

Special Issue Reprint

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# Tectonic–Magmatic Evolution and Mineralization Effect in the Southern Central Asian Orogenic Belt

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Edited by  
Jiafu Chen, Nan Ju and Zhonghai Zhao

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# **Tectonic–Magmatic Evolution and Mineralization Effect in the Southern Central Asian Orogenic Belt**





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Editors

**Jiafu Chen**

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# Preface

Orogenic research, including the temporal and spatial features of orogens, has long been a major task of the international community because it deals with the fundamental principles of the formation and growth of continents. The Central Asian Orogenic Belt (CAOB), also known as the Central Asian Orogenic System or the Altaid Tectonic Collage, occupies a broad area between the Siberian, Baltic, North China, and Tarim cratons. It is the largest accretionary orogen and one of the most important sites of Phanerozoic crustal growth in the world. It is the result of long-lived multi-stage tectonic evolution, including Proterozoic to Paleozoic accretion and collision, Mesozoic intracontinental modification, and Cenozoic rapid deformation and uplift. The accretionary and collisional orogenesis of its early history generated a huge orogenic collage consisting of diverse tectonic units including island arcs, ophiolites, accretionary prisms, seamounts, oceanic plateaus, and micro-continents. These incorporated orogenic components preserved valuable detailed information on orogenic processes and continental crust growth, which make the CAOB a key region for the understanding of continental evolution, mantle–crust interaction, and associated mineralization.

Abundant high-quality data (such as zircon U-Pb ages, whole-rock geochemistry, and Sr-Nd-Pb-Hf-O isotopes) have recently been obtained from various orogens in the CAOB, with the rapid advancement of testing technology. It has been accepted that the accretionary orogenic process is very complex, and more in-depth work is needed. The south CAOB is constituted by several key terranes, microcontinents, arcs, and suture zones, including the Kazakhstan–West Junggar orocline system, Tianshan orogenic belt, Beishan orogenic belt, Xing–Meng orogenic belt, and the northern margin of the North China Craton. The architecture of these orogens remains controversial, in particular, in terms of their crustal composition, deformation, metamorphism, sedimentation, kinematics, and ore deposit genesis. The final closure time and subduction process of the Paleo–Asian Ocean still requires further discussion and more evidence. Furthermore, the south CAOB has experienced superimposition of different orogenic domains and has been overprinted by younger tectonism, the mechanism of which remains to be understood. Thus, we assembled papers for this Special Issue of *Minerals*, which provide new geologic, geophysical, petrological, geochronological, and other data and examine advances on tectonic evolution and the mineralization effect of the south domain of the CAOB.

We appreciate the efforts made by all authors, reviewers, and editors.

**Jiafu Chen, Nan Ju, and Zhonghai Zhao**

*Editors*





## Editorial

# Editorial for Special Issue “Tectonic–Magmatic Evolution and Mineralization Effect in the Southern Central Asian Orogenic Belt”

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The Central Asian Orogenic Belt (CAOB), one of the world's largest orogens, extending from the Ural Mountains in the west to the Russian and the Chinese Far East, is the result of long-lived multi-stage tectonic evolution, including Proterozoic to Paleozoic accretion and collision, Mesozoic intracontinental modification, and Cenozoic rapid deformation and uplift [1–3]. The accretionary and collisional orogenesis of its early history generated a huge orogenic collage consisting of diverse tectonic units, including island arcs, ophiolites, accretionary prisms, seamounts, oceanic plateaus, and micro-continents. These incorporated orogenic components have preserved valuable detailed information on the orogenic process and continental crust growth, which makes the CAOB a key region for understanding continental evolution, mantle–crust interaction, and the associated mineralization.

However, the architecture of the CAOB remains controversial, particularly in terms of its crustal composition, deformation, metamorphism, sedimentation, and kinematics. Furthermore, the CAOB has experienced the superimposition of different orogenic domains and has been overprinted by younger tectonism, the mechanism of which is still not understood [3]. We have assembled papers for this Special Issue of Minerals that provide new geologic, geophysical, petrological, and geochronological data and study advances in tectonic evolution and the mineralization effect in the south domain of CAOB. For this Special Issue, we have collected 15 papers, encompassing the archipelago system of the West Junggar orogenic belt, Tianshan orogenic belt, Beishan orogenic belt, and Xing-Meng orogenic belt and the northern margin of the North China Craton.

Liu et al. (Contribution 1) report zircon U–Pb chronological and geochemical research on the volcano-sedimentary strata of the Middle Devonian Kulumudi Formation in West Junggar. The zircon U–Pb age of the lithic crystal tuff is  $386 \pm 2$  Ma, and the maximum depositional age of the sandstone is  $341 \pm 3$  Ma, indicating that this rock unit should be redefined as belonging to the Lower Carboniferous Jiangbasitao Formation. Geochemical data and Zircon Hf isotopic data indicate that the Kulumudi Formation and Jiangbasitao Formation were both formed in a juvenile arc setting with ocean–continent subduction. It is further concluded that the southward subduction of the ocean basin represented by the Darbut–Karamay ophiolitic mélange beneath the newly accreted arc crustal segments produced a juvenile arc.

Wang et al. (Contribution 2) conducted zircon U–Pb dating, whole-rock geochemical analysis, and molybdenite Re–Os isotope chronological analysis to constrain the magma origins and the timing of mineralization for the Yuhaxi Mo (Cu) deposit in the eastern Dananhu–Tousuquan island arc, Eastern Tianshan. Zircon U–Pb dating suggests that the emplaced ages of the Yuhaxi monzonitic granite, diorite, and granite are  $359 \pm 2$  Ma,  $299 \pm 2$  Ma, and  $307 \pm 2$  Ma, respectively. The Re–Os dating of molybdenite yields a well-constrained  $^{187}\text{Re}$ – $^{187}\text{Os}$  isochron age of  $354 \pm 7$  Ma. Geochemical data suggest that

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the Yuhaixi Mo (Cu) deposit was likely sourced from the juvenile lower crust and was formed in an arc setting.

Wu et al. (Contribution 3) present a systematic study of granodiorites and bimodal volcanic rocks from the north Huitongshan–Zhangfangshan ophiolitic belt in the Southern Beishan orogenic belt. The bimodal volcanic rocks consist of rhyolite and basaltic andesite. The Early Permian granodiorites ( $289 \pm 2$  Ma) and rhyolite ( $272 \pm 2$  Ma) have geochemical features similar to those of typical A<sub>2</sub>-type granitoids. The authors conclude that the Early Permian Zhangfangshan granodiorites and Baishantang bimodal volcanic rocks formed in a post-collision extensional setting and the Huitongshan–Zhangfangshan ocean had been closed before the Early Permian.

Chen et al. (Contribution 4) report new geochronological and geochemical results for the Early Devonian plutons from the Luotuoquan complex in the eastern segment of the Southern Beishan orogenic belt, including monzogranite (405 Ma) and syenogranite (399 Ma). Geochemical data enable the authors to state that these A-type granites might occur in a post-collisional extension setting. They further point out that the closure of the Beishan Ocean occurred before the Early Devonian.

Wang et al. (Contribution 5) present petrographic, geochronologic, and whole-rock elemental analyses and Sr–Nd–Hf–O isotopic composition analyses for Paleozoic Huashigou granitoids in the South Qilian along the northeastern margin of the Tibetan Plateau. They conclude that the Late Devonian ( $369 \pm 4$  Ma) and Middle Permian ( $262 \pm 1$  Ma) granitic rocks were formed in the orogenic–post-orogenic extensional setting after the closure of the Paleo-Tethys Ocean and were derived from the partial melting of crustal materials at different depths.

Wang et al. (Contribution 6) present a geochronological and geochemical study on Early Cretaceous volcanic rocks ( $129 \pm 1$  Ma) from the Longjiang formation in the middle of the Da Hinggan mountains, which belongs to the Zhalantun Duobaoshan island arc. Geochemical data enable the authors to state that these rocks were formed in a superimposed post-collisional and continental arc environment, possibly associated with the Mongol–Okhotsk Ocean closure and the oblique subduction of the Pacific Plate.

Wang et al. (Contribution 7) report new geochronological, geochemical, and isotopic results for the monzogranites ( $209 \pm 1$  Ma) and rhyolitic porphyries ( $170 \pm 1$  Ma) associated with the Wunugetu deposit, situated in the southern Erguna block. They conclude that the Wunugetu deposit was formed in an active continental margin setting and was influenced by the Late Triassic–Middle Jurassic southeastward subduction of the Mongol–Okhotsk Ocean.

Zhao et al. (Contribution 8) conducted skarn mineralogy, fluid inclusion (FI), and H–O isotopic analyses for the Da’anhe deposit in the eastern section of the Xingmeng orogenic belt. The data enable the authors to state that the Da’anhe deposit is a calcareous reduced skarn Au deposit related to the metasomatism of gabbro–dioritic magma and marble in the middle-deep part of the crust. They further point out that the distinctive nature of the ore-forming magma (source, reducing conditions, and high-water content:  $\Delta FMQ = 0.17$ ,  $\log(fO_2) = -15.11$ , water content = 6.80 wt.%) was key to the formation of the Da’anhe skarn gold deposit.

Na et al. (Contribution 9) studied the geochronology, petrology, and geochemistry of the Hadayang schists ( $360 \pm 2$  Ma and  $355 \pm 3$  Ma) in the eastern Xing’an block. Geochemical data indicate that the magma source of the schists was a mantle that consisted of both spinel and garnet lherzolite, with a partial melting degree of 1–5% and that it had undergone olivine, orthopyroxene, and plagioclase fractional crystallization. They conclude that Late Devonian–Early Carboniferous basic–intermediate magmatic rocks in the eastern Xing’an block were formed in an intracontinental extension tectonic setting similar to that of the North American Basin and Range basalt.

Zhang et al. (Contribution 10) conducted molybdenite Re–Os dating, H–O–S–Pb isotopic compositions, and fluid inclusion (FI) analyses on the Lower Urgen molybdenum deposit, which is situated in the northern Great Xing’an Range. Systematic data indicate that

the Lower Urgen molybdenum deposit is coeval with Late Jurassic–Early Cretaceous molybdenum mineralization events in NE China and that the hydrothermal process can be divided into three stages. Isotopic data suggest that the ore-forming fluids were initially of magmatic origin, with the increasing incorporation of meteoric water, and that the ore-forming materials originated from granitic magmas.

Pan et al. (Contribution 11) conducted a systematic investigation into sedimentary rocks from the Heilongjiang Complex, NE China. They identified two episodes of orogenic events including crustal thickening, magmatic flare-up, and landward migration. The Permian crustal thickening event was caused by a shallowing subducting slab angle and thus triggered magmatic flare-ups. The shallow slab subduction enhanced plate coupling and caused the westward subduction of the Mudanjiang Oceanic Plate, generating the second flare-up in this region and the crustal thickening event.

Li et al. (Contribution 12) reported new geochronological and geochemical results for the Middle Silurian–Middle Devonian magmatic rocks in Yitong County, Jilin Province, NE China, including tonalite, basalt, andesite, and metamorphic olivine-bearing basalt. Geochemical data enable the authors to state that the Middle–Late Silurian magmatic rocks were formed in an active continental margin environment influenced by the southward subduction of the Paleo-Asian Ocean, while the Middle Devonian volcanic rocks formed in an extensional environment after the arc–continent collision.

Chen et al. (Contribution 13) conducted a systematic investigation into Permian granitic rocks in the Chifeng area, located at the junction of the Xing’an–Mongolian orogenic belt and the northern margin of the North China Craton. They conclude that the Permian tectono-magmatic evolution of the Paleo-Asian Ocean can be divided into three events: (1) Early Permian granite formed in a subduction setting; (2) Middle Permian granite formed in a syn-collision setting; and (3) Late Permian–Early Triassic granite formed in an extensional setting induced by the slab break-off responsible for the closing of the PAO.

Yu et al. (Contribution 14) present in situ pyrite trace element and sulfur isotope composition measurements from the Beiwagou Pb–Zn Deposit, Liaodong Peninsula, Northeast China. They suggest that most mineralization events occurred due to the compaction and lithification during diagenesis, which led the sulfate to undergo thermochemical sulfate reduction, a loss of permeability, and vertical dewatering.

Tang et al. (Contribution 15) conducted geochronological, geochemical, and apatite fission track thermochronology studies on sandstone from the Upper Triassic Dajianggang Formation at the northeastern margin of the North China Plate, and they conclude that the main source of the Dajianggang Formation was the Late Triassic magmatic arc of the Changchun–Yanji suture zone, possibly mixed with materials from the northern margin of the North China Craton in a convergent tectonic setting. They further point out that the orogenic process in the study area ceased during the Late Triassic period and that the remote effect of Pacific subduction did not impact the study area until 30 Ma.

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#### List of Contributions:

1. Liu, B.; Hou, L.X.; Xu, Y.; Ju, N.; Ma, J.X.; Xie, Z.H.; Hong, Y.B.H. Zircon U–Pb–Hf Isotopes and Whole-Rock Geochemistry of the “Kulumudi Formation” from the Laofengkou Area (West Junggar): Implications of the Construction of a Juvenile Arc in the Junggar–Balkhash Ocean. *Minerals* **2024**, *14*, 14. <https://doi.org/10.3390/min14010014>.
2. Wang, D.; Xue, C.; Zhao, Y.; Li, C.; Xi, B.; Yang, Y.; Tian, Q.; Kang, X.; Wu, X. Ore Genesis and the Magmatism of the Yuhaixi Mo(Cu) Deposit in Eastern Tianshan, NW China: Constraints from Geology, Geochemistry, Zircon U–Pb and Molybdenite Re–Os Dating. *Minerals* **2023**, *13*, 1368. <https://doi.org/10.3390/min13111368>.

