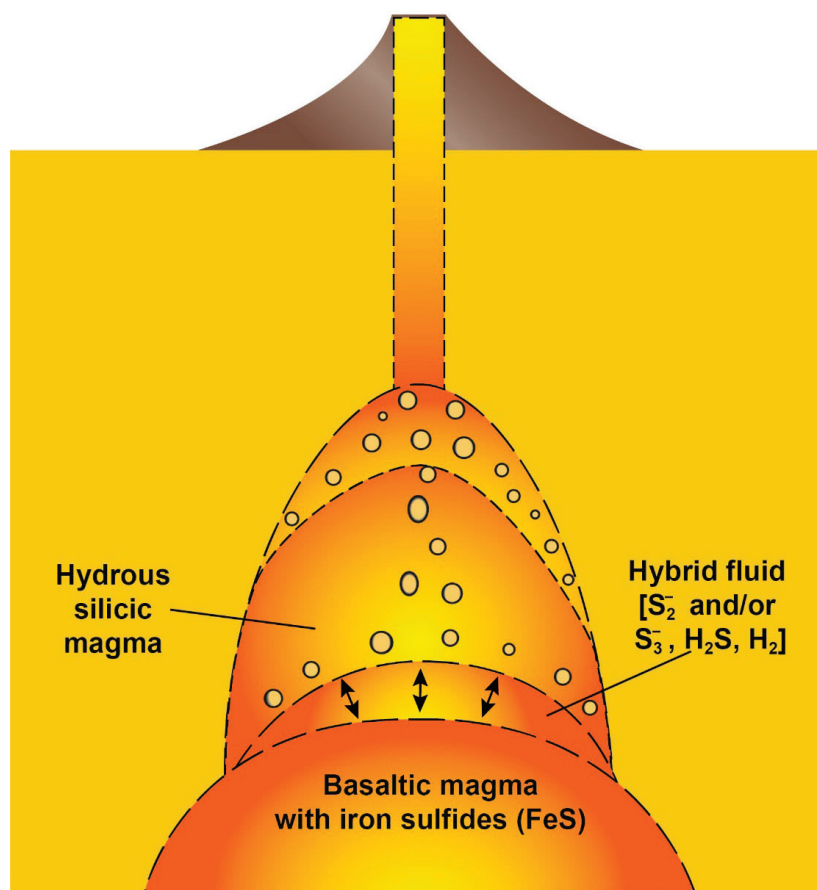


Figure 3. The principal schema of magma mixing triggering explosive eruptions. The following reactions are suggested to control liberation of the hybrid fluid triggering explosive eruptions: (1) $2 \text{FeS}(\text{po}) + 2 \text{H}_2\text{O} = 2 \text{FeO}(\text{melt}) + \text{S}_2^- + \text{H}^+ + 1.5 \text{H}_2$ and (2) $3 \text{FeS}(\text{po}) + 3 \text{H}_2\text{O} = 3 \text{FeO}(\text{melt}) + \text{S}_3^- + \text{H}^+ + 2.5 \text{H}_2$ and (3) $\text{S}_3^- + 0.75 \text{O}_2 + 2.5 \text{H}_2\text{O} = \text{SO}_4^{2-}(\text{fluid/melt}) + 2 \text{H}_2\text{S} + \text{H}^+$ or (4) $8 \text{S}_3^- + 20 \text{H}_2\text{O} = 19 \text{H}_2\text{S} + 5 \text{SO}_4^{2-}(\text{fluid/melt}) + 2 \text{H}^+$ and (5) $8 \text{S}_2^- + 2 \text{H}^+ + 12 \text{H}_2\text{O} = 13 \text{H}_2\text{S} + 3 \text{SO}_4^{2-}(\text{fluid/melt})$. The arrows indicate a zone of S-rich magma and fluid production, and the circles indicate the fluid phase degassing.

5.2. Sulfur-Loving (Chalcophile) Metal-Rich Magma Formation

The observed sulfide dissolution reaction mechanism, generating magma that is rich in sulfur, has to be enriched with the associated chalcophile metals of Au, Cu, and Pt [4,31,42–44], derived from the dissolving sulfide components. Such a hybrid, S-rich magma can promote the production of an S-rich fluid that is highly enriched in chalcophile metals, resulting in porphyry ore deposit formation [38,45–47]. Thus, magma mixing and sulfide dissolution can be the main physical-chemical mechanism of chalcophile metal transport from the mantle to the crust. This conclusion is also consistent with the recently described behavior of S and Cu in the mantle–crust transition zone, which is a zone of sulfide segregation and sulfide-controlled metal storage [48], and it is in agreement with the Au–Cu-rich nature of adakite magmas [41,45]. The described sulfide dissolution mechanism can thus be considered to be the main physicochemical process, explaining how sulfur behaves during magma–fluid–crustal interaction. This mechanism can be considered to be one of the physical-chemical mechanisms that controls crustal metallogeny.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min15090989/s1>, Table S1: Experimental conditions, starting material, resulting phases and diffusion coefficients; Table S2: Micro-Raman data; Table S3: EPMA data; Table S4: Numerical data on diffusion coefficients; Table S5: Thermodynamic modeling.

Funding: This research was supported by Institut National des Sciences de l'Univers—Centre National d'Études Spatiales (INSU-CNES, France; 2022–2023) PLAGIOGRAN grant to A.Y.B. This article is funded by the European Union (ERC, PLANETAFELSIC, project 101141259) to AYB. Views and opinions expressed are, however, those of the author(s) only and do not necessarily reflect those of the European Union or the European Research Council. Neither the European Union nor the granting authority can be held responsible for them.

Data Availability Statement: All data needed to evaluate conclusions in the paper are supported by the paper and the Supplementary Materials (Tables S1–S5). Additional data related to this paper may be requested from the author, Anastassia Y. Borisova.

Acknowledgments: Three anonymous reviewers and L. Dubrovinsky are thanked. The author thanks N. Zagrtidenov, A. Colin, G. Pokrovski, M. Portnyagin for help in the experiment preparation and important suggestions and comments on the initial versions of this manuscript.

Conflicts of Interest: The author declares no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

EPMA	Electron Probe Microanalysis
FTIR	Fourier Transform Infrared Spectroscopy
XANES	X-ray absorption near edge structure