3. Wu, L.; Zhai, X.; Wang, E.; Chen, W.; Song, G.; Zheng, F.; Zhao, J.; Wang, J.; Wang, H. Early Permian Post-Collision Extensional Setting in the Southern Beishan Orogenic Belt: Evidence from the Zhangfangshan Granodiorite and the Baishantang Bimodal Volcanic Rocks. *Minerals* **2023**, *13*, 1468. <https://doi.org/10.3390/min13121468>.
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7. Wang, Q.; Yang, Y.; Fu, Q.; Zhang, Z.; Guo, X.; Wu, T.; Chai, L.; Zhou, Y.; An, Y. Origin and Geological Implications of Monzogranites and Rhyolitic Porphyries in the Wunugetu Porphyry Copper–Molybdenum Deposit, Northeast China: Evidence from Zircon U–Pb–Hf Isotopes and Whole-Rock Geochemistry. *Minerals* **2024**, *14*, 310. <https://doi.org/10.3390/min14030310>.
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## Article

# Zircon U-Pb-Hf Isotopes and Whole-Rock Geochemistry of the “Kulumudi Formation” from the Laofengkou Area (West Junggar): Implications of the Construction of a Juvenile Arc in the Junggar–Balkhash Ocean

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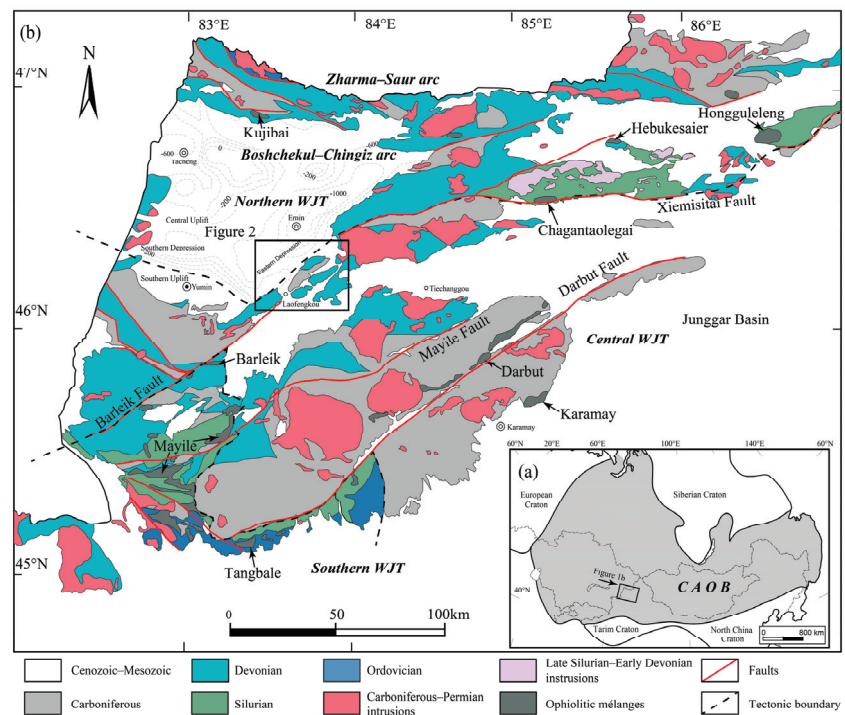
**Abstract:** The properties of ancient magmatic arcs are crucial for understanding the tectonic evolution of the Central Asian Orogenic Belt. The Middle Devonian Kulumudi Formation in the Laofengkou area of West Junggar lacks accurate chronological data constraints, which hampers the knowledge of the nature of the Late Paleozoic magmatic arcs in the West Junggar and circum-Balkhash areas. In this contribution, samples of pyroclastic rocks and sedimentary rocks were collected from the volcano–sedimentary strata of the Kulumudi Formation. Petrography, zircon U-Pb-Hf isotopic analysis and whole-rock geochemistry were carried out to constrain the age and the tectonic setting of the Kulumudi Formation. The zircon U-Pb age of the lithic crystal tuff from the Kulumudi Formation on the northeast side of the Alemale Mountains was  $386 \pm 2$  Ma, accurately indicating that this rock unit formed during the Middle Devonian. However, the fine sandstone near the Huojierte Mongolian Township, originally assigned as the “Kulumudi Formation”, yielded a maximum depositional age of  $341 \pm 3$  Ma. Combined with the stratigraphic contact, this rock unit was redefined to belong to the Lower Carboniferous Jiangbasitao Formation. According to the whole-rock geochemistry study, the lithic crystal tuff of the Kulumudi Formation was characterized as medium potassium–calc–alkaline series rock, which is relatively enriched in light rare earth elements and large ion lithophile elements (i.e., Rb, Ba, K) and depleted in high-field-strength elements (i.e., Nb, Ta, Ti), showing similar geochemical characteristics to the volcanic arc rocks. By contrast, the fine sandstone from the Jiangbasitao Formation had  $\text{Al}_2\text{O}_3/\text{SiO}_2$  (0.25–0.29) and  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  (1.29–1.72) ratios close to those derived from the continental arc and active continental margin and was characterized as part of the continental arc field in the La-Th-Sc and Th-Sc-Zr/10 tectonic discrimination diagrams. Zircon Hf isotope analysis showed that the  $\varepsilon_{\text{Hf}}(t)$  values of the Kulumudi Formation were +5.6–+12.8, and those of the Jiangbasitao Formation were +11.43–+15.48, both of which show highly positive juvenile characteristics. The above data indicate that the Kulumudi Formation and Jiangbasitao Formation both formed in a juvenile arc setting with ocean–continent subduction. Combined with the previous work, it was concluded that the southward subduction of the ocean basin represented by the Darbut–Karamay ophiolitic mélanges beneath the newly accreted arc crustal segments produced a juvenile arc with positive Hf isotope characteristics.

**Keywords:** Kulumudi Formation; West Junggar; Junggar–Balkhash Ocean; Central Asian Orogenic Belt; Hf isotope



## 1. Introduction

The Central Asian Orogenic Belt (CAOB), or the Altai [1], is located between the Siberian Craton, the European Craton and the Tarim–North China Craton (Figure 1a). It is characterized by the significant accretion of arcs (both intra-oceanic and continental), accretionary complexes, seamounts and oceanic plateaus since the Neoproterozoic, which formed during the long-term evolution of the Paleo-Asian Ocean [2,3]. The CAOB is a complex collage that consists of three major oroclines, including the Kazakhstan Orocline [4], the Mongolian Orocline [5] and the NE China Orocline [6]. Among these, the formation of the Kazakhstan Orocline has been attributed to the large-angle bending of the Devonian–Carboniferous magmatic arcs during the Late Paleozoic consumption of the Junggar–Balkhash Ocean (the southwestern branch of the Paleo-Asian Ocean) [2,4,7–10]. These two Devonian–Carboniferous magmatic arcs are difficult to reconstruct using a traditional study of igneous rocks because of the long-term subduction erosion [11]. However, the arc-derived sedimentary rocks retained on the surface might have recorded information about the provenances [11,12]. By using whole-rock geochemical compositions and detrital zircon U–Pb–Hf isotope characteristics of these arc-related sedimentary rocks, we can trace the properties of ancient magmatic arcs. Moreover, compared with the well-accepted Early-to-Middle-Devonian outer arc belt (OAB) with a Precambrian continental basement, the basement nature of the Late-Devonian-to-Carboniferous inner arc belt (IAB) remains debated [9,10,13].

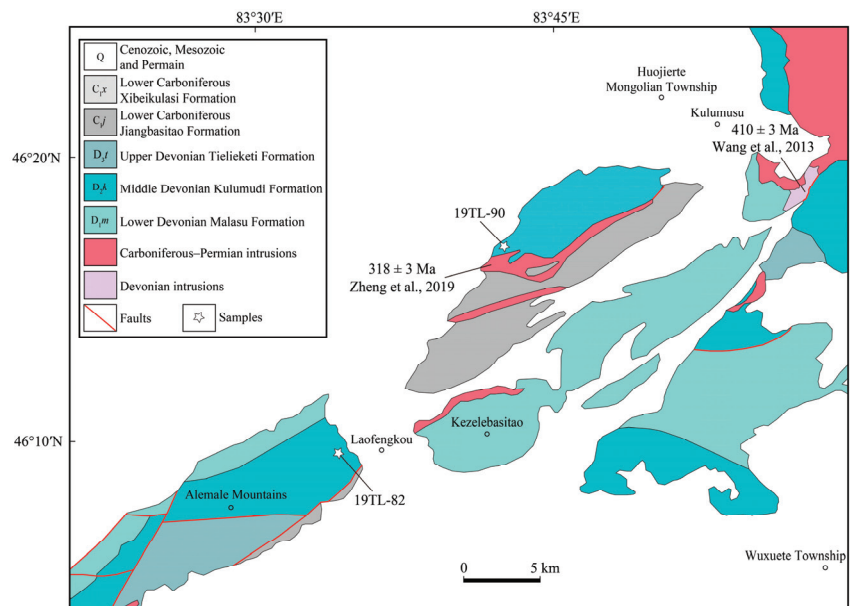


**Figure 1.** (a) Simplified tectonic map of the Central Asian Orogenic Belt (modified after [14]). (b) Geological map of the West Junggar terrane (modified after [15]).

The West Junggar Terrane (WJT) in the southwestern CAOB is located on the northern limb of the Kazakhstan Orocline (Figure 1a) [9,10]. The WJT is characterized by widespread Paleozoic accretionary complexes and Carboniferous–Permian intrusive rocks (Figure 1b), and its formation was closely associated with the subduction and closure of the Junggar–Balkhash Ocean [2,7,16–18]. Current research on the tectonic evolution of the WJT

focuses on the Ediacaran–Early Paleozoic [15,17,19,20] and Carboniferous–Permian periods [14,18,21]. It is generally accepted that the Ediacaran–Early Paleozoic evolution of the WJT was dominated by a single or multiple intra-oceanic arc(s) [15,17,19,20,22,23]. Previous work showed that the WJT was a place of active convergence during the Early Carboniferous [24,25], while the Late Carboniferous–Permian tectonic setting was suggested to be a post-collisional [25–27] or continuous normal/ridge-related subduction system [7,28,29]. However, relatively little research has been focused on the Devonian tectonic evolution of the WJT [9,30]. Therefore, a timely study of the Devonian tectonic setting is the key to understanding the whole Paleozoic tectonic evolution of the Junggar–Balkhash Ocean.

The Laofengkou area is located in the central part of the WJT, where the Late Paleozoic volcano–sedimentary strata and the Carboniferous–Permian intrusive rocks are extensively outcropping (Figure 2), but the accurate sedimentary age of the Middle Devonian Kulumudi Formation is still unclear. In this contribution, samples of pyroclastic rocks and sedimentary rocks were collected from the Middle Devonian Kulumudi Formation (Figure 2). Petrography, zircon U–Pb–Hf isotopic and whole-rock geochemistry analyses were carried out to accurately constrain the age and tectonic setting of the Middle Devonian Kulumudi Formation, which could provide new insights into the Late Paleozoic evolution of West Junggar. Combined with published data from the West Junggar and circum-Balkhash areas, the nature of the Late Paleozoic magmatic arcs in the tectonic frame of the Kazakhstan Orocline is discussed.



**Figure 2.** Geological map of the Laofengkou area (modified after [31]). Published age data are from [22,32].

## 2. Geological Setting and Sampling

### 2.1. Tectonic Units of the WJT

The WJT is located at the junction of the Siberian and Kazakhstan–Yili plates (Figure 1a), sandwiched between the North Tianshan and the Irtysh–Zaisan suture zones. According to juvenile Sr–Nd–Hf isotopic data, the WJT has been interpreted to lack of ancient Precambrian continental basement [16,33,34]. Taking the Chagantaolegai ophiolite mélangé [35,36] and the Barleik–Mayile–Tangbale ophiolite mélanges as the tectonic boundary (Figure 1b; [21,37]), the WJT can be divided into the northern, central and southern parts.

The northern WJT is composed of the Zharma–Saur arc and Boshchekul–Chingiz arc from north to south, which are separated by the EW-trending Kujibai–Hebukesaier–Hongguleleng ophiolitic mélanges [36,38]. The Zharma–Saur arc (346–321 Ma [24]) formed during the southward subduction of the Irtysh–Zaisan Ocean [2,24,39,40], while the Boshchekul–Chingiz arc is supposed to be related to the northward subduction of the Junggar–Balkhash Ocean [2,41] or the southward subduction of the Irtysh–Zaisan Ocean [42,43] during the Late Silurian–Early Devonian period.

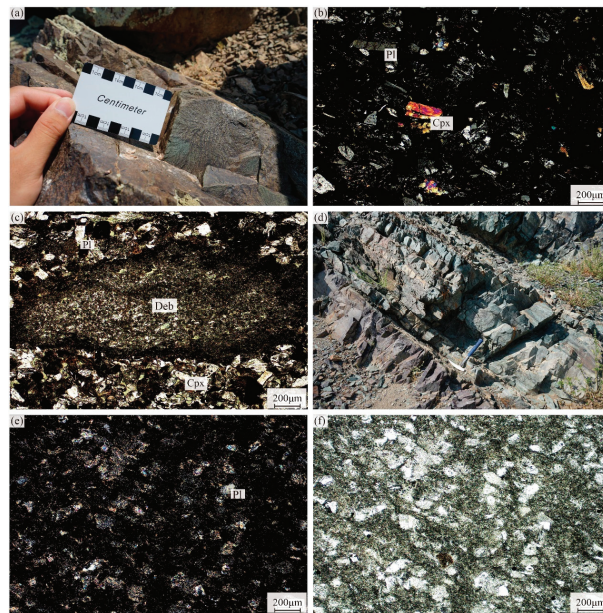
The central WJT is dominated by the Late Paleozoic accretionary complexes (Figure 1b) and Late Carboniferous–Early Permian granitoids [26,27]. Based on the recent identification of Late Devonian diorite (~368 Ma) with typical juvenile Nd isotopes, the central WJT was suggested to be the eastern extension of the northern limb of the IAB [9]. The Devonian–Early Carboniferous Karamay and Darbut ophiolitic mélanges [44–47] occur in the accretionary complexes and represent the youngest ophiolite mélanges in the WJT. The Paleozoic volcano–sedimentary sequences of the central WJT can be divided into the Mayile Mountains area and Karamay area. In the Mayile Mountains area, the Devonian strata are dominated by the Kulumudi and Tielieketi formations, comprising a set of clastic and volcanic rocks under neritic to marine environments [21,31,37,48–50]. The zircon U–Pb ages of the tuffs from the Tielieketi Formation range from ~369 to 363 Ma [21,50], and the maximum depositional age of this formation is ~356 Ma [21]. The Lower Carboniferous strata include the Heishantou and Jiangbasitao formations, and the zircon U–Pb ages of tuffs from the latter are ~336 to 339 Ma [51]. The Paleozoic strata exposed in the Karamay area include the Carboniferous and Permian volcano–sedimentary rocks. The Lower Carboniferous strata consist of the Tailegula, Baogutu and Xibeikulasi formations, and there are different understandings of the stratigraphic sequences among them [52–55]. A limited outcrop of the Upper Carboniferous Molaoba Formation shows typical fluvial sedimentary characteristics [21]. Upwards, Permian volcano–sedimentary sequences are a set of intermediate-acid terrestrial volcanic rocks containing fossils of Angara flora [56,57].