References

1. Sparks, S.R.J.; Sigurdsson, H.; Wilson, L. Magma mixing: A mechanism for triggering acid explosive eruptions. *Nature* **1977**, *267*, 315–318. [CrossRef]
2. Matthews, S.J.; Jones, A.P.; Bristow, C.S. A simple magma-mixing model for sulphur behaviour in calc-alkaline volcanic rocks: Mineralogical evidence from Mount Pinatubo 1991 eruption. *J. Geol. Soc.* **1992**, *149*, 863–866.
3. Hattori, K. High-sulfur magma, a product of fluid discharge from underlying mafic magma: Evidence from Mount Pinatubo, Philippines. *Geology* **1993**, *21*, 1083–1086. [CrossRef]
4. Kress, V. Magma mixing as a source for Pinatubo sulfur. *Nature* **1997**, *389*, 591–593. [CrossRef]
5. Hattori, K.; Sato, H. Magma evolution recorded in plagioclase zoning in 1991 Pinatubo eruption products. *Am. Mineral.* **1996**, *81*, 982–994. [CrossRef]
6. Bluth, G.J.S.; Doiron, S.D.; Schnetzler, C.C.; Krueger, A.J.; Walter, L.S. Global tracking of the SO₂ clouds from the June 1991 Mount Pinatubo eruption. *Geophys. Res. Lett.* **1992**, *19*, 151–154. [CrossRef]
7. Pallister, J.S.; Hoblitt, R.P.; Reyes, A.G. A basalt trigger for the 1991 eruptions of Pinatubo volcano? *Nature* **1992**, *356*, 426–428. [CrossRef]
8. Borisova, A.Y.; Toutain, J.-P.; Dubessy, J.; Pallister, J.; Zwick, A.; Salvi, S. H₂O–CO₂–S fluid triggering the 1991 Mount Pinatubo climactic eruption (Philippines). *Bull. Volcanol.* **2014**, *76*, 800. [CrossRef]
9. Johnson, M.C.; Anderson, A.T., Jr.; Rutherford, M.J. Pre-eruptive volatile contents of magmas. In *Reviews in Mineralogy, Volatiles in Magmas*; Carroll, M.R., Holloway, J.R., Eds.; De Gruyter: Berlin, Germany, 1994; pp. 281–323.
10. Van Hoose, A.E.; Streck, M.J.; Pallister, J.S.; Wälle, M. Sulfur evolution of the 1991 Pinatubo magmas based on apatite. *J. Volcanol. Geotherm. Res.* **2013**, *257*, 72–89. [CrossRef]
11. Borisova, A.Y.; Zagrtidenov, N.R.; Toplis, M.J.; Ceuleneer, G.; Safonov, O.G.; Pokrovski, G.S.; Bychkov, A.Y. Hydrated peridotite–basaltic melt interaction Part II: Fast assimilation of serpentized mantle by basaltic magma. *Front. Earth Sci.* **2020**, *8*, 84. [CrossRef]
12. Borisova, A.Y.; Zagrtidenov, N.R.; Toplis, M.J.; Bohrsen, W.A.; Nédélec, A.; Safonov, O.G.; Pokrovski, G.S.; Ceuleneer, G.; Bindeman, I.N.; Melnik, O.E.; et al. Hydrated Peridotite–Basaltic Melt Interaction Part I: Planetary Felsic Crust Formation at Shallow Depth. *Front. Earth Sci.* **2021**, *9*, 640464. [CrossRef]
13. Vikentyev, I.; Vikent'eva, O.; Tyukova, E.; Nikolsky, M.; Ivanova, J.; Sidorova, N.; Palyanova, G. Noble metal speciations in hydrothermal sulphides. *Minerals* **2021**, *11*, 488. [CrossRef]
14. Borisova, A.Y.; Pokrovski, G.S.; Pichavant, M.; Freydier, R.; Candaudap, F. Amorphous Materials: Properties, Structure, and Durability. Arsenic enrichment in hydrous peraluminous melts: Insights from femtosecond laser ablation-inductively coupled plasma-quadrupole mass spectrometry, and in situ X-ray absorption fine structure spectroscopy. *Am. Mineral.* **2010**, *95*, 1095–1104.

15. Bromiley, G.; Hilaret, N.; McCammon, C. Solubility of hydrogen and ferric iron in rutile and TiO₂ (II): Implications for phase assemblages during ultrahigh-pressure metamorphism and for the stability of silica polymorphs in the lower mantle. *Geophys. Res. Lett.* **2004**, *31*, 310. [CrossRef]
16. Matjuschkin, V.; Woodland, A.B.; Yaxley, G.M. Methane-bearing fluids in the upper mantle: An experimental approach. *Contrib. Mineral Petrol.* **2019**, *174*, 1. [CrossRef]
17. Pokrovski, G.S.; Dubrovinsky, L.S. The S³⁺-ion is stable in geological fluids at elevated temperatures and pressures. *Science* **2011**, *331*, 1052–1054. [CrossRef] [PubMed]
18. Colin, A.; Schmidt, C.; Pokrovski, G.S.; Wilke, M.; Borisova, A.Y.; Toplis, M.J. In situ determination of sulfur speciation and partitioning in aqueous fluid-silicate melt systems. *Geochem. Persp. Lett.* **2020**, *14*, 31–35. [CrossRef]
19. King, P.L.; Ramsey, M.S.; McMillan, P.F.; Swayze, G. Laboratory Fourier transform infrared spectroscopy methods for geologic samples. *Infrared Spectrosc. Geochem. Explor. Remote Sens.* **2004**, *33*, 57–91.
20. Jarosewich, E.; Nelen, J.A.; Norberg, J.A. Reference samples for electron microprobe analysis. *Geostand. Newsl.* **1980**, *4*, 43–47. [CrossRef]
21. Jochum, K.P.; Weis, U.; Stoll, B.; Kuzmin, D.; Yang, Q.; Raczek, I.;ENZWEILER, J. Determination of reference values for NIST SRM 610–617 glasses following ISO guidelines. *Geostand. Geoanalytical Res.* **2011**, *35*, 397–429. [CrossRef]
22. Shvarov, Y.V. A suite of programs, OptimA, OptimB, OptimC, and OptimS compatible with the Unitherm database, for deriving the thermodynamic properties of aqueous species from solubility, potentiometry and spectroscopy measurements. *Appl. Geochem.* **2015**, *55*, 17–27.
23. Helgeson, H.C.; Kirkham, D.H.; Flowers, G.C. Theoretical prediction of thermodynamic behavior of aqueous electrolytes at high temperatures and pressures. IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 5 kb and 600 °C. *Am. J. Sci.* **1981**, *281*, 1249–1516.
24. Holland, T.J.B.; Powell, R. An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids. *J. Metamorph. Geol.* **2011**, *29*, 333–383. [CrossRef]
25. Chio, C.H.; Sharma, S.K.; Muenow, D.W. The hydrates and deuterates of ferrous sulfate (FeSO₄): A Raman spectroscopic study. *J. Raman Spectrosc.* **2007**, *38*, 87–99.
26. Harrison, T.M.; Watson, E.B. Kinetics of zircon dissolution and zirconium diffusion in granitic melts of variable water content. *Contrib. Mineral. Petrol.* **1983**, *84*, 66–72.
27. Borisova, A.Y.; Bindeman, I.N.; Toplis, M.J.; Zagrtchenov, N.R.; Guignard, J.; Safonov, O.G.; Bychkov, A.Y.; Shcheka, S.; Melnik, O.E.; Marchelli, M.; et al. Zircon survival in shallow asthenosphere and deep lithosphere. *Am. Mineral.* **2020**, *105*, 1662–1671.
28. Lierenfeld, M.B.; Zajacz, Z.; Bachmann, O.; Ulmer, P. Sulfur diffusion in dacitic melt at various oxidation states: Implications for volcanic degassing. *Geochim. Cosmochim. Acta* **2018**, *226*, 50–68.
29. Ni, H.; Zhang, Y. H₂O diffusion models in rhyolitic melt with new high pressure data. *Chem. Geol.* **2008**, *250*, 68–78. [CrossRef]
30. Zajacz, Z. The effect of melt composition on the partitioning of oxidized sulfur between silicate melts and magmatic volatiles. *Geochim. Cosmochim. Acta* **2015**, *158*, 223–244. [CrossRef]
31. Xu, T.; Liu, X.; Xiong, X.; Wang, J. Sulfur dissolution capacity of highly hydrated and fluid-saturated dacitic magmas at the lower crust and implications for porphyry deposit formation. *Geochim. Cosmochim. Acta* **2022**, *333*, 107–123. [CrossRef]
32. De Hoog, J.C.M.; Hattori, K.H.; Hoblitt, R.P. Oxidized sulfur-rich mafic magma at Mount Pinatubo, Philippines. *Contrib. Mineral. Petrol.* **2004**, *146*, 750–761. [CrossRef]
33. Pallister, J.S.; Hoblitt, R.P.; Meeker, G.P.; Knight, R.J.; Siems, D.F. Magma mixing at Mount Pinatubo: Petrographic and chemical evidence from the 1991 deposits. In *FIRE and MUD Eruptions and Lahars of Mount Pinatubo, Philippines*; U.S. Geological Survey: Reston, VA, USA, 1996; pp. 687–731. Available online: <https://pubs.usgs.gov/pinatubo/index.html> (accessed on 12 September 2025).
34. Di Muro, A.; Pallister, J.; Villemant, B.; Newhall, C.; Semet, M.; Martinez, M.; Mariet, C. Pre-1991 sulfur transfer between mafic injections and dacite magma in the Mt. Pinatubo reservoir. *J. Volcanol. Geotherm. Res.* **2008**, *175*, 517–540. [CrossRef]
35. Jégo, S.; Dasgupta, R. The fate of sulfur during fluid-present melting of subducting basaltic crust at variable oxygen fugacity. *J. Petrol.* **2014**, *55*, 1019–1050.
36. Hervo, M.; Quennehen, B.; Kristiansen, N.I.; Boulon, J.; Stohl, A.; Fréville, P.; Pichon, J.-M.; Picard, D.; Labazuy, P.; Gouhier, M.; et al. Physical and optical properties of 2010 Eyjafjallajökull volcanic eruption aerosol: Ground-based, Lidar and airborne measurements in France. *Atmos. Chem. Phys.* **2012**, *12*, 1721–1736. [CrossRef]
37. Gerlach, T.M.; Westrich, H.R.; Symonds, R.B. Fire and mud: Eruptions and lahars of Mount Pinatubo. *Philippines* **1996**, *415*, 33.
38. Li, L.; Liu, X.; Xu, T.; Xiong, X.; Wang, J.; Li, L. Sulfur partitioning between aqueous fluids and felsic melts at high pressures: Implications for sulfur migration in subduction zones. *Sci. Rep.* **2025**, *15*, 4273. [CrossRef]
39. Prouteau, G.; Scaillet, B.; Pichavant, M.; Maury, R. Evidence for mantle metasomatism by hydrous silicic melts derived from subducted oceanic crust. *Nature* **2001**, *410*, 197–200. [CrossRef]