The southern WJT contains the Ediacaran–Silurian arc and accretionary complexes. The records of intra-oceanic arc magmatism are mainly distributed in the Barleik (540–502 Ma [22,37,58]), Mayile (530–515 Ma [20,23]) and Tangbale (572–549 Ma [22,23]) areas. The accretionary complexes are mainly composed of the Barleik, Mayile and Tangbale SSZ-type ophiolite mélanges from north to south and the subduction-related metamorphic rocks (504–492 Ma [17]). Previous studies have found that the oldest ophiolitic mélanges of the southern WJT formed at 572 to 512 Ma [20,59–61], suggesting that the initial intra-oceanic subduction of the Junggar–Balkhash Ocean occurred in the Ediacaran [15]. Recently, the occurrences of quartz diorites with adakitic geochemical features (394–390 Ma [10]) were interpreted as supporting evidence of an eastern extension of the Kazakhstan OAB in the southern WJT.

## 2.2. Geology of the Study Area

The Laofengkou area is located in the northeast of the Mayile Mountains in the central WJT and is dominated by the Devonian–Early Carboniferous strata and granitoid intrusions (Figure 2). The Middle Devonian Kulumudi Formation is composed of littoral–shallow marine terrigenous sedimentary rocks, pyroclastic rocks with a small amount of limestone and acid volcanic rocks [31]. The zircon U–Pb age of the tuff for the Kulumudi Formation near the Laofengkou area (Tiechanggou area, Figure 1b) is  $379 \pm 5$  Ma [48]. In terms of the Laofengkou area, the Middle Devonian Kulumudi Formation exposed northeast of the Alemale Mountains consists of tuffaceous siltstone and lithic crystal tuff (Figure 3a). Meanwhile, the Kulumudi Formation is composed of fine sandstone interbedded with sandstone southwest of the Huojierte Mongolian Township (Figure 3d).





**Figure 3.** Photomicrographs and field photographs of the dark green lithic crystal tuff (a–c) and gray-green fine sandstone (d–f). Pl—plagioclase; Cpx—clinopyroxene; Deb—debris.

### 2.3. Sample Description

Samples were collected from the above locations (Figure 2), including the lithic crystal tuff and fine sandstone. The dark green lithic crystal tuff (19TL-82, 46°7'48" N, 83°35'57" E) had a tuffaceous texture and massive structure (Figure 3a), which was mainly composed of crystal debris (65%), lithic debris (25%) and volcanic ashes (10%) (Figure 3b,c). The crystal debris consisted of plagioclase (0.2–0.7 mm) and clinopyroxene (~0.2 mm). Locally, this sample had undergone clayization. The gray-green fine sandstone (19TL-90, 46°17'20" N, 83°42'22" E) showed a fine-grained texture and massive structure (Figure 3d). It developed plenty of xenomorphous carbonate minerals and a few plagioclases with altered edges and polysynthetic twins (Figure 3e,f).

## 3. Analytical Methods

### 3.1. Zircon U–Pb and Lu–Hf Isotope Analysis

Representative zircon grains were selected from the samples according to their color, shape and integrity; mounted in epoxy resin; and polished. The zircon grains with obvious oscillating zoning under cathodoluminescence (CL) images were considered. Zircon U–Pb dating and trace element analyses were undertaken using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at Beijing Createch Testing Technology Co., Ltd., Beijing, China, using a RESolution 193 nm laser ablation system attached to an Agilent 7500 ICP-MS instrument. The laser spot was 24 µm in diameter, and the frequency was 10 Hz. The energy density was about 10 J/cm<sup>2</sup>. GJ-1 standard zircons were used during the experiments. Offline data calculations and concordia diagrams were processed using the ICPMSDataCal program [62] and Isoplot 4.0, respectively. The zircon U–Pb data and rare earth element compositions are summarized in Table S1 and Table S2, respectively.

In situ zircon Hf isotope analysis was carried out using a RESolution SE 193 laser-ablation system attached to a Nu Plasma II multiple collector ICP-MS instrument at State Key Laboratory of Continental Dynamics, Northwest University, Xi'an, China. Zircon GJ-1 was used as the standard sample. The laser spot was 43 µm in diameter and the energy density was 6 J/cm<sup>2</sup>. The detailed experimental process and related parameters are

described by [63,64]. A two-stage model was selected for the depleted-mantle-based Hf model ages ( $T_{DM}$ ) calculation. The zircon Hf data are summarized in Table S3.

### 3.2. Whole-Rock Major and Trace Element Analysis

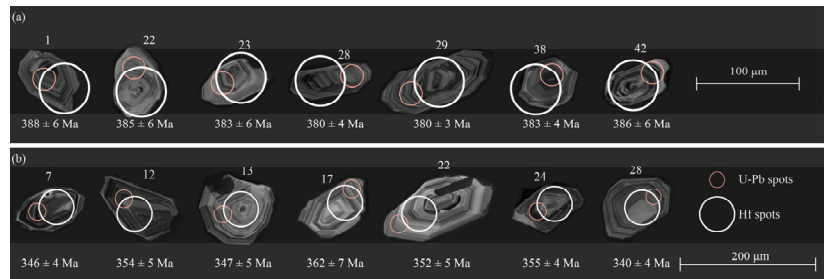
The whole-rock major and trace element compositions were determined at Beijing Createch Testing Technology Co., Ltd., Beijing, China. Major elements were analyzed using a Shimadzu X-ray fluorescence spectrometer with an accuracy better than 5%. The trace elements were determined using an Analyticjena PQMS elite ICP-MS with an accuracy better than 5%. The analytical data are presented in Table S4.

## 4. Analytical Results

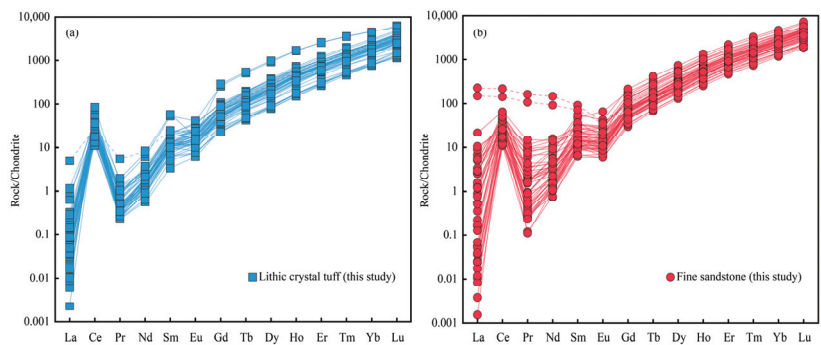
### 4.1. Zircon U-Pb and Lu-Hf Isotope Analysis

#### 4.1.1. Zircon U-Pb Ages

Zircons from the lithic crystal tuff (19TL-82) were mainly euhedral and prismatic with lengths of 50–150  $\mu\text{m}$  and showed obvious oscillatory zoning (Figure 4a), which is typical of tuff origin [65]. Based on REE patterns (Table S2), zircons shown by the solid lines exhibited positive Ce and slightly negative Eu anomalies, which is typical of igneous origin (Figure 5a). This is consistent with their Th/U ratios (0.31–0.97, Table S1). Zircons shown by the dotted line were relatively rich in La (Figure 5a), which might have been subjected to hydrothermal metasomatism or metamorphism at a later stage [66], and were excluded from consideration. This sample yielded 30 valid zircon ages ranging from  $380 \pm 4$  Ma to  $421 \pm 7$  Ma ( $^{206}\text{Pb}/^{238}\text{U}$  age, Table S1), of which the older age of  $421 \pm 7$  Ma might have been derived from an inherited zircon. The weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of the remaining 29 zircons was  $386 \pm 2$  Ma (MSWD = 1.20, Figure 6a,b), representing that the lithic crystal tuff formed during the Middle Devonian.

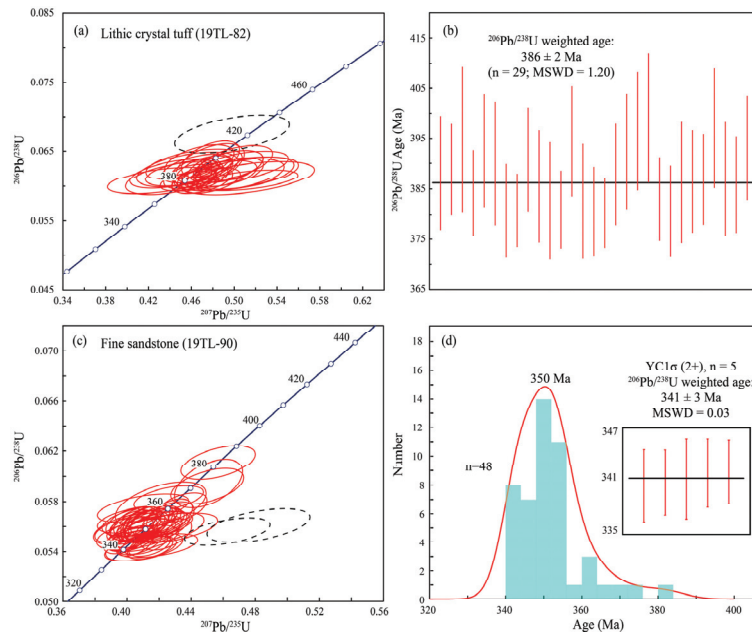


**Figure 4.** Cathodoluminescence (CL) images of representative zircons of the lithic crystal tuff (a) and fine sandstone (b).



**Figure 5.** Chondrite-normalized REE patterns of the zircons of the lithic crystal tuff (a) and fine sandstone (b). Chondrite normalization values are from [67].

Detrital zircons from the fine sandstone (19TL-90) were mainly euhedral and short prismatic, with clear oscillating zoning and 50–200  $\mu\text{m}$  in length (Figure 4b). Zircons shown by the dotted lines were also not considered (Figure 5b, Table S2). The sample yielded 48 usable zircon ages with a variation from  $340 \pm 4$  Ma to  $382 \pm 5$  Ma, with Th/U ratios ranging from 0.40 to 1.11 (Table S1). The Early Carboniferous ages comprised the largest population (41 of the 48 results, Table S1) and exhibited a single peak at 350 Ma (Figure 6c,d). The maximum depositional age of this sandstone was  $341 \pm 3$  Ma ( $^{206}\text{Pb}/^{238}\text{U}$  age,  $n = 5$ ) using the weighted mean age of the youngest cluster of two or more grain ages ( $n \geq 2$ ) overlapping in age at  $1\sigma$  (YC1 $\sigma$  (2+)).



**Figure 6.** Zircon U-Pb concordia diagrams and weighted average age diagrams of the lithic crystal tuff (a,b) and fine sandstone (c,d). The red solid circles represent valid zircon ages that were used for further discussion, whereas the black dotted ones were not considered during the calculation.

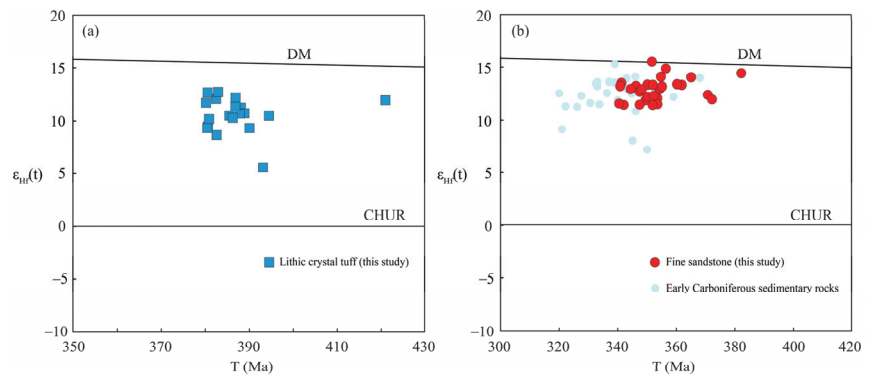
#### 4.1.2. Hf Isotopes

Nineteen zircon grains from the lithic crystal tuff that were selected for U-Pb dating were analyzed for in situ Lu-Hf isotopic compositions. They had initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios from 0.282685 to 0.282895 (Table S3) and exhibited  $\epsilon_{\text{Hf}}(t)$  values from +5.6 to +12.8 (Figure 7a). All zircon grains were characterized by young Hf model ages of 564–1032 Ma (Table S3).

Twenty-eight detrital zircon grains from the fine sandstone had initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios from 0.282931 to 0.282991 (Table S3) and their  $\epsilon_{\text{Hf}}(t)$  values ranged from +11.4 to +15.5, consistent with the Early Carboniferous sedimentary rocks in the adjacent area (Figure 7b). These detrital zircons had comparable young Hf model ages of 366–626 Ma (Table S3).

#### 4.2. Whole-Rock Major and Trace Element Analysis

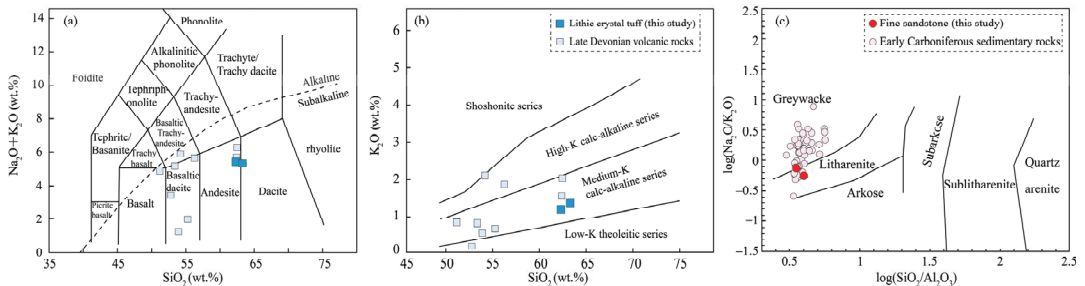
The whole-rock geochemical analysis was carried out for the lithic crystal tuff (19TL-80/81) and fine sandstone (19TL-88/89). To avoid the influence of loss on ignition (LOI), all contents for major oxides were recalculated after deducting the LOI. Whole-rock geochemical data are shown in Table S4.