40. Jenner, F.E. Cumulate causes for the low contents of sulfide-loving elements in the continental crust. *Nat. Geosci.* **2017**, *10*, 524–529. [CrossRef]
41. Liu, S.A.; Rudnick, R.L.; Liu, W.R.; Teng, F.Z.; Wu, T.H.; Wang, Z.Z. Copper isotope evidence for sulfide fractionation and lower crustal foundering in making continental crust. *Sci. Adv.* **2023**, *9*, eadg6995. [CrossRef]
42. Pokrovski, G.S.; Kokh, M.A.; Guillaume, D.; Borisova, A.Y.; Gisquet, P.; Hazemann, J.L.; Dubessy, J. Sulfur radical species form gold deposits on Earth. *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 13484–13489. [CrossRef] [PubMed]
43. Pokrovski, G.S.; Kokh, M.A.; Desmaele, E.; Laskar, C.; Bazarkina, E.F.; Borisova, A.Y.; Saitta, A.M. The trisulfur radical ion S₃—controls platinum transport by hydrothermal fluids. *Proc. Natl. Acad. Sci. USA* **2021**, *118*, e2109768118. [CrossRef]
44. Chiaradia, M.; Caricchi, L. Supergiant porphyry copper deposits are failed large eruptions. *Commun. Earth Environ.* **2022**, *3*, 107. [CrossRef]
45. Borisova, A.Y.; Pichavant, M.; Polvé, M.; Wiedenbeck, M.; Freydier, R.; Candaudap, F. Trace element geochemistry of the 1991 Mt. Pinatubo silicic melts, Philippines: Implications for ore-forming potential of adakitic magmatism. *Geochim. Cosmochim. Acta* **2006**, *70*, 3702–3716. [CrossRef]
46. Borisova, A.Y.; Martel, C.; Gouy, S.; Pratomo, I.; Sumarti, S.; Toutain, J.P.; Bindeman, I.N.; de Parseval, P.; Métaxian, J.P. Highly explosive 2010 Merapi eruption: Evidence for shallow-level crustal assimilation and hybrid fluid. *J. Volcanol. Geotherm. Res.* **2013**, *261*, 193–208. [CrossRef]
47. He, D.Y.; Qiu, K.F.; Simon, A.C.; Pokrovski, G.S.; Yu, H.C.; Connolly, J.A.; Deng, J. Mantle oxidation by sulfur drives the formation of giant gold deposits in subduction zones. *Proc. Natl. Acad. Sci. USA* **2024**, *121*, e2404731121. [CrossRef] [PubMed]
48. Pieterek, B.; Tribuzio, R.; Matusiak-Malek, M.; Ciałela, J.; Horn, I.; Weyer, S.; Strauss, H.; Kuhn, T.; Muszyński, A. Underplated melts control sulfide segregation at the continental crust-mantle transition. *Commun. Earth Environ.* **2024**, *5*, 45. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Extreme Element Enrichment by the Interaction of Supercritical Fluids from the Mantle with Crustal Rocks

Rainer Thomas ^{1,*} and Adolf Rericha ²¹ Im Waldwinkel 8, D-14662 Friesack, Germany² Alemannenstraße 4a, D-14612 Falkensee, Germany

* Correspondence: rainerthomas@t-online.de

Abstract: We show that supercritical fluids or melts are verifiable by critical high-temperature and high-pressure minerals like diamond, lonsdaleite, and others in crustal rocks as foreign minerals. In combination with the pseudo-binary solvus curves (temperature versus water content of silicate melts) with the Lorentzian distribution of some ore-forming elements, which are untypical for hydrothermal forming processes, we have solid proof for the interaction of mantle fluids and crustal rocks (granites). In this contribution, we restrict ourselves to a small number of critical observations, in particular on cassiterite polytypes.

Keywords: supercritical fluid; mantle-crust interaction; enrichment of tin; cotunnite-type cassiterite; Raman spectroscopy

1. Introduction

Since the development of the method for the determination of water in glass and silicate melt inclusions [1], the further improvement of this method [2,3], and the completion of the determination of boric acid [H₃BO₃] [4], we can show that many pegmatites form a pseudo-binary solvus curve in the coordinates water concentration versus temperature. Beginning with the work on the determination of beryllium in pegmatitic melt inclusions [5], it has become more evident from year to year that the solvus curves are also regularly related to trace and some main elements. The maximum of elements are clearly associated with the solvus crest, forming Gaussian or Lorentzian element distribution patterns [6,7]. Figures 1 and 2 exemplarily show such solvus curves and the corresponding Lorentzian distribution of tin. The connection between solvus and, e.g., the Lorentzian distribution is in [8], presented as a three-dimensional plot outlined.

Table 1 provides the parameters for the Lorentzian distribution of Sn (ppm) for Ehrenfriedersdorf pegmatite.

The Clarke number of Sn for granitic rocks is three ppm [9]. Tin granites of the Erzgebirge have a value of about 200 ppm [10]). The offset is already 2.5-fold higher than the Sn value of highly specialized tin granites.

The relationship between solvus and Lorentzian distribution of elements, here Sn, is typical for pegmatites, and we interpret that as the first hint for the interaction of supercritical fluids with granites and other crustal rocks. At the solvus crest (critical point, CP), we observe the highest element enrichment, here about 0.6 (mol/mol) SnO₂. Further studies confirmed that the highest measured Sn value was 16,430 ppm at 26.5 (g/g) H₂O, corresponding to 1.39 (mol/mol) SnO₂. That means, at least, that the Lorentzian distribution is a first approximation. Much work is necessary to solve these complex questions. Such

distributions (pseudo-binary solvus curves (H_2O -silicate melt versus temperature and Lorentzian element distribution)) are untypical for processes in the normal hydrothermal state, which is far away from the supercritical state here considered. High values for tin solubility were obtained by [11], with hydrothermal diamond anvil cells and by using alkali carbonate aqueous solutions. They received for the Li_2CO_3 - H_2O system 0.41 (mol/mol) SnO_2 at about 790 °C and 795 MPa. These values are much lower than the supercritical conditions; however, they are not far from the supercritical state.

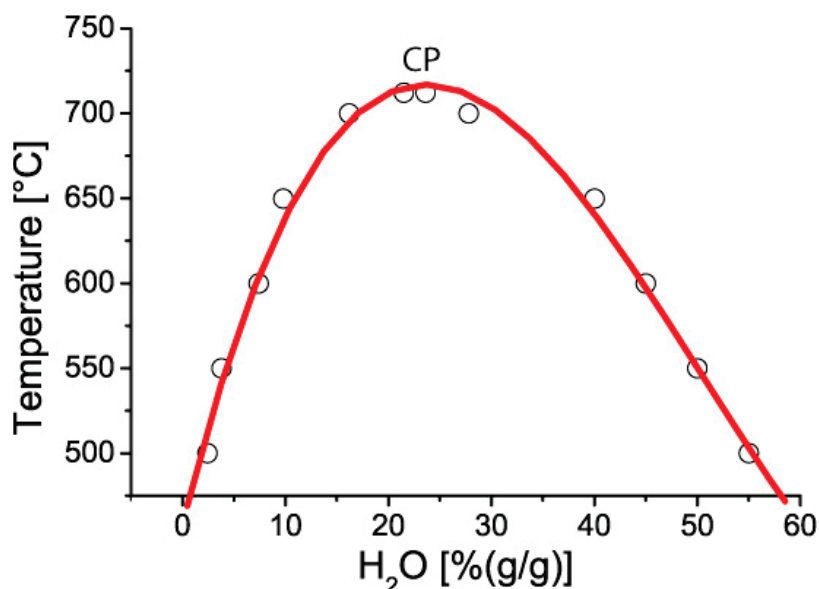


Figure 1. Solvus curve for the pegmatite-system Ehrenfriedersdorf (Sauberg mine).

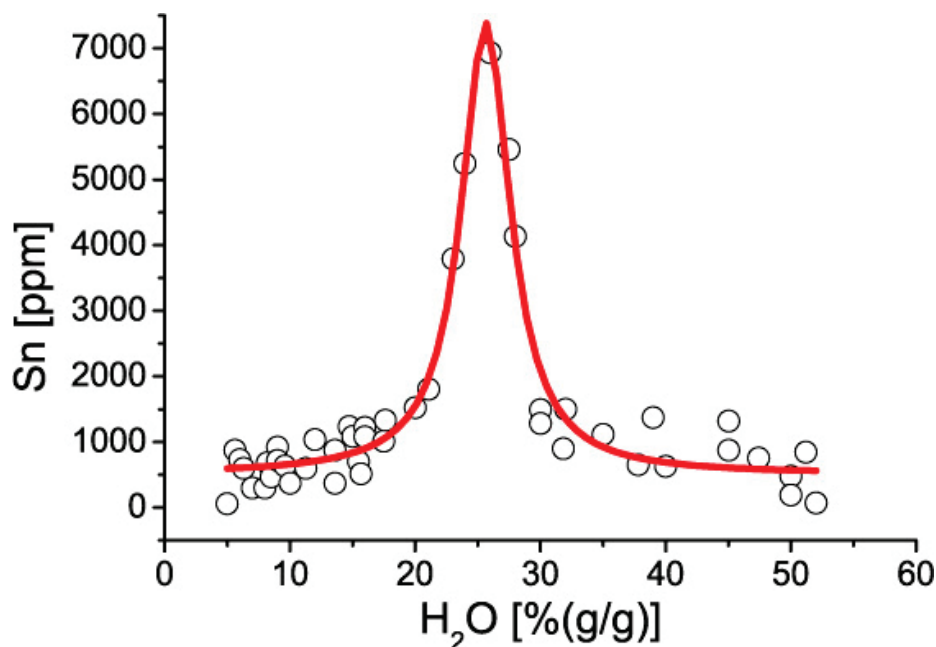


Figure 2. Tin distribution in the pegmatite system Ehrenfriedersdorf (Sauberg mine). The Lorentzian maximum corresponds to about 0.6% (mol/mol) SnO_2 .

Table 1. Lorentzian fit parameters for the Sn distribution.

Area	Center	Width	Offset	Height	R ²
51,522	25.6% H_2O	4.77% H_2O	504 ppm Sn	6882 ppm	0.9455

Studies on alkali chlorides and carbonates in diamonds [12,13] have resulted in further studies on hints to the interaction of supercritical fluids and crustal rocks. Experimental and theoretical works on the problem of supercritical fluids are in [11,14,15]. The historical development of research on supercritical fluids has been given by [16].

Studies on the Rønne pegmatite (Bornholm Island) yield clear proof that alkali carbonate-rich (NaHCO_3 , Li_2CO_3 and others) supercritical fluids, together with ^{13}C -rich diamond, take part in the formation of pegmatites [17].

Starting with new research on the prismatic rock from Waldheim/Saxony [18], the first author found clear indications that supercritical fluids or melts have influenced the well-known metamorphic rock. Hints for that are slight spheric and total smooth, polished-like mineral inclusions such as diamond, reidite, coesite, and stishovite. These findings initiate the search for such smooth spherical mineral inclusions in crustal rocks. The first object was granite from Greifenstein, near Ehrenfriedersdorf, Central Erzgebirge, Germany.

2. Sample Materials and Methodology

2.1. Sample Materials

The sample material used here is a tetragonal yellow-colored cassiterite crystal (sample Sn 40 from the Mining Academie Freiberg, cited in [19], 1 cm in diameter from Krupka (Krušnohoří Mining District/Czech Republic). All other sample material is mentioned in the text and cited in the corresponding references. More information on the Krupka deposit is in [20–22].

2.2. Methodology

For the preparation of the presented results, we used only microscopic and Raman spectroscopic techniques.

2.3. Raman Spectroscopy

We performed all microscopic and Raman spectroscopic studies with a petrographic polarization microscope with a rotating stage coupled with the EnSpectr Raman spectrometer R532 (Enhanced Spectrometry, Inc., Mountain View, CA, USA) in reflection and transmission. The Raman spectra were recorded in the spectral range of 0–4000 cm^{-1} using an up-to-50 mW single-mode 532 nm laser, an entrance aperture of 20 μm , a holographic grating of 1800 g/mm, and spectral resolution ranging from 4 to 6 cm^{-1} . Generally, we used an objective lens with a magnification of 100 $\times$ —the Olympus long-distance LMPLFLN100 $\times$ objective (Olympus, Tokyo, Japan). The laser power on the sample is adjustable down to 0.02 mW. The Raman band positions were calibrated before and after each series of measurements using the Si band of a semiconductor-grade silicon single-crystal. The run-to-run repeatability of the line position (based on 20 measurements each) is $\pm 0.3 \text{ cm}^{-1}$ for Si ($520.4 \pm 0.3 \text{ cm}^{-1}$) and 0.4 cm^{-1} for diamond ($1332.7 \pm 0.4 \text{ cm}^{-1}$ over the range of 80–2000 cm^{-1}). The FWHM = $4.26 \pm 0.42 \text{ cm}^{-1}$. FWHM is the Full-Width at Half Maximum. We also used a water-clear natural diamond crystal (Mining Academy Freiberg: 2453/37 from Brazil) as a diamond reference (for more information, see [23,24]).

3. Results

The solvus curves and the Lorentzian element distribution patterns (up to now for about 20 element and molecule groups derived [6,7]) alone are not enough to say that the supercritical fluids come from mantle depths. At high temperatures, where water-rich pegmatite melts form, the supercritical state can create and work. Therefore, further proof

is necessary. This comes from the evidence of mantle minerals in ore deposit minerals trapped at low-pressure crustal regions.