**Figure 7.** The  $\epsilon_{\text{Hf}}(t)$  vs.  $T$  (Ma) diagrams of the lithic crystal tuff (a) and fine sandstone (b). Data for the Early Carboniferous sedimentary rocks are from [68].

#### 4.2.1. Major Elements

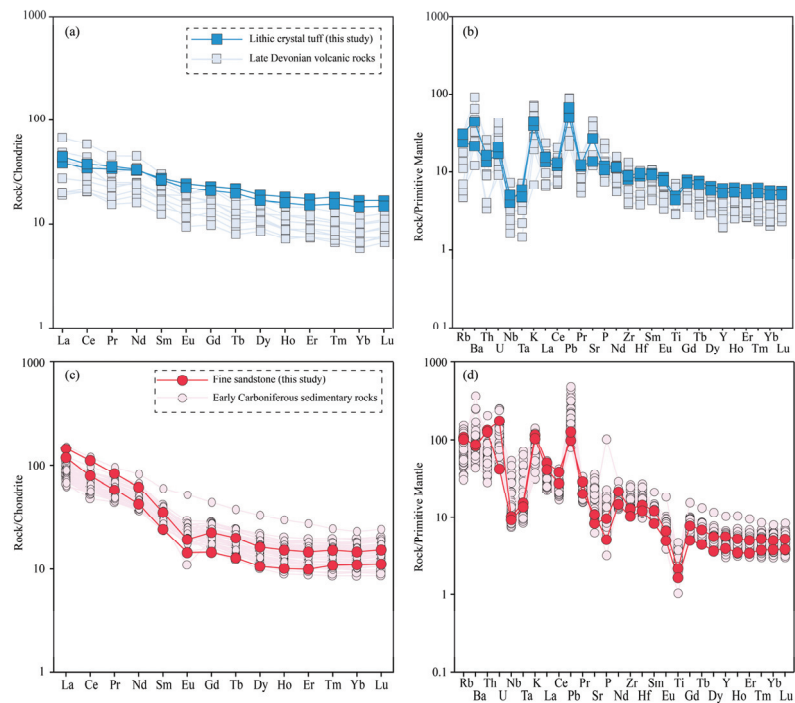
The lithic crystal tuff samples (19TL-80/81) had high  $\text{SiO}_2$  contents (62.32–63.29 wt.%) and medium  $\text{Na}_2\text{O}$  (3.93–4.23 wt.%) and  $\text{K}_2\text{O}$  (1.18–1.36 wt.%) contents. Their  $\text{MgO}$  contents ranged from 2.38 wt.% to 2.73 wt.%, with a relatively high  $\text{Mg\#}$  value of 56. They were plotted in the andesite and dacite fields (Figure 8a) and medium-K calc-alkaline series field (Figure 8b). The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (3.50–3.97) of the fine sandstone samples (19TL-88/89) were comparatively low. These fine sandstone samples had medium  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  and relatively high  $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$  ratios, and thus, were plotted in the litharenite fields (Figure 8c).



**Figure 8.** TAS classification diagram ((a), from [69]),  $\text{SiO}_2$  vs.  $\text{K}_2\text{O}$  diagram of the lithic crystal tuff ((b), from [70]);  $\lg[w(\text{Na}_2\text{O})/(\text{K}_2\text{O})]$  vs.  $\lg[w(\text{SiO}_2)/w(\text{Al}_2\text{O}_3)]$  diagram ((c), from [71]) of the fine sandstone. Data for the Late Devonian volcanic rocks and the Early Carboniferous clastic rocks are from [50] and [68,72], respectively.

#### 4.2.2. Trace Elements

The lithic crystal tuff samples showed enrichment of light rare earth elements (LREEs) and depletion of heavy rare earth elements (HREEs) with  $\delta\text{Eu}$  values of 0.94–0.97 (Figure 9a), implying the absence of obvious Eu anomalies. They were rich in large-ion lithophile elements (LILEs, i.e., Rb, Ba, K) and depleted in high-field-strength elements (HFSEs, i.e., Nb, Ta, Ti), showing similar geochemical characteristics to those of volcanic arc rocks (Figure 9b). The fine sandstone samples had enriched LREEs and relatively flat HREEs (Figure 9c). The  $\delta\text{Eu}$  values ranged from 0.66 to 0.74, indicating an obvious Eu negative anomaly, similar to that of open PAAS ( $\delta\text{Eu} = 0.65$  [73]). The samples were also deficient in HFSEs (i.e., Nb, Ta, Ti) (Figure 9d) and exhibited low ferromagnesian trace element concentrations (Sc, 8.0–8.9; Co, 9.8–11.9; Ni, 4.5–6.5).



**Figure 9.** Chondrite-normalized REE patterns (a,c) and primitive-mantle-normalized spidergrams (b,d) of the lithic crystal tuff and fine sandstone. Data for Later Devonian volcanic rocks and Early Carboniferous sedimentary rocks are from [50] and [68,72], respectively.

## 5. Discussion

### 5.1. Sedimentary Age of the Kulumudi Formation

Previous work on the stratigraphy of the Middle Devonian Kulumudi Formation was mainly based on the lithostratigraphic correlation and paleontological fossils [31,74]. Among these fossils, occurrences of *Barradeophylum* sp., *Pachyfavosites* sp., *Paraspirifer* sp., *Psilophyton bella* (*Tchirkoua*) *Aneurophyton* aff. *Germanicak* Etw., etc., indicate typical Middle Devonian characteristics [31,74]. In this study, the zircon U-Pb dating result for the lithic crystal tuff from the Middle Devonian Kulumudi Formation was  $386 \pm 2$  Ma (Figure 6b), indicating that the stratum northeast of the Alemale Mountains belongs to the Middle Devonian, which is consistent with previous results [31,74].

Differently, based on the detrital zircon ages, the maximum depositional age of detrital zircons from the fine sandstone was  $341 \pm 3$  Ma (Figure 6c). This result shows that the stratum originally assigned as the “Kulumudi Formation” southwest of the Huojierte Mongolian Township was formed during the Early Carboniferous. Indeed, the result is similar to the age of the adjacent Lower Carboniferous Jiangbasitao Formation ( $336 \pm 3$  Ma,  $339 \pm 2$  Ma [51]). Importantly, the originally assigned “Kulumudi Formation” and the Lower Carboniferous Jiangbasitao Formation were invaded by the Late Carboniferous intrusive rocks ( $318 \pm 3$  Ma [22]) together (Figure 2). The Jiangbasitao Formation is a set of terrigenous sedimentary rocks mainly composed of the conglomerate, sandy conglomerate, carbonaceous shale, argillaceous siltstone and fine sandstone [31], which is consistent with the rocks observed southwest of the Huojierte Mongolian Township. Thus, our new chronological data, together with the above lithologic correlation, indicate that parts of the “Kulumudi Formation” should be redefined as the Lower Carboniferous Jiangbasitao Formation.



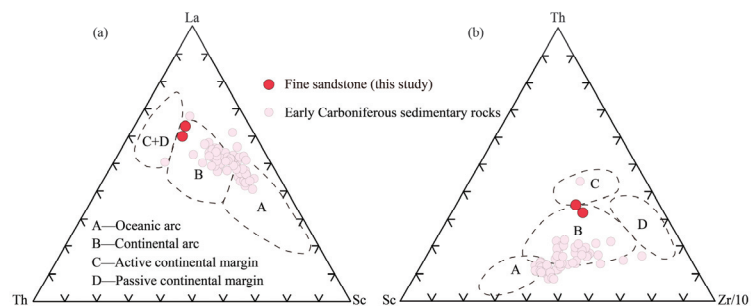
## 5.2. Tectonic Setting

### 5.2.1. The Middle Devonian Kulumudi Formation

The lithic crystal tuff samples (~386 Ma) of the Middle Devonian Kulumudi Formation were plotted in the andesite and dacite fields in the TAS classification diagram (Figure 8a), and thus, they belonged to the medium potassium calc-alkaline series (Figure 8b). These samples were rich in LREEs and LILEs and depleted in HREEs and HFSEs (Figure 9a,b), indicating geochemical characteristics similar to the volcanic arc rocks [75]. Furthermore, the samples had relatively low Nb/La ratios (0.32–0.34) and high La/Ta (35.53–53.82) and Th/Nb ratios (0.38–0.39), confirming that they were formed in a subduction-related setting [76]. Their high Ba/La values (16.47–29.58) also imply a strong effect on the magma source area from a subduction zone or related fluids [77]. Furthermore, the  $\varepsilon_{\text{Hf}}(t)$  values of the zircons from the lithic crystal tuff show highly positive characteristics, ranging from +5.6 to +12.8 (Figure 7a), indicating the feature of a juvenile arc. Considering the whole-rock geochemistry and Hf isotope analysis, the lithic crystal tuff from the Middle Devonian Kulumudi Formation is suggested to be formed in a juvenile arc setting.

### 5.2.2. The Early Carboniferous Jiangbasitao Formation

The chemical index of alteration (CIA) and index of compositional variability (ICV) can be used to assess the weathering intensity and source composition of the sedimentary rocks. The relatively low CIA values (63.06–63.97) for the fine sandstone from the Jiangbasitao Formation suggest a low degree of chemical weathering. The high ICV values ranging from 1.40–1.45 indicate an immature source. Their  $\delta\text{Eu}$  values ranged from 0.66 to 0.74 and clear Nb-Ta negative anomalies (Figure 9d), similar to many subduction-related compositionally intermediate lavas [75]. The contents and ratios of major and trace elements in clastic rocks can distinguish different tectonic settings, such as oceanic arc, continental arc, active continental margin and passive continental margin [78,79]. The contents of  $\text{TiO}_2$  (0.38–0.50 wt.%) in fine sandstone samples from the Jiangbasitao Formation were similar to those in active continental margin and continental arc [80]. The  $\text{Al}_2\text{O}_3/\text{SiO}_2$  (0.25–0.29) and  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  (1.29–1.72) ratios were close to those derived from the continental arc and active continental margin, respectively [80]. Moreover, all samples were plotted in the continental arc field in the La-Th-Sc and Th-Sc-Zr/10 tectonic discrimination diagrams (Figure 10a,b). The highly positive  $\varepsilon_{\text{Hf}}(t)$  values (+11.4 to +15.5) of the detrital zircons from the fine sandstone suggest a juvenile arc (Figure 7b), which is consistent with the interpretation that the Early Carboniferous sedimentary rocks from the Darbut area were derived from a juvenile arc setting (Figure 7b). Thus, combined with published data from adjacent areas [68,72]), the new whole-rock geochemistry and Hf isotope analysis suggest an Early Carboniferous juvenile arc in the central WJT rather than a continental arc with Precambrian basement [13].



**Figure 10.** Discrimination diagrams of the La-Th-Sc (a) and Th-Sc-Zr/10 (b) (from [80]). A—oceanic arc; B—continental arc; C—active continental margin; D—passive continental margin. Data for Early Carboniferous sedimentary rocks are from [68,72].

### 5.3. Tectonic Evolution of West Junggar during the Middle Devonian–Early Carboniferous

During the Ediacaran–Cambrian period, the southern WJT was suggested to be a southward intra-oceanic subduction setting in the Tangbale area, forming the Tangbale ophiolitic mélange (572–531 Ma [15,20,59–61]). With the northward migration of the subduction zone, the Mayile ophiolite mélange (516–517 Ma [20,81]) and Barleik ophiolite mélange ( $512 \pm 7$  Ma [81]) gradually formed. These Ediacaran–Early Paleozoic SSZ-type ophiolitic mélanges, combined with the intra-oceanic arc igneous rocks [23] and subduction-related metamorphic rocks [17], clearly indicate an intra-oceanic arc setting for the southern WJT [15]. Meanwhile, the northward subduction of the oceanic crust of the Junggar–Balkhash Ocean formed the Middle Silurian to Early Devonian Boshchekul–Chingiz arc [41].

There are different interpretations of the ocean basin represented by the Darbut–Karamay ophiolite mélanges during the Devonian and Early Carboniferous. Some researchers interpret the basin as a residual ocean basin trapped by the Junggar–Balkhash Ocean under the constraint of the Kazakhstan Orocline [46], based on the fact that the Lower Carboniferous continuous volcano–sedimentary strata are developed on both sides of the Darbut ophiolite mélange [45,82]. Alternatively, the opening of the Devonian Karamay back-arc ocean basin [41] was suggested to result from the continuous lithosphere extension during the Early–Middle Devonian. Regardless of the residual ocean basin or back-arc ocean basin model, a consensus has been reached about the existence of an Early Devonian–Early Carboniferous oceanic basin in the central WJT. Importantly, previous studies found that the Middle Devonian Kulumudi Formation unconformably overlies the Ediacaran–Early Paleozoic accretionary complexes in the southern and central WJT [20,49,83], indicating that the Ediacaran–Early Paleozoic intra-oceanic subduction had ended before the Middle Devonian [15]. Such a pre-Middle Devonian lateral accretion of juvenile oceanic arc crust was further evidenced by recent dating results of detrital zircons from the southern WJT [12]. A major sedimentary transition from Middle–Late Silurian bathyal facies to Devonian overall littoral–terrestrial facies [49] and the absence of Late Silurian arc-related volcanism also support a pre-Late Silurian termination of the intra-oceanic subduction–accretion processes.