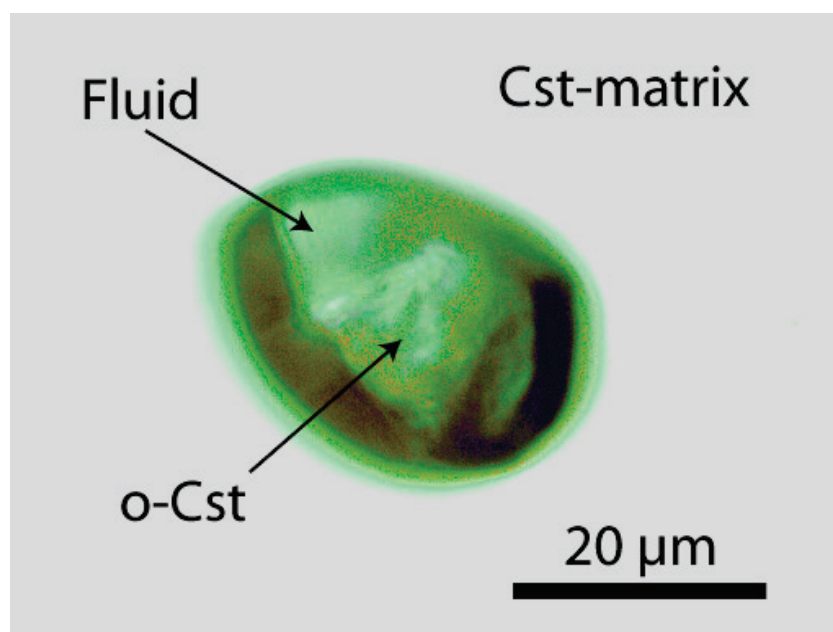
In the Greifenstein granite (1–2 kbar: shallow intrusion level [25]), we found spherical minerals like high-pressure cristobalite, coesite, diamond, lonsdaleite, kumdykolite, moissanite, high-pressure beryl, zircon, zircon-reidite, and OH-dominated topaz [24]. Because such minerals and their unique form cannot be formed at the crustal range, we interpret that as hints of the impact of supercritical fluids or melts coming from the mantle region. The first signs of the participation of mantle components come from [26]. These authors found, however, no compelling pieces of evidence for their statement.

The present author, together with some coauthors, has shown that the supercritical fluids/melts bring together untypical minerals (diamond, moissanite, and many others), especially high-temperature water, CO_2 , and CH_4 , into the crustal region. Thus, we often found orthorhombic cassiterite, diamond, and graphite inclusion in the Variscan cassiterites of the German Erzgebirge, Krušnohoří, and Slavkovský les (Czech Republic) regions. In 18 cassiterite samples from there, we could show that inclusions of orthorhombic cassiterite (CaCl_2 polytype Pnm, PbO_2 -polytype Pbcn, ZrO_2 -polytype Pbca, and cotunnite-polytype Pnma-I) are widespread (for the SnO_2 -polytypes, see [27]. The Pnma-I (cotunnite-type of cassiterite) is from other orthorhombic polytypes that are relatively rare. There is also often graphite, diamond, and sometimes moissanite primarily present. In the sample Sn-40, we could also prove complex C-B-N carbide phases (see [28]). Figure 3a–e show such inclusion of orthorhombic cassiterite in normal tetragonal, pale-yellow-colored cassiterite (Sn 40, in [19]) from Krupka (Krušnohoří Mining District/Czech Republic).

Figure 3b shows a typical Raman spectrum of a tetragonal cassiterite host (Sn-40) with the typical Raman bands at 632 and 775 cm^{-1} .

The cotunnite-type cassiterite (Pnma-I) shows the Raman main band at significantly lower values (626 versus 632 cm^{-1}).

Figure 3d represents the Raman bands of the cotunnite-type cassiterite (Pnma-I) in the low-frequency range.



(a)

Figure 3. Cont.

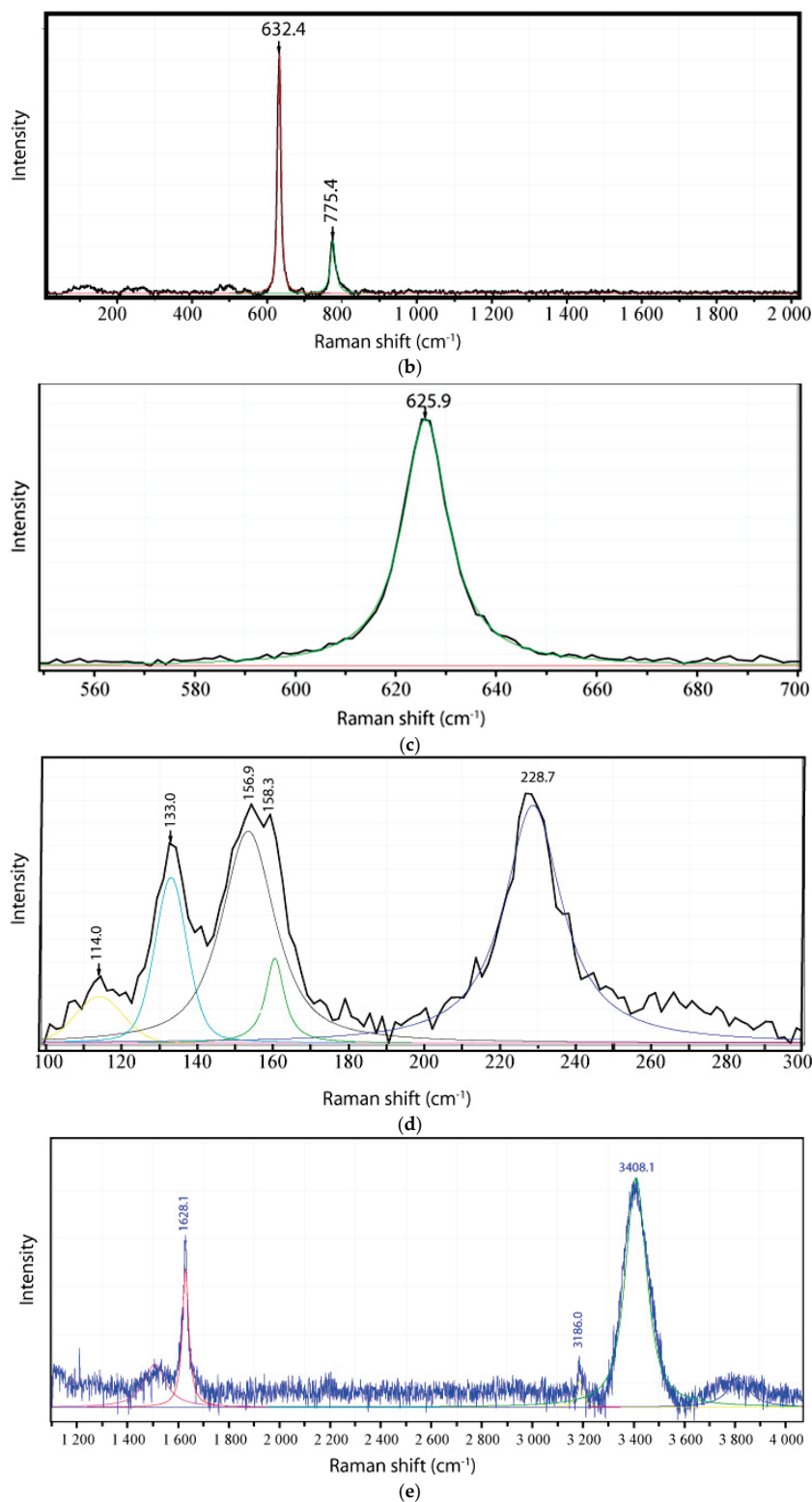


Figure 3. (a). A tetragonal cassiterite matrix (Cst-matrix) of sample Sn-40 with fluid inclusion containing a large orthorhombic cassiterite (o-Cst) crystal with some H₂¹⁶O-rich fluid [29]. The o-Cst is mainly the polymorph Pnma-I (cotunnite-type of cassiterite)—a high-pressure and high-temperature polymorph phase (15 GPa, 1200 K) of cassiterite (see [27,30]). (b). Raman spectrum of the tetragonal matrix cassiterite (Sn-40) from Krupka (Krušnohoří Mining District/Czech Republic). (c). Raman spectrum of the cotunnite-type cassiterite (main line). (d). The low-frequency range of the Raman spectrum of the cotunnite-type cassiterite. (e). Water bands in the high-frequency range of the Raman spectrum of the cotunnite-type cassiterite. The band at 1628 cm⁻¹ corresponds to the ν_2 bending modes and at 3408 cm⁻¹ mainly to the ν_1 vibration.

To completion, the Raman spectrum Figure 3e shows the two typical OH bands ν_2 bending vibration (H-O-H) at 1628 and ν_1 at 3408 cm^{-1} .

Table 2 shows the Raman main lines of the orthorhombic cassiterite (Pnma-I)—from the cotunnite polytype of cassiterite (see [27])—10 measurements.

Table 2. Raman shift (cm^{-1}) of an orthorhombic cassiterite inclusion in yellow tetragonal cassiterite from Krupka (Krušnohoří Mining District/Czech Republic).

Orthorhombic Cassiterite (Pnma-I) as Inclusion in Cassiterite from Krupka		
Raman Band	Raman Mode	Relative Intensity
138.2 ± 2.2	A_g	vs
159.5 ± 2.6	B_{1g}	vs
232.0 ± 2.4	A_g	s
474.0 ± 4.8	B_{1g}	w
625.8 ± 2.0	A_g	vs
691.3 ± 0.6	B_{1g}	vw

Remark: The Raman lines are not stable under the 532 nm laser (50 mW). The best data can be obtained with a low laser power of 0.3 mW on samples and a long measuring time of 2000 s. Here is a change in the Pbcn-cassiterite polytype. vs—very strong; s—strong; w—weak; vw—very weak.

The cotunnite-type cassiterite inclusion also contains remnants of other orthorhombic cassiterite polymorphs, such as the CaCl_2 -type cassiterite (see [31]). According to [27,30], the formation of the cotunnite-type polymorph of cassiterite happens at about 19.7 GPa and 1200 K.

During the transition from a supercritical state to a critical and under-critical state, chemical and physical processes happen, which cannot be solved at the moment. As an example, the formation of moissanite whiskers in beryl in the Variscan tin deposit Ehrenfriedersdorf, Sauberg mine, can be referenced [32]. The growth of moissanite at temperatures lower than 700 °C is untypical.

At this point, we remember that the fundamental physical properties of supercritical fluids, like viscosity and diffusivity, must go in the direction of zero and infinite, respectively (e.g., [14]). This basic behavior of supercritical fluids determines all other properties of such fluid—ascend velocity, solubility behavior, complex formation, surface tension, and many others (see [8]).

Furthermore, ref. [20] has clearly shown with his sketches (Figure D in this contribution) that the amount and distribution of small and large pegmatite bodies in the Sauberg mine near Ehrenfriedersdorf cannot be formed by the water of the surrounding granites. A different, intense source of water is necessary. Starting with the interpretation of the origin of mantle minerals in the prismatic granulite von Waldheim/Saxony, it would be more evident that supercritical fluids have had a more significant impact as of now, though. The question of where the ore elements come from immediately follows. Is the classic idea correct that, for example, Sn comes from the so-called surrounding tin granite alone? Or do we have a different or second source? And is the high level of 200 ppm Sn in specialized granites not the result of the interaction of supercritical fluids with granites in the upper crust itself?

Scientific proof [31] clearly shows that in many tin deposits of the German Erzgebirge and from Krušnohoří Mining District, Czech Republic, the Sn comes as high-pressure and high-temperature orthorhombic cassiterite together with supercritical fluids, also bearing dissolved tin and other elements from a depth corresponding to a pressure of 15 GPa or more, which demands a reassessment of the conventional wisdom up to now.

4. Discussion

Our careful study of samples from the tin deposits of the Erzgebirge Mts., Germany, shows that many minerals (quartz, topaz, and cassiterite) contain high-temperature and high-pressure minerals, which is unmistakable proof of the interaction between mantle and crust by supercritical fluids or melts.

Figure 4 shows such a diamond crystal in cassiterite and the corresponding Raman spectrum. Often, we find in cassiterite crystals, besides the rare diamond crystals from the Variscan Erzgebirge and the Slavkovský les, North Bohemia (Czech Republic), orthorhombic cassiterite inclusions in tetragonal cassiterite [31], demonstrating that at least a part of the cassiterite comes from mantle depths indicated by the high-pressure (~15 GPa or more) formation of orthorhombic cassiterite.

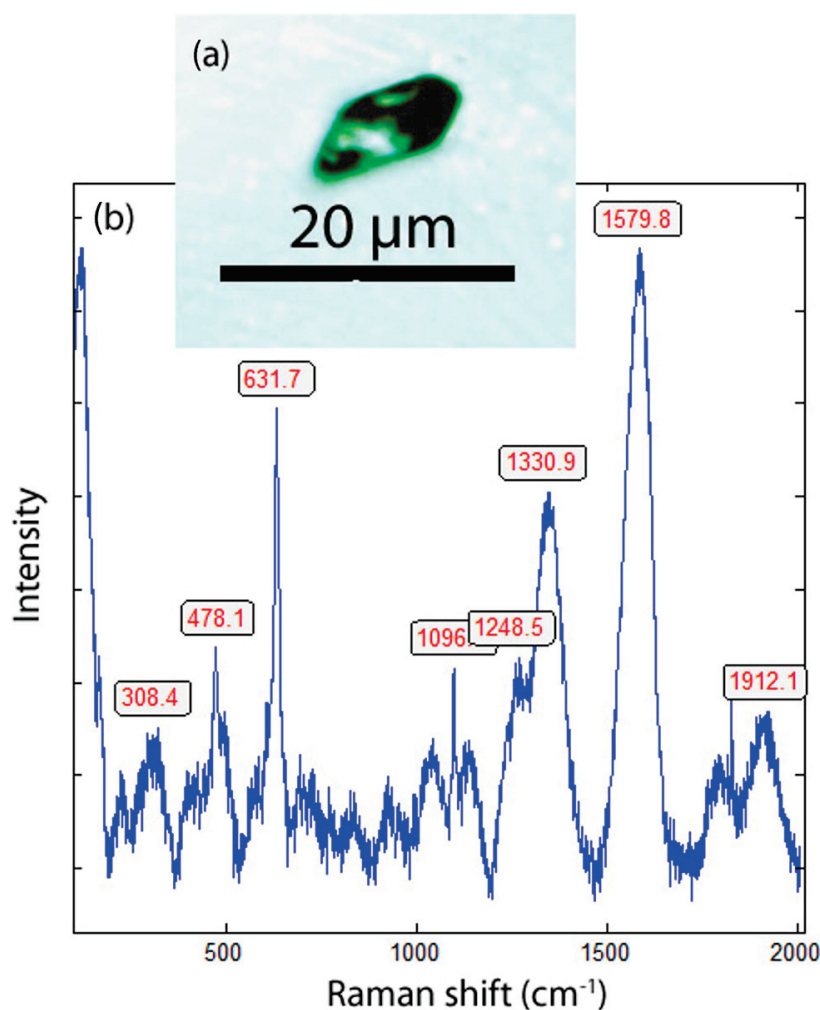


Figure 4. Diamond crystal (a) in cassiterite (Sn-49) from Slavkovský les–North Bohemia (Czech Republic) and the corresponding Raman spectrum (b). The 631.7 cm^{−1} Raman line is from the cassiterite matrix, the 1330.9 cm^{−1} line is from diamond, and the 1580 cm^{−1} line is from graphite.