Since the Early Devonian, the oceanic crust represented by the Darbut–Karamay ophiolitic mélanges has subducted southward, forming the active continental margin in the southern and central WJT. Early–Middle Devonian adakitic magmatism (394–390 Ma) with high positive  $\varepsilon_{\text{Hf}}(t)$  values of +5.6 to +10.3 was newly recognized in the southern WJT and their formation was contributed to the partial melting of a juvenile and slightly thickened lower crust as the eastern extension of the Kazakhstan Early–Middle Devonian OAB [10]. Similarly, Liu and Han [9] suggested that the tectonic setting of the central WJT (northern IAB) evolved to a juvenile Late Devonian IAB built on Ediacaran–Early Paleozoic accreted terranes (intra-oceanic arcs and accretionary complexes), contrasting with the Yili (southern IAB) and Balkhash (central IAB) arcs built on a Precambrian continental basement. Combined with the above-published results, the positive  $\varepsilon_{\text{Hf}}(t)$  values of the studied Middle Devonian tuff (+5.6–+12.8) and Early Carboniferous sandstone (+11.4–+15.5) show typical juvenile arc characteristics, indicating that the active continental margin of central WJT lacked ancient continental basement during the Middle Devonian–Early Carboniferous subduction [9,10]. The occurrences of only two ancient zircons for pyroxene diorite (408 Ma [13]) from the central WJT may not indicate a Precambrian basement. Thus, it was concluded that the southward subduction of the ocean basin represented by the Darbut–Karamay ophiolitic mélanges beneath the newly accreted arc crustal segments resulted in a juvenile arc with positive Hf isotope characteristics.

## 6. Conclusions

- (1) The lithic crystal tuff from the Kulumudi Formation northeast of the Alemale Mountains in the Laofengkou area yielded a zircon U–Pb age of  $386 \pm 2$  Ma and was formed during the Middle Devonian. The maximum depositional age for the fine sandstone originally assigned into the “Kulumudi Formation” southwest of the Huo-

jierte Mongolian Township was  $341 \pm 3$  Ma, belonging to the Lower Carboniferous Jiangbasitao Formation.

- (2) According to the whole-rock geochemistry and Hf isotope analysis, the Middle Devonian Kulumudi Formation and Lower Carboniferous Jiangbasitao Formation formed in a juvenile arc setting related to the ocean–continent subduction.
- (3) During the Middle Devonian to Early Carboniferous, the ocean basin represented by the Darbut–Karamay ophiolitic mélanges subducted southward beneath the newly accreted arc crustal segments, forming a juvenile arc with positive Hf isotopic characteristics.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14010014/s1>, Table S1: Zircon U–Pb data of pyroclastic rocks and sedimentary rocks from the Laofengkou area, West Junggar; Table S2: Rare earth element compositions ( $\times 10^{-6}$ ) of zircons for pyroclastic rocks and sedimentary rocks from the Laofengkou area, West Junggar; Table S3: Zircon in situ Lu–Hf isotope compositions for pyroclastic rocks and sedimentary rocks from the Laofengkou area, West Junggar; Table S4: Whole-rock major (wt.%) and trace element ( $\times 10^{-6}$ ) compositions for pyroclastic rocks and sedimentary rocks from the Laofengkou area, West Junggar.

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## Article

# Ore Genesis and the Magmatism of the Yuhaxi Mo(Cu) Deposit in Eastern Tianshan, NW China: Constraints from Geology, Geochemistry, Zircon U-Pb and Molybdenite Re-Os Dating

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**Abstract:** The Yuhaxi Mo(Cu) deposit is a new discovery in the eastern section of the Dananhu-Tousuquan island arc, Eastern Tianshan. However, the genesis of the Yuhaxi Mo(Cu) deposit is still not fully understood. The Yuhaxi intrusion is composed of monzonitic granites, diorites, granites, and gabbro dikes, among which disseminated or veinlet Mo and Cu mineralization is mainly hosted by the monzonitic granites. The LA-ICP-MS zircon U-Pb dating yields emplacement ages of  $359.4 \pm 1.6$  Ma for the monzonitic granite,  $298.8 \pm 1.8$  Ma for the diorite, and  $307.0 \pm 2.3$  Ma for the granite. The Re-Os dating of molybdenite hosted by monzonitic granite yields a well-constrained  $^{187}\text{Re}$ - $^{187}\text{Os}$  isochron age of  $354.1 \pm 6.8$  Ma (MSWD = 1.7) with a weighted average age of  $344.5 \pm 3.1$  Ma. The Mo mineralization is closely associated with the Yuhaxi monzonitic granite. The Yuhaxi monzonitic granite rocks are characterized by high silica ( $\text{SiO}_2 > 70$  wt.%), low MgO (0.23–0.36), Ni, Cr contents, and they are enriched in light rare earth elements (LREEs) and large ion lithophile elements (LILEs: e.g., K, Ba, Pb and Sr), and depleted in heavy rare earth elements (HREEs) and high field-strength elements (HFSEs: e.g., Nb, Ta and Ti). They are weak peraluminous and have high  $\epsilon\text{Hf}(t)$  (11.37–17.59) and  $\epsilon\text{Nd}(t)$  (1.36–7.75) values, and varied initial  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7037–0.7128) values. The Yuhaxi post-ore granites exhibit similar geochemical and isotopic signatures to the Yuhaxi monzonitic granite. These characteristics suggest that the Yuhaxi felsic rocks are likely sourced from the partial melting of the juvenile lower crust. The Yuhaxi diorite has low  $\text{SiO}_2$ , and  $\text{K}_2\text{O}$  contents, relatively high  $\text{Na}_2\text{O}$ , MgO ( $\text{Mg}^\# = 45$ –53) contents, and depletions in HFSE (e.g., Nb, Ta, and Ti). These geochemical features, coupled with isotopic data such as low initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $\leq 0.7043$ ), high  $\epsilon\text{Nd}(t)$  (2.5 to 3.0) and  $\epsilon\text{Hf}(t)$  ( $\geq 11.6$ ) values, and young Hf model ages, suggest that their parental magmas possibly originated from the partial melting of the depleted lithospheric mantle that was metasomatized by hydrous melts or fluids from the subducting oceanic plate. Integrating our new results with previous works on the Dananhu-Tousuquan island arc belt, we suggest that the Yuhaxi Mo(Cu) deposit is likely sourced from the juvenile lower crust, which was formed in an arc setting, where the bipolar subduction of the North Tianshan oceanic slab forms the Dananhu-Tousuquan belt to the north and the Aqishan-Yamansu belt to the south. The eastern section of the Dananhu-Tousuquan island arc is a promising target for late Paleozoic porphyry Mo(Cu) deposits.

**Keywords:** LA-ICP-MS zircon U-Pb dating; geochemistry; Sr-Nd-Hf isotope; molybdenite Re-Os dating; Yuhaxi Mo deposit; Eastern Tianshan

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## 1. Introduction

Porphyry ore deposits are the primary source of Cu, Mo, and Au [1–3]. Porphyry-type deposits commonly form in the young continental and oceanic arcs [4], and they are



usually associated with magmatic–hydrothermal fluids exsolved from relatively oxidized intermediate-felsic magmas with high oxidation states [1,4]. However, porphyry Mo(Cu) deposits in the margins of North China Craton mainly occurred in a post-collision extension setting and the ore-forming magmas stemmed from an old lower crust source [5–14]. Therefore, the origin and evolution processes of ore-forming magmas and their tectonic setting are significant for understanding the formation of economic porphyry deposits [1,2,4].

Recently, numerous early Paleozoic porphyry Cu-Mo deposits have been discovered in the Eastern Tianshan, southern margin of the Central Asian Orogenic Belt (CAOB). These porphyry-type deposits are closely related to the Paleozoic intermediate to felsic magmatic hydrothermal activity in the Eastern Tianshan [15–17]. The Dananhu-Tousuquan arc belt (DTA) is located in the northern part of the Eastern Tianshan, which hosts Tuwu-Yandong, Fuxing, Linglong, Chihu, Yuhai porphyry deposits. Previous studies are mainly focused on these porphyry deposits in the middle section, which have revealed that most of the porphyry Cu-Mo deposits were likely related to the subduction of the North Tianshan Oceanic plate in the late Paleozoic [4–10]. However, the genesis of the porphyry Mo(Cu) deposits in the eastern section of the DTA has not been fully understood.

The Yuhaxi porphyry Mo(Cu) deposit is a new discovery in the eastern section of the DTA, which provides a good opportunity for investigating the generation mechanisms for the porphyry Mo deposits in this section [10–14]. In this study, zircon LA-ICP-MS U-Pb dating and trace elements, zircon Hf isotope compositions, whole-rock geochemical data, and molybdenite Re-Os isotope dating were carried out to constrain the magma origins and the timing of mineralization in the Yuhaxi Mo(Cu) deposit. This study provides new insights on the evolution of the DTA and its potential for porphyry Mo(Cu) mineralization in Eastern Tianshan.

## 2. Geological Settings

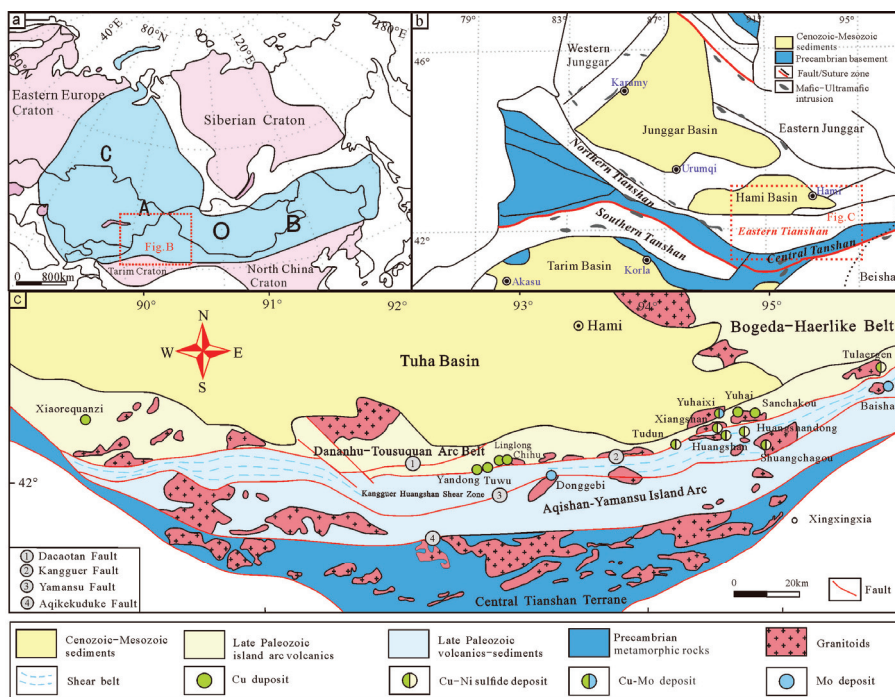
### 2.1. Regional Geology

The CAO, which is placed between the European and Siberian Cratons in the north and the North China and Tarim Cratons in the south, is the largest Phanerozoic accretionary orogenic belt in the world [8]. The west–east trending Eastern Tianshan orogenic belt is situated in the southern margin of the CAO. The Eastern Tianshan is a Paleozoic island arc system, which is located between the Jungar Basin and the Tarim Craton (Figure 1), characterized by a series of complicated tectonic history, which has witnessed multiple stages of subduction and collisional events [11–17]. It can be divided into three major tectonic zones from the north to the south: the Bogeda-Haerlike belt, the Jueluotage belt, and the Central Tianshan block (Figure 1c). The Eastern Tianshan belt withstands a series of E–W trending faults, including the Kanggur, the Yamansu, the Dacotan, and the Aqikekuduke faults [12]. The Dananhu-Tousuquan island arc belt mainly consists of Devonian to Carboniferous sedimentary–volcanic rocks. The Devonian Dananhu Formation consists of basaltic to andesitic volcanic rocks, which were overlain by the Carboniferous Gandun Formation sedimentary rocks and Qie’shan Group basaltic–andesitic volcanic/pyroclastic rocks and sedimentary rocks. Most of the Cu-Mo deposits in the Eastern Tianshan porphyry are hosted in the middle section of the Dananhu-Tousuquan island arc belt [15,18–25]. The Kangguer shear zone mainly comprises volcanic–sedimentary rocks of the Carboniferous Gandun and Wutongwozi formations, and volcanic and pyroclastic rocks of the Carboniferous Yamansu Formation [15,16]. Most rocks were metamorphosed and ductile deformed in the Kangguer shear zone [11,15]. The Aqishan-Yamansu belt comprises bimodal volcanic rocks of the Carboniferous Yamansu Formation, as well as clastic rocks, andesitic tuff, and the Permian Kula Formation marine and terrestrial clastic rocks [15,25–29].