Figure 5 shows an orthorhombic (Pbcn polytype) cassiterite crystal in the tetragonal cassiterite matrix (Sn-40) from Krupka with diamond and graphite inclusions. Most orthorhombic cassiterites show replacement structures by the tetragonal cassiterite. Some cassiterite crystals contain up to 20 [(vol/vol)] orthorhombic cassiterite phases (e.g., Sn-49).

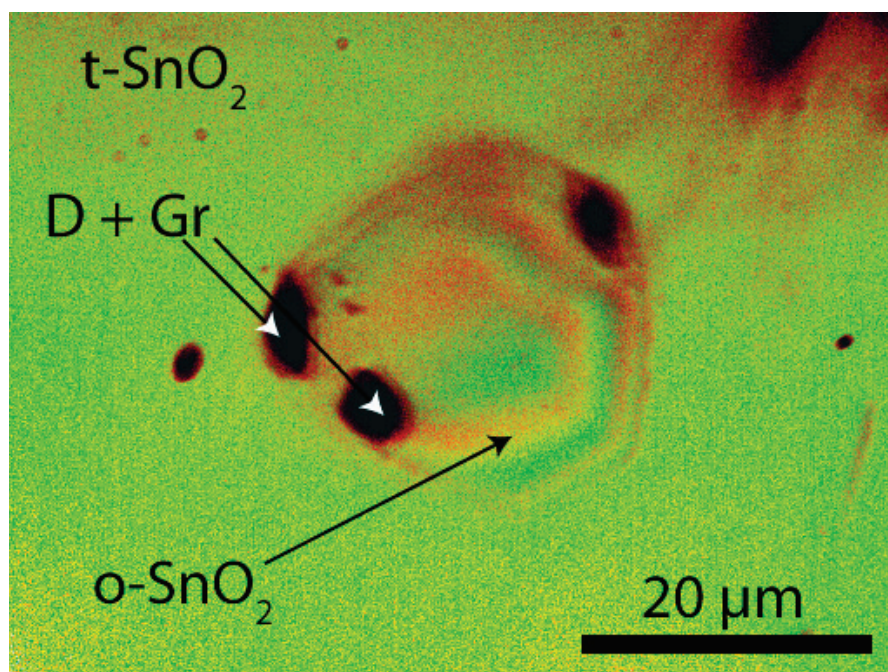


Figure 5. Orthorhombic cassiterite (o-SnO₂) in tetragonal cassiterite (t-SnO₂) with inclusions of diamond (D) at 1332.9 cm^{−1} and graphite (Gr) at 1581.8 cm^{−1} in the sample Sn-40 from Krupka.

The observation of high-pressure and high-temperature minerals is not only related to the Variscan Erzgebirge and the Krušnohoří Mining District, Czech Republic region. We found such proof in the Königshain granite, in some quartz veins of the Lusatian Mts, and also in East Thuringia [33]. During the newest Raman studies on the pegmatites related to the Rønne granite (Bornholm Island), the first author found much ¹³C-rich diamond and ¹³C-rich graphite and other surprising findings like NaDCO₃[−] rich phases and ¹³C-rich CO₂ [17].

All these results obtained in the last three years, together with the coauthors' findings, show that the meaning of supercritical fluids or melts in the case of Variscan tin deposits was not taken into account. Obviously, supercritical fluids play an essential role in the formation of pegmatites and other high-temperature ore deposits. Besides critical high-temperature and high-pressure minerals like diamond and lonsdaleite, we also found inclusions of ore-forming minerals (different cassiterite polytypes, caracolite [Na₃Pb₂(SO₄)₃Cl], REE-phosphates, and many others; see [24]). Furthermore, the presence of inclusions or remnants of high-pressure and high-temperature SnO₂ polymorphs of **rutile-type** → **CaCl₂-type** → pyrite-type → **ZrO₂ orthorhombic phase I** → **cotunnite-type** [27,30] demonstrate that high-pressure phases (CaCl₂- and cotunnite-type) are essential pieces of evidence for the transport of this ore mineral from mantle depths to the crust region. This observation shows further clear indications that the element solubility in supercritical phases can have extreme values, and the concentration of tin indicated in the form of a Lorentzian curve with the maximum at the solvus crest is not the highest Sn concentration in the supercritical fluid. This concentration reflects the transition from the supercritical to critical state.

This results in the following question: Are the typical fluid inclusions in cassiterite only (e.g., [19]) proof of the recrystallization and re-deposition of cassiterite under hydrothermal conditions? Up to now, the tin-rich melt inclusions in cassiterite or the high-pressure and high-temperature polymorphs of cassiterite inclusions do not feature in genetic discussions. Is there an analog situation like the emerald formation via supercritical fluids in the Habachtal, Austria [34], where the dominant fluid inclusions represent only the secondary

processes and the up-to-now ignored melt inclusions are the primary inclusions generated by supercritical fluids? By this acceptance of supercritical fluids, the contradiction between regional geology and the observation of high-temperature indications can be solved. The proof of diamond (1329.2 cm^{-1} with an FWHM = 76.3 cm^{-1}) by the first author in the Habachtal emerald supports this statement.

Compared to diamond and lonsdaleite inclusions, which are indicative of mantle origin, different high-pressure and high-temperature cassiterite polymorphs are pressure and temperature sensors for the origin of supercritical fluids.

Author Contributions: R.T and A.R. designed the project; R.T. performed the Raman analyses; both authors contributed to the interpretation and did comprehensive editing and have read and agreed to the published version of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: The research received no external funding.

Data Availability Statement: Data are contained within the article.