### 2.2. Ore Deposit Geology

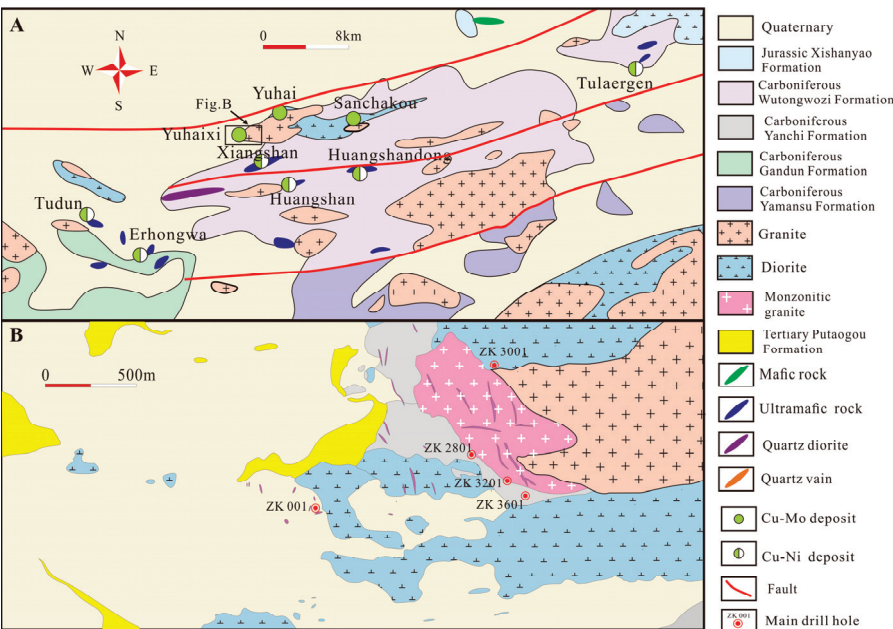
The Yuhaxi Mo(Cu) deposit is located in the eastern section of the Dananhu-Tousuquan arc belt, approximately 110 km southeast of Hami City, Xinjiang (Figure 1b). The main lithostratigraphic units in the area include granulite, hornblende schist of the lower Carboniferous

Yanchi Formation, and glutenite of the Tertiary Putaogou Formation (Figure 2A; [5]). The intrusive complex at Yuhaixi is intermediate to felsic in composition (Figure 2B). In the middle and eastern area, various granitoid intrusions occur as stocks and dikes that cover an area of approximately 3 km<sup>2</sup>. These intrusions are composed of monzonitic granite, granite, diorite (Figure 2B). The monzonitic granites host most of the Mo and Cu mineralization at Yuhaixi. Postmineralization plutons comprising granite and diorite intruded the mineralized monzonitic granite. The gabbro dikes mark the final stage of magmatic activity, having intruded the monzonitic granite and the Yanchi Formation (Figure 2B). In the study area, the monzonitic granite and granite generally exhibit low or moderate degrees of alteration. The monzonitic granite is primarily composed of plagioclase (~25%), K-feldspar (~35%), quartz (~25%), and biotite (~5%), with accessory apatite and zircon (Figure 4A,D). The diorite is light gray to gray-white in color and has a microgranular or aphanitic groundmass. It mainly consists of plagioclase (~45%), hornblende (~20%), quartz (~15%), and biotite (~15%), with minor accessory minerals (Figure 4B,E). The granite is coarse-grained and shows typical equigranular texture. It consists of plagioclase (~35%), quartz (~30%), and biotite (~5%), with negligible magnetite, apatite, and zircon (Figure 4C,F). The Yuhaixi intrusive complex has been affected by subordinate faults associated with the regional-scale Kanggur fault [27–37]. The early NE-trending fault dips 65° to 85° and is inferred to be the predominant structure in the Yuhaixi area (Figure 2A). Geologic surveying defined that the ore zone consists of 6 orebodies, which is based on the drill hole ZK3201 and ZK3601. Each individual orebody is about 2–10 m thick (Figure 3A,B). The monzonitic granite have a genetic relationship with disseminated molybdenite and chalcopyrite (Figure 4G–I) and associated hydrothermal alterations (Figure 4I–K).

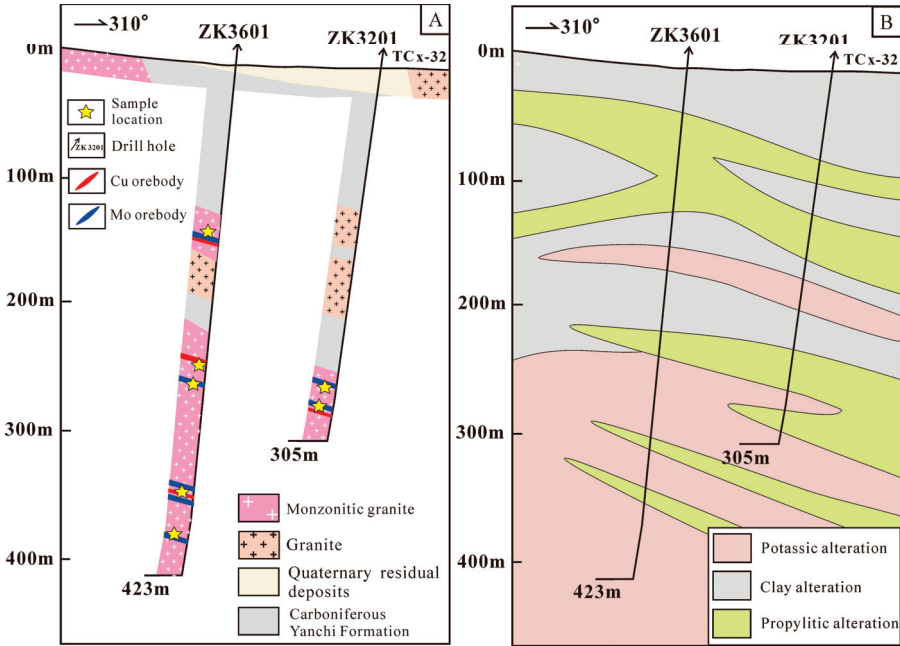


**Figure 1.** (a) Location of Central Asian Orogenic Belt (CAOB) [4]; (b) geological map of NW China showing the main tectonic units; (c) geological map of Eastern Tianshan showing major tectonic units, faults and copper deposits (modified from [12]).

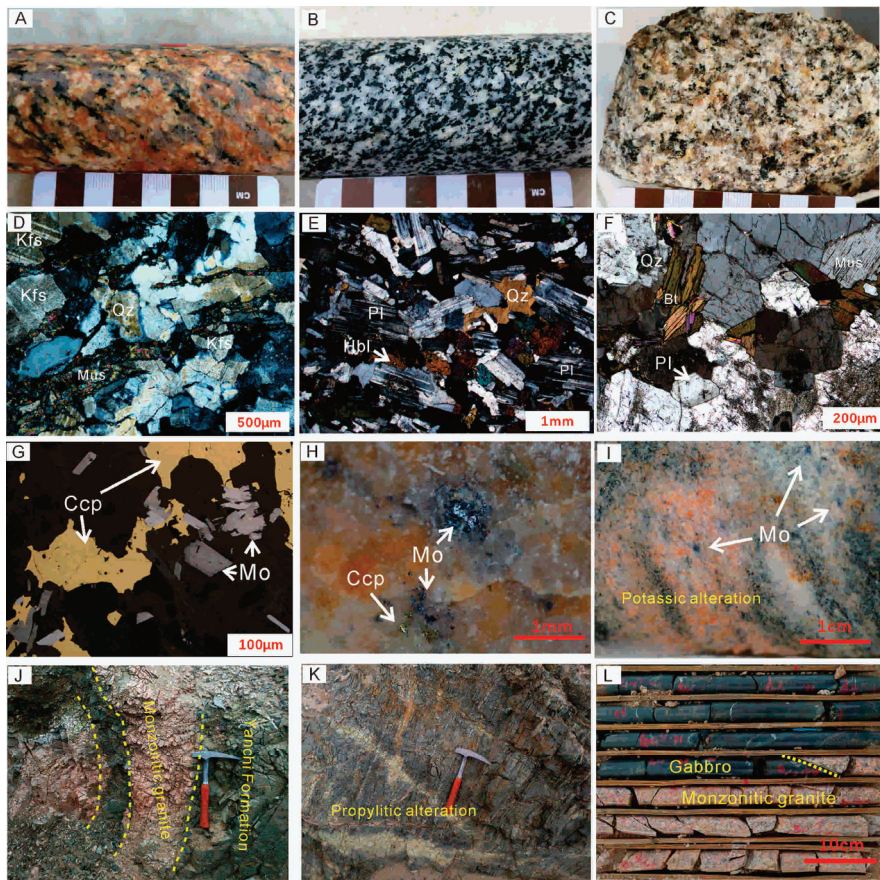




**Figure 2.** (A) Geological map of the Yuhaxi region showing the distribution of Cu and Cu–Ni deposits. (B) Simplified geological map of the Yuhaxi Mo(Cu) deposit (modified from [30]).



**Figure 3.** Geologic cross section of the ZK3601 and ZK3201 exploration lines across the Yuhaxi porphyry Mo deposit with lithology and mineralization (A) and alteration (B).



**Figure 4.** Field, hand specimen, and microscope photos of magmatic intrusions in the Yuhaixi area. (A–C) Hand specimen of the monzonitic granite (A), diorite (B), granite (C). (D) Photomicrograph of the monzonitic granite, showing K-feldspar, quartz, and muscovite phenocrysts under cross-polarized light. (E) Photomicrograph of the diorite, showing plagioclase, quartz, and hornblende phenocrysts under cross-polarized light. (F) Photomicrograph of the granite, showing biotite, quartz, and plagioclase phenocrysts under cross-polarized light. (G) Photomicrograph of the anhedronal chalcopyrite and euhedral molybdenite assemblages under reflected light. Abbreviations: Group; Qtz, quartz; Pl, plagioclase; Bt, biotite; Mus, muscovite; Kfs, K-feldspar; Ccp, chalcopyrite; Mo, molybdenite. (H,I) The molybdenite in the monzonitic granite hand specimen, with potassic alteration. (J) The Carboniferous Yanchi Formation rocks and the monzonitic granite in the exploratory trench. (K) Propylitic alteration in the exploratory trench. (L) The gabbro dike intruded into early monzonitic granite.

### 3. Materials and Methods

#### 3.1. Sampling

Three representative intrusive samples (YHX-ZK-1, ZK001-412, 721-6) from the Yuhaixi outcrops (granite) and drill holes (monzonitic granite, diorite) were collected for zircon LA-ICP-MS U-Pb dating, trace element and Hf isotope analyses. Nine samples, including monzonitic granite (Sample No. YHX-ZK-14, YHX-ZK2, YHX-ZK3), diorite (Sample No. ZK001-25, ZK001-350, ZK001-396), and granite (Sample No. 721-1, 721-3, 721-5), were chosen for major and trace element analysis and Sr-Nd isotope analyses. In addition, nine

molybdenite samples from Mo orebodies of the Yuhaixi deposit were collected from the disseminated ores for Re-Os isotope analyses.

### 3.2. Zircon U-Pb Dating and Trace Elements

Three samples, including one monzonitic granite (sample YHX-ZK-1), one diorite (sample ZK001-1), and one granite (721-6), were chosen for the zircon LA-ICP-MS U-Pb dating and trace element analysis.

The zircon grains were separated by conventional density and magnetic techniques and then carefully hand-picked under a binocular microscope. Subsequently, they were mounted on epoxy resin discs and polished to expose the crystal cross-sections at the Langfang Regional Geological Survey. The selection of potential target sites for the U-Pb dating of all the mounted zircons were based on photomicrographs of both transmitted and reflected light, as well as cathodoluminescence (CL) images. Zircon U-Pb dating and trace element analyses were conducted using an Agilent 7500 a inductively coupled plasma mass spectrometer (ICP-MS) simultaneously coupled with a GeoLas 2005 at the Tianjin Institute of Geology and Mineral Resources. The analytical procedures were described in [38]. Laser ablation was operated at a constant energy of 60 mJ, with a repetition rate of 4 Hz and a spot diameter of 32  $\mu\text{m}$ . Zircons 91500 and GJ-1, NIST SRM 610 [30] were used as external standards. Zircon 91500 was analyzed twice for every six analyses in order to calibrate the isotope fractionation. NIST SRM 610 was analyzed once every eight analyses to make the instrumental drift and mass discrimination correction of the trace element analysis. Individual errors in analyses were cited at the  $1\sigma$  level, and the weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  ages were quoted at the 95% confidence level. The ICPMSDataCal software GeoLas 2005 were used for the adjustment of background and ablation signals, time drift correction [38]. Concordia diagrams and weighted mean calculations were determined using Isoplot 3.0 [39]. Zircon Ce anomalies were calculated using the method of the lattice strain model [17].

### 3.3. Zircon Hf Isotopes

In situ Hf isotope analyses were conducted using a Neptune MC-ICP-MS and New Wave UP 213 ultraviolet LA-MC-ICP-MS at the National Research Center for Geoanalysis, Beijing, China. The analysis was undertaken on the adjacent spots used for the LA-ICP-MS zircon U-Pb dating to match the Hf isotope data with the U-Pb ages. The ablated samples wrapped in helium were transported from the laser ablation chamber to the ICP-MS torch via a mixing chamber of Argon. Based on the zircon size, the stationary beam spot size was set to either 40 or 50  $\mu\text{m}$ . During testing, GJ-1 international standard [30] zircon samples were used as a reference for the instrumental mass bias correction. The weighted average of the  $^{176}\text{Hf}/^{177}\text{Hf}$  of the GJ-1 zircon samples was  $0.281017 \pm 0.000007$  (2 SD,  $n = 10$ ), which is consistent with the values reported by [18]. More detailed operating conditions for the MC-ICP-MS instrument, the laser ablation system, and the analytical method are given in [39,40].

### 3.4. Whole-Rock Major and Trace Elements

Whole-rock major and trace elements analyses were performed at the National Research Center for Geoanalysis, Beijing, China. The samples were powdered to approximately 200 mesh before testing. The major elements were determined using a Philips PW 2404 X-ray fluorescence (XRF) spectrometer with a rhodium X-ray source. The trace elements and the rare earth elements were determined using an Element-I plasma mass spectrometer (Finnigan-MAT Ltd., Bremen, German); two national geological standard reference samples, GSR-3 and GSR-15, were used for the analytical quality control purpose. The analytical precision for the major elements is better than 1% and for the trace elements is better than 5%, and the analytical procedures were described by [19].

### 3.5. Whole-Rock Sr-Nd Isotopes

Sr–Nd isotopic analyses were carried out using a Neptune multi-collector ICP-MS at the National Research Center for Geoanalysis, Beijing, China, using analytical procedures described by [40]. The Separation of the Sr and REE were performed using cation columns, and the Nd fractions were further separated using HDEHP-coated Kef columns. The measured  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios were normalized to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1193$  and  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7217$ , respectively. The reported  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios were adjusted to the NBS SRM 987 standard  $^{87}\text{Sr}/^{86}\text{Sr} = 0.71027$  and the Shin Etsu JNdi-1 standard  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512116$  [11], respectively.

### 3.6. Re-Os Isotopic Analyses

Nine molybdenite samples were collected from the Yuhai porphyry Mo(Cu) deposits for Re–Os isotope analyses. Among them, five molybdenite samples came from drill holes ZK3601. Four molybdenite samples came from drill hole ZK3201. The photographs and photomicrographs of the representative samples are shown in Figure 4. Molybdenite occurs as disseminations in monzonitic granite or quartz veinlets and molybdenite is cogenetic with chalcopyrite (Figure 4H). The molybdenite was magnetically separated and then handpicked under a binocular microscope at the Langfang Regional Geological Survey. Fresh, nonoxidized molybdenite powders (<0.1 mm in size and purity >99%) were used for Re–Os isotope analyses.  $^{187}\text{Re}$  and  $^{187}\text{Os}$  concentrations of molybdenite were measured using a TJA PQ ExCell ICP-MS at the Re–Os Laboratory of National Research Center of Geoanalysis, Chinese Academy of Geological Sciences, Beijing. The chemical separation of the Re and Os and the analytical procedure were in accordance with [18]. The weighed molybdenite samples were loaded into a Carius tube through a thin-neck long funnel. The mixed  $^{190}\text{Os}$  and  $^{185}\text{Re}$  spike solutions and 2 mL HCl and 4 mL  $\text{HNO}_4$  were loaded, while the bottom part of the tube was frozen at  $-50\text{ }^\circ\text{C}$  to  $-80\text{ }^\circ\text{C}$  in an ethanol–liquid nitrogen slush, and the top was sealed using an oxygen–propane torch. The tube was then placed in a stainless-steel jacket and heated for 24 h at  $230\text{ }^\circ\text{C}$ . After 24 h and upon cooling, the sample-bearing tubes were opened to transfer the supernatants out and the Os was separated using the method of direct distillation from the Carius tube for 50 min and trapped in 2 mL of water that was used for the ICP-MS (X-Series) determination of the Os isotope ratio. After that, the residual Re-bearing solution was saved in a 150 mL Teflon beaker for Re separation. The residual Re-bearing solution was heated to near-dryness. The acetone phase was transferred to a 150 mL Teflon beaker that contained 1 mL of water. Finally, the solution was picked up in 2%  $\text{HNO}_3$ , which was used for the ICP-MS(X-Series) determination of the Re isotope ratio.

The average blanks for the method were ca. 3 pg Re and ca. 0.5 pg Os. The working conditions of the instrument were controlled by the reference material JDC, which produced a measured value of  $139.8 \pm 2.0$  Ma, which is consistent with the recommended value of  $139.6 \pm 3.8$  Ma [41]. The analytical uncertainty in the Re–Os model ages includes 1.02% uncertainty (at 95% confidence level) for the  $^{187}\text{Re}$  decay constant. The Re–Os model ages were calculated following the equation:  $t = [\ln(1 + ^{187}\text{Os}/^{187}\text{Re})]/\lambda$ , where  $\lambda$  is the decay constant of  $^{187}\text{Re}$  ( $\lambda\text{ }^{187}\text{Re} = 1.666 \times 10^{-11}\text{ year}^{-1}$ ; [41]) and denotes the age. The Re–Os isochron ages were calculated using the least-squares method [42], employing the program ISOPLOT 3.0 [23].

## 4. Results

### 4.1. Zircon U–Pb Dating and Zircon Trace Elements

The Yuhai monzonitic granite sample (YHX-ZK-1), diorite sample (ZK001-412), and granite sample (721-6) were selected for LA-ICP-MS zircon U–Pb dating, and the analytical data are listed in Table 1. Most of the zircon grains are euhedral–subhedral and show prismatic forms (100–200  $\mu\text{m}$  long) with aspect ratios of 3:1 to 3:2 and characterized by clear oscillatory growth zoning in the CL images (Figure 5). All samples have varying



U(58–453 ppm) and Th (30–417 ppm) contents with high Th/U ratios (>0.3), which is consistent with a magmatic origin [21].

**Table 1.** Whole-rock geochemical data of the studied intrusive rocks in the Yuhaixi Mo(Cu) deposit (major elements: wt.%; trace elements: ppm).

| Rock Type                            | Monzonitic Granite |          |          |          | Diorite   |           | Granite |        |        |
|--------------------------------------|--------------------|----------|----------|----------|-----------|-----------|---------|--------|--------|
| Sample No.                           | YHX-ZK-1           | YHX-ZK-2 | YHX-ZK-3 | ZK001-25 | ZK001-350 | ZK001-396 | 721-1   | 721-3  | 721-5  |
| SiO <sub>2</sub>                     | 74.2               | 76.57    | 74.64    | 53.55    | 54.58     | 54.16     | 74.16   | 73.79  | 73.75  |
| TiO <sub>2</sub>                     | 0.17               | 0.18     | 0.14     | 0.95     | 0.94      | 0.8       | 0.2     | 0.18   | 0.18   |
| Al <sub>2</sub> O <sub>3</sub>       | 13.57              | 12.42    | 12.9     | 17.98    | 17.33     | 17.59     | 13.77   | 14.15  | 14.17  |
| TFe <sub>2</sub> O <sub>3</sub>      | 1.23               | 1.31     | 1        | 8.69     | 8.37      | 7.9       | 1.49    | 1.4    | 1.39   |
| MnO                                  | 0.03               | 0.06     | 0.03     | 0.17     | 0.16      | 0.14      | 0.08    | 0.06   | 0.06   |
| MgO                                  | 0.28               | 0.36     | 0.23     | 4.06     | 4.84      | 5.06      | 0.45    | 0.39   | 0.39   |
| CaO                                  | 1.23               | 1.12     | 1.9      | 7.97     | 7.8       | 7.61      | 1.65    | 1.63   | 1.64   |
| Na <sub>2</sub> O                    | 3.33               | 3.39     | 2.77     | 3.86     | 4.11      | 4.11      | 4.46    | 4.57   | 4.55   |
| K <sub>2</sub> O                     | 4.97               | 3.75     | 4.53     | 1.15     | 0.9       | 1.14      | 2.65    | 2.7    | 2.81   |
| P <sub>2</sub> O <sub>5</sub>        | 0.04               | 0.05     | 0.04     | 0.24     | 0.16      | 0.25      | 0.07    | 0.07   | 0.07   |
| LOI                                  | 0.63               | 0.73     | 1.82     | 1.12     | 0.8       | 1.02      | 0.5     | 0.47   | 0.5    |
| TOTAL                                | 99.68              | 99.94    | 99.98    | 99.74    | 99.99     | 99.77     | 99.48   | 99.41  | 99.52  |
| Na <sub>2</sub> O + K <sub>2</sub> O | 8.3                | 7.14     | 7.29     | 5.01     | 5.01      | 5.25      | 7.11    | 7.28   | 7.37   |
| Mg <sup>#</sup>                      | 28.87              | 32.88    | 29.08    | 45.44    | 50.76     | 53.31     | 35      | 33.18  | 33.34  |
| A/CNK                                | 1.04               | 1.05     | 1.06     | 0.81     | 0.79      | 0.81      | 1.04    | 1.05   | 1.05   |
| A/NK                                 | 1.25               | 1.2      | 1.29     | 2.37     | 2.24      | 2.2       | 1.35    | 1.35   | 1.27   |
| Li                                   | 5.44               | 6.67     | 1.31     | 8.67     | 10.66     | 8.71      | 13.79   | 16.67  | 12.95  |
| Be                                   | 0.89               | 2.39     | 0.94     | 0.97     | 1.02      | 0.96      | 1.05    | 1.52   | 1.04   |
| Sc                                   | 2.15               | 3.53     | 1.14     | 19.92    | 24.87     | 23.37     | 1.38    | 2.6    | 1.38   |
| V                                    | 10.66              | 12.16    | 9.27     | 201.07   | 241.97    | 116.9     | 8.35    | 8.39   | 7.22   |
| Cr                                   | 19.13              | 0.78     | 10.53    | 22.33    | 67.75     | 129.44    | 5.68    | 8.87   | 4.1    |
| Co                                   | 1.97               | 1.01     | 0.56     | 22.83    | 30.73     | 29.04     | 1.01    | 1.03   | 0.88   |
| Ni                                   | 0.11               | 0.73     | 0.86     | 18.48    | 46.27     | 81.17     | 0.26    | 1.81   | 1.52   |
| Cu                                   | 114.22             | 37.2     | 10.2     | 65.43    | 132.91    | 55.89     | 2.01    | 1.23   | 2.88   |
| Zn                                   | 15.83              | 74.89    | 27.69    | 103.43   | 102.49    | 105.55    | 68.29   | 44.17  | 49.97  |
| Ga                                   | 14.88              | 15.67    | 11.72    | 22.98    | 23.43     | 24.02     | 15.15   | 16.25  | 15.12  |
| Rb                                   | 64.57              | 75.8     | 64.65    | 25.2     | 17.69     | 25.25     | 45.6    | 62.97  | 45.83  |
| Sr                                   | 188.36             | 168.2    | 137.76   | 833.76   | 784.8     | 940.51    | 379.1   | 400.17 | 371.33 |
| Y                                    | 7.83               | 14.27    | 5.77     | 28.58    | 25.65     | 24.64     | 19.57   | 18.59  | 19.64  |
| Zr                                   | 94.78              | 114.16   | 89.03    | 364.46   | 160.19    | 23.13     | 120.58  | 110.57 | 114.79 |
| Nb                                   | 5.35               | 12.47    | 5.34     | 4.52     | 5.26      | 4.15      | 5.4     | 6.28   | 4.93   |
| Cs                                   | 0.24               | 0.4      | 0.4      | 0.51     | 0.5       | 0.57      | 0.39    | 1.39   | 0.38   |
| Ba                                   | 853                | 592      | 598      | 369      | 314       | 436       | 1248    | 1277   | 1333   |
| La                                   | 27.76              | 27.03    | 17.31    | 18.18    | 19.09     | 15.35     | 20.76   | 35.15  | 27.57  |
| Ce                                   | 51.7               | 59       | 38.94    | 45.57    | 47.45     | 41.31     | 45.29   | 68.09  | 53.25  |
| Pr                                   | 5.86               | 6.19     | 3.93     | 6.63     | 6.78      | 6.23      | 4.71    | 8.11   | 6.57   |
| Nd                                   | 21.54              | 22.74    | 14.66    | 30.25    | 30.26     | 28.08     | 18.11   | 30.56  | 25.29  |
| Sm                                   | 3.39               | 4.1      | 2.56     | 6.66     | 6.09      | 5.78      | 3.35    | 5.4    | 4.51   |
| Eu                                   | 1.15               | 0.86     | 0.82     | 1.91     | 1.57      | 1.58      | 1.4     | 1.54   | 1.51   |
| Gd                                   | 2.94               | 3.4      | 2.14     | 5.46     | 5.05      | 4.69      | 2.99    | 4.43   | 3.96   |
| Tb                                   | 0.36               | 0.49     | 0.27     | 0.9      | 0.83      | 0.79      | 0.49    | 0.64   | 0.6    |
| Dy                                   | 1.64               | 2.58     | 1.16     | 5.67     | 4.84      | 4.65      | 2.98    | 3.42   | 3.47   |
| Ho                                   | 0.3                | 0.52     | 0.22     | 1.2      | 0.99      | 0.94      | 0.67    | 0.67   | 0.71   |
| Er                                   | 0.81               | 1.43     | 0.6      | 3.3      | 2.77      | 2.57      | 1.97    | 1.87   | 1.97   |
| Tm                                   | 0.11               | 0.22     | 0.08     | 0.49     | 0.41      | 0.37      | 0.3     | 0.28   | 0.29   |
| Yb                                   | 0.67               | 1.45     | 0.53     | 3.12     | 2.71      | 2.42      | 1.99    | 1.73   | 1.95   |
| Lu                                   | 0.11               | 0.24     | 0.08     | 0.48     | 0.44      | 0.39      | 0.33    | 0.28   | 0.32   |
| Hf                                   | 2.77               | 3.64     | 2.5      | 8.98     | 4.93      | 1.27      | 3.67    | 3.46   | 3.54   |

Table 1. Cont.

| Rock Type            | Monzonitic Granite |          |          |          | Diorite   |           | Granite |        |        |
|----------------------|--------------------|----------|----------|----------|-----------|-----------|---------|--------|--------|
| Sample No.           | YHX-ZK-1           | YHX-ZK-2 | YHX-ZK-3 | ZK001-25 | ZK001-350 | ZK001-396 | 721-1   | 721-3  | 721-5  |
| Ta                   | 0.3                | 1.34     | 0.29     | 0.32     | 0.34      | 0.25      | 0.31    | 0.48   | 0.3    |
| Tl                   | 0.21               | 0.24     | 0.19     | 0.09     | 0.06      | 0.08      | 0.18    | 0.2    | 0.16   |
| Pb                   | 15.31              | 11.3     | 11.69    | 6.2      | 5.45      | 8.02      | 8.42    | 9.44   | 8.78   |
| Bi                   | 0.05               | 0.03     | 0.03     | 0.12     | 0.1       | 0.26      | 0.02    | 0.04   | 0.02   |
| Th                   | 5.77               | 8.18     | 5.8      | 3.06     | 3.35      | 1.18      | 5.21    | 9.97   | 7.37   |
| U                    | 1.13               | 1.95     | 0.99     | 2.19     | 1.46      | 0.83      | 1.19    | 1.82   | 1.46   |
| (La/Yb) <sub>N</sub> | 27.9               | 12.55    | 21.98    | 3.92     | 4.74      | 4.28      | 7.02    | 13.71  | 9.54   |
| (Tb/Yb) <sub>N</sub> | 2.37               | 1.5      | 2.24     | 1.29     | 1.36      | 1.45      | 1.1     | 1.63   | 1.36   |
| (La/Sm) <sub>N</sub> | 5.15               | 4.15     | 4.26     | 1.72     | 1.97      | 1.67      | 3.9     | 4.09   | 3.84   |
| Th/Ce                | 0.11               | 0.14     | 0.15     | 0.07     | 0.07      | 0.03      | 0.12    | 0.15   | 0.14   |
| Th/U                 | 5.12               | 4.2      | 5.84     | 1.4      | 2.29      | 1.42      | 4.39    | 5.48   | 5.05   |
| Ce/Pb                | 3.38               | 5.22     | 3.33     | 7.35     | 8.7       | 5.15      | 5.38    | 7.22   | 6.06   |
| ΣREE                 | 118.34             | 130.24   | 83.29    | 129.82   | 129.29    | 115.14    | 105.33  | 162.16 | 131.97 |
| Eu                   | 1.09               | 0.68     | 1.05     | 0.94     | 0.84      | 0.9       | 1.33    | 0.94   | 1.07   |
| Sr/Y                 | 24.05              | 11.78    | 23.88    | 29.17    | 30.59     | 38.17     | 19.38   | 21.53  | 18.91  |

Note:  $Mg^{\#} = 100 \times (MgO/40.3044)/(MgO/40.3044 + 0.8998 \times Fe_2O_3^T/71.8440)$ .