Acknowledgments: We thank James (Jim) Webster (1955–2019), geologist and curator at the American Museum of Natural History, for his aid with our work on pegmatites and tin granites.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Thomas, R. Determination of water contents of granite melt inclusions by confocal laser Raman microprobe spectroscopy. *Am. Mineral.* **2000**, *85*, 868–872. [CrossRef]
2. Thomas, R.; Kamenetsky, V.S.; Davidson, P. Laser Raman spectroscopic measurements of water in unexposed glass inclusions. *Am. Mineral.* **2006**, *91*, 467–470. [CrossRef]
3. Thomas, S.-M.; Koch-Müller, M.; Reichart, P.; Rhede, D.; Thomas, R.; Wirth, R.; Matsyuk, S. IR calibration for water determination in olivine, r-GeO_2 , and SiO_2 polymorphs. *Phys. Chem. Miner.* **2009**, *36*, 489–509. [CrossRef]
4. Thomas, R. Determination of the H_3BO_3 concentration in fluid and melt inclusions in granite pegmatites by laser Raman microprobe spectroscopy. *Am. Mineral.* **2002**, *87*, 56–68. [CrossRef]
5. Thomas, R.; Webster, J.D.; Davidson, R. Be-daughter minerals in fluid and melt inclusions: Implications for the enrichment of Be in granite-pegmatite systems. *Contrib. Mineral. Petrol.* **2011**, *161*, 483–495. [CrossRef]
6. Thomas, R.; Davidson, P.; Appel, K. The enhanced element enrichment in the supercritical states of granite-pegmatite systems. *Acta Geochim.* **2019**, *38*, 335–349. [CrossRef]
7. Thomas, R.; Davidson, P.; Rericha, A.; Voznyak, D.K. Water-rich melt inclusions as “frozen” samples of the supercritical state in granites and pegmatites reveal extreme element enrichment resulting under non-equilibrium conditions. *Mineral. J.* **2022**, *44*, 3–15. [CrossRef]
8. Thomas, R.; Rericha, A. Meaning of supercritical fluids in pegmatite formation and critical-element redistribution. *Geol. Earth Mar. Sci.* **2024**, *6*, 1–5.
9. Rösler, J.H.; Lange, H. *Geochemische Tabellen*; VEB Deutscher Verlag für Grundstoffindustrie: Leipzig, Germany, 1975; 675p.
10. Ni, H.; Zhang, L.; Xiong, X.; Mao, Z.; Wang, J. Supercritical fluids at subduction zones: Evidence, formation conditions, and physicochemical properties. *Earth Sci. Rev.* **2017**, *167*, 62–71. [CrossRef]
11. Sun, Y.; Liu, X.; Lu, X. Structures and transport properties of supercritical $\text{SiO}_2\text{-H}_2\text{O}$ and $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$ fluids. *Am. Mineral.* **2023**, *108*, 1871–1880. [CrossRef]
12. Kamenetsky, M.B.; Sobolev, A.V.; Kamenetsky, V.S.; Maas, R.; Danyushevsky, L.V.; Thomas, R.; Pokhilenko, N.P.; Sobolev, N.V. Kimberlite melts rich in alkali chlorides and carbonates: A potent metasomatic agent in the mantle. *Geology* **2004**, *32*, 845–848. [CrossRef]
13. Kaminsky, F.; Wirth, R.; Marsyuk, S.; Schreiber, A.; Thomas, R. Nyerereite and nahcolite inclusions in diamond: Evidence for lower-mantle carbonatitic magmas. *Mineral. Mag.* **2009**, *73*, 521–540. [CrossRef]
14. Bolmatov, D.; Brazhkin, V.V.; Trachenko, K. Thermodynamic behaviour of supercritical matter. *Nat. Commun.* **2013**, *4*, 2331. [CrossRef] [PubMed]
15. Ni, H. Introduction to advances in the study of supercritical geofluids. *Science China. Earth Sci.* **2023**, *66*, 2391–2394.
16. Sengers, J.L. *How Fluids Unmix: Discoveries by the School of Van der Waals and Kamerlingh Onnes*; Koninklijke Nederlandse Akademie van Wetenschappen: Amsterdam, The Netherlands, 2002; 302p.

17. Thomas, R. ^{13}C -rich diamond in a pegmatite from Rønne, Bornholm Island: Proof for the interaction between mantle and crust. *Geol. Earth Mar. Sci.* **2024**, *6*, 1–3.
18. Thomas, R.; Grew, E. Coesite inclusions in prismatine from Waldheim, Germany: New constraints on the pressure-temperature evolution of the Saxony Granulite Complex. In Proceedings of the 3rd European Mineralogical Conference in Cracow, Cracow, Poland, 29 August–2 September 2021; Book of Abstracts: 391.
19. Thomas, R. *Ergebnisse der Thermobarometrischen Untersuchungen an Flüssigkeitseinschlüssen in Mineralen der Postmagmatischen Zinn-Wolfram-Mineralisation des Erzgebirges*; Freiburger Forschungshefte C370; Bergakademie Freiberg: Freiberg, Germany, 1982; 85p.
20. Schröcke, H. Zur Paragenese erzgebirgischer Zinnlagerstätten. *Neues Jahrb. Mineral. Abh.* **1954**, *87*, 33–109.
21. Baumann, L.; Kuschka, E.; Seifert, T. *Lagerstätten des Erzgebirges*; Enke: Stuttgart, Germany, 2000; 300p.
22. Kotlánová, M.K.; Dolníček, Z.; René, M.; Prochaska, W.; Ulmanová, J.; Kapusta, J.; Maček, V.; Kropác, K. Fluid evolution of greisen from Krupka Sn-W ore district, Bohemian Massif (Czech Republic). *Minerals* **2024**, *14*, 86. [CrossRef]
23. Thomas, R.; Davidson, P.; Rericha, A.; Recknagel, U. Water-rich coesite in prismatine-granulite from Waldheim/Saxony. *Veröffentlichungen Naturkunde Mus. Chemnitz* **2022**, *45*, 67–80.
24. Thomas, R.; Davidson, P.; Rericha, A.; Recknagel, U. Mineral inclusions in a crustal granite: Evidence for a novel transcrustal transport mechanism. *Geosciences* **2023**, *13*, 94. [CrossRef]
25. Thomas, R.; Klemm, W. Microthermometric study of silicate melt inclusions in Variscan granites from SE Germany: Volatile contents and entrapment conditions. *J. Petrol.* **1997**, *38*, 1753–1765. [CrossRef]
26. Schütze, H.; Stiehl, G.; Wetzels, K.; Beuge, P.; Haberlandt, R.; Gerstenberger, H.; Tischendorf, G.; Wand, U.; Mühle, K.; Rösler, H.-J.; et al. Isotopen- und elementgeochemische sowie radiogeochronologische Aussagen zur Herkunft des Ehrenfriedersdorfer Granites.–Ableitung erster Modellvorstellungen. *ZFI-Mitteilungen Leipz.* **1983**, *76*, 232–254.
27. Balakrishnan, K.; Veerapandy, V.; Fjellvag, H.; Vajeeston, P. First-principles exploration into the physical and chemical properties of certain newly identified SnO_2 polymorphs. *ACS Publ.* **2022**, *7*, 10382–10393. [CrossRef] [PubMed]
28. Werninghaus, T. MicroRaman Spectroscopy Investigations of Hard Coatings. Ph.D. Thesis, TU Chemnitz-Zwickau, Chemnitz, Germany, 1997; 163p.
29. Brooker, M.H.; Hancock, G.; Rice, B.C.; Shapter, J. Raman frequency and intensity studies of liquid H_2O , H_2^{18}O and D_2O . *J. Raman Spectrosc.* **1989**, *20*, 683–694. [CrossRef]
30. Shieh, S.R.; Kubo, A.; Duffy, T.S.; Prakapenka, V.B.; Shen, G. High-pressure phases in SnO_2 to 117 GPa. *Phys. Rev. B* **2006**, *73*, 014105-1–014105-7. [CrossRef]
31. Thomas, R. Rhomboedric cassiterite as inclusions in tetragonal cassiterite from Slavkovský les–North Bohemia (Czech Republic). *Geol. Earth Mar. Sci.* **2024**, *6*, 1–6.
32. Thomas, R. Growth of SiC whiskers in beryl by a natural supercritical VLS process. *Asp. Min. Miner. Sci.* **2023**, *11*, 1292–1297.
33. Thomas, R.; Leh, M. The formation of some quartz veins in the Lusatian Massif, E-Germany by supercritical fluids/melts bearing lonsdaleite and diamond and comparison with other similar formations in Middle-Saxonian and Thuringian/E-Germany. *Geol. Earth Mar. Sci.* **2024**, *6*, 1–7.
34. Thomas, R.; Davidson, P.; Rericha, A. Emerald from the Habachtal: New observations. *Mineral. Petrol.* **2020**, *114*, 161–173. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

MDPI AG
Grosspeteranlage 5
4052 Basel
Switzerland
Tel.: +41 61 683 77 34

Minerals Editorial Office
E-mail: minerals@mdpi.com
www.mdpi.com/journal/minerals



Disclaimer/Publisher's Note: The title and front matter of this reprint are at the discretion of the Guest Editors. The publisher is not responsible for their content or any associated concerns. The statements, opinions and data contained in all individual articles are solely those of the individual Editors and contributors and not of MDPI. MDPI disclaims responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.



Academic Open
Access Publishing

mdpi.com

ISBN 978-3-7258-8836-8