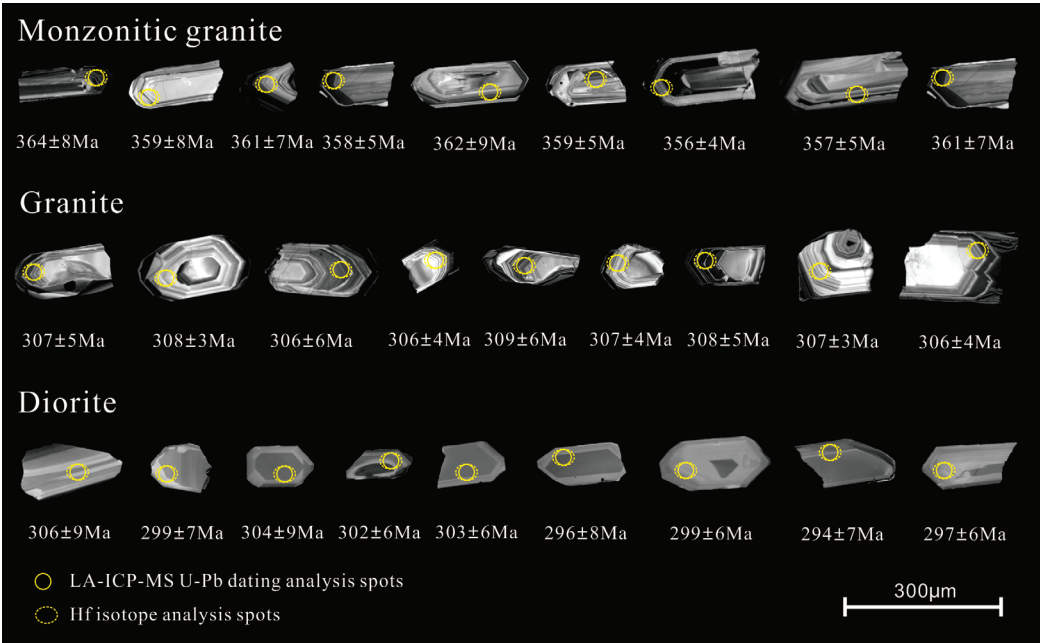
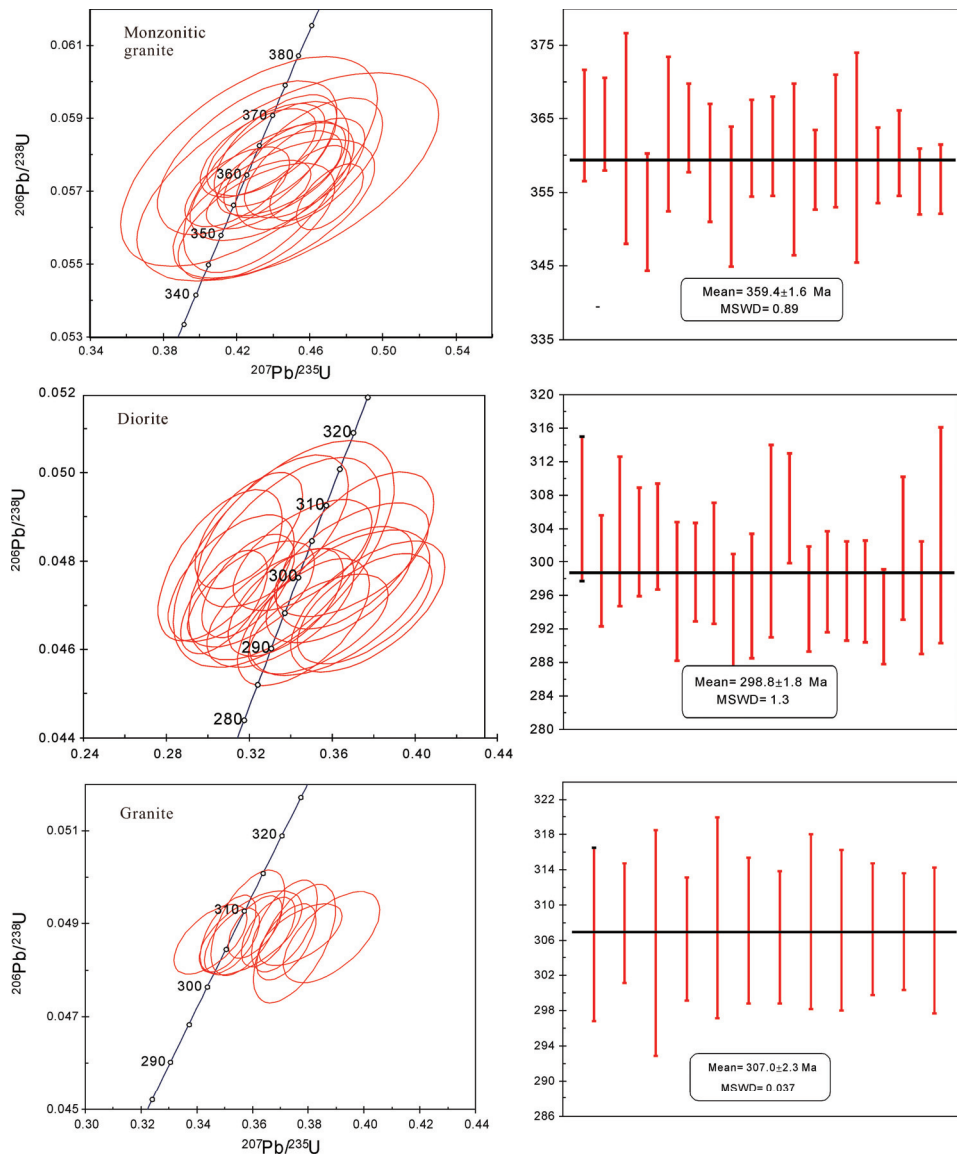


Figure 5. Cathodoluminescence images of representative zircon grains of the Yuhaxi showing the inner structures and analyzed spots.

Except for two discordant spot (02, 05), the remaining 17 analyses from the monzonitic granite sample (YHX-ZK-1) yielded concordant  $^{206}Pb/^{238}U$  ages varying from 352 to 362 Ma (Figure 6), with a weighted mean age of  $359.4 \pm 1.6$  Ma (MSWD = 0.89), which is interpreted as the best estimate of emplacement age for the Yuhaxi monzonitic granite.





**Figure 6.** U-Pb concordia diagrams and weighted average ages of the zircons from monzonitic granite, diorite, and granite in the Yuhaixi porphyry Mo(Cu) deposit.

Except for three discordant spots (07, 09, 11), the remaining 12 analytical spots from the granite sample (721-6) had  $^{206}\text{Pb}/^{238}\text{U}$  ages ranging from 306 to 309 Ma (Figure 6), with a weighted mean age of  $307.0 \pm 2.3$  Ma (MSWD = 0.037).

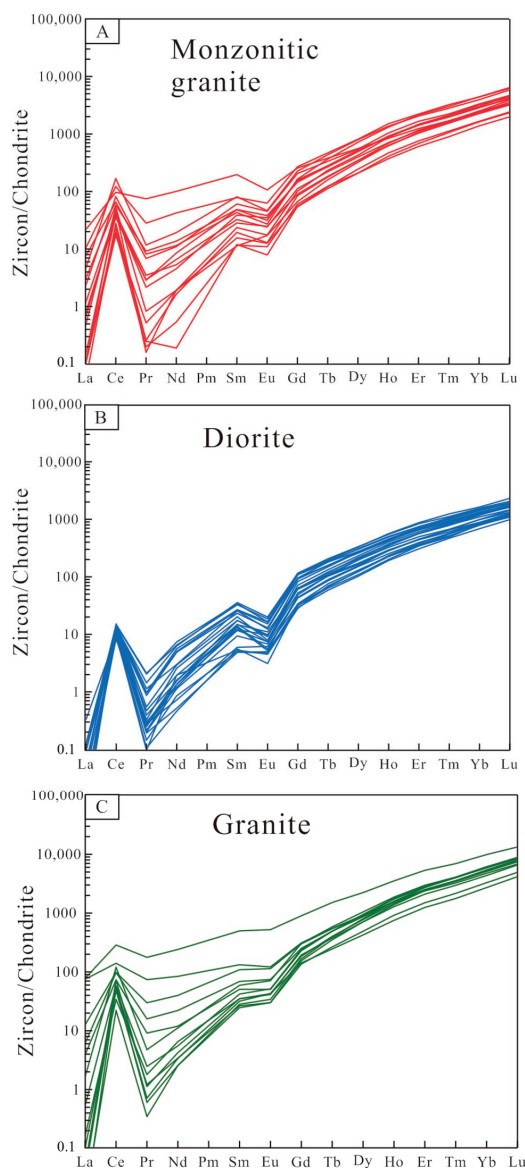
Except for three discordant spots (03, 07 and 16), the remaining 19 analytical spots from the diorite sample (ZK001-412) had  $^{206}\text{Pb}/^{238}\text{U}$  ages ranging from 296 to 306 Ma. (Figure 6), with a weighted mean age of  $298.8 \pm 1.8$  Ma (MSWD = 1.3) (Table 2).

Table 2. LA-ICP-MS zircon U–Pb data for the studied intrusive rocks in the Yuhaxi Mo(Cu) deposit.

| Spot     | Element ( $\times 10^{-6}$ ) |      |      | Isotope Ratio                    |            |                                  | Apparent Age (Ma) |                                  |            |                                  |            |    |     |    |
|----------|------------------------------|------|------|----------------------------------|------------|----------------------------------|-------------------|----------------------------------|------------|----------------------------------|------------|----|-----|----|
|          | Pb                           | Th   | U    | $^{207}\text{Pb}/^{235}\text{U}$ | 1 $\sigma$ | $^{206}\text{Pb}/^{238}\text{U}$ | 1 $\sigma$        | $^{207}\text{Pb}/^{235}\text{U}$ | 1 $\sigma$ | $^{206}\text{Pb}/^{238}\text{U}$ | 1 $\sigma$ |    |     |    |
| YHX-1-1  | 97                           | 849  | 1156 | 0.0034                           | 0.4414     | 0.0273                           | 0.0581            | 0.0012                           | 398        | 173                              | 371        | 19 | 364 | 8  |
| YHX-1-2  | 23                           | 174  | 302  | 0.0033                           | 0.4362     | 0.0264                           | 0.0581            | 0.001                            | 369        | 134                              | 368        | 19 | 364 | 6  |
| YHX-1-3  | 26                           | 108  | 348  | 0.0071                           | 0.4269     | 0.0573                           | 0.0578            | 0.0023                           | 309        | 281                              | 361        | 41 | 362 | 14 |
| YHX-1-4  | 20                           | 137  | 265  | 0.0043                           | 0.4309     | 0.0348                           | 0.0562            | 0.0013                           | 383        | 180                              | 364        | 25 | 352 | 8  |
| YHX-1-5  | 14                           | 120  | 173  | 0.0558                           | 0.4258     | 0.0401                           | 0.0579            | 0.0017                           | 456        | 275                              | 360        | 29 | 363 | 11 |
| YHX-1-6  | 74                           | 835  | 840  | 0.0532                           | 0.4319     | 0.0259                           | 0.058             | 0.001                            | 345        | 145                              | 365        | 18 | 364 | 6  |
| YHX-1-7  | 7                            | 41   | 89   | 0.0568                           | 0.4393     | 0.0366                           | 0.0573            | 0.0013                           | 487        | 236                              | 370        | 26 | 359 | 8  |
| YHX-1-8  | 8                            | 46   | 102  | 0.0548                           | 0.4404     | 0.0449                           | 0.0565            | 0.0016                           | 406        | 227                              | 371        | 32 | 354 | 10 |
| YHX-1-9  | 13                           | 69   | 182  | 0.0561                           | 0.4465     | 0.027                            | 0.0576            | 0.0011                           | 457        | 155                              | 375        | 19 | 361 | 7  |
| YHX-1-10 | 90                           | 535  | 1167 | 0.0559                           | 0.4573     | 0.0267                           | 0.0576            | 0.0011                           | 450        | 127                              | 382        | 19 | 361 | 7  |
| YHX-1-11 | 20                           | 144  | 245  | 0.0546                           | 0.436      | 0.0369                           | 0.0571            | 0.0019                           | 398        | 210                              | 367        | 26 | 358 | 12 |
| YHX-1-12 | 16                           | 95   | 218  | 0.0531                           | 0.4203     | 0.0234                           | 0.0571            | 0.0009                           | 345        | 144                              | 356        | 17 | 358 | 5  |
| YHX-1-13 | 18                           | 106  | 232  | 0.059                            | 0.4598     | 0.0328                           | 0.0578            | 0.0015                           | 565        | 183                              | 384        | 23 | 362 | 9  |
| YHX-1-14 | 12                           | 68   | 157  | 0.0571                           | 0.448      | 0.0673                           | 0.0574            | 0.0023                           | 494        | 356                              | 376        | 47 | 360 | 14 |
| YHX-1-15 | 104                          | 1050 | 1184 | 0.0577                           | 0.4602     | 0.0181                           | 0.0572            | 0.0008                           | 517        | 83                               | 384        | 13 | 359 | 5  |
| YHX-1-16 | 14                           | 92   | 182  | 0.0564                           | 0.4436     | 0.0279                           | 0.0575            | 0.001                            | 478        | 146                              | 373        | 20 | 360 | 6  |
| YHX-1-17 | 235                          | 1618 | 3001 | 0.0594                           | 0.471      | 0.0151                           | 0.0568            | 0.0007                           | 583        | 74                               | 392        | 10 | 356 | 4  |
| YHX-1-18 | 25                           | 241  | 307  | 0.0543                           | 0.4322     | 0.0234                           | 0.0569            | 0.0008                           | 389        | 122                              | 365        | 17 | 357 | 5  |
| Diorite  |                              |      |      |                                  |            |                                  |                   |                                  |            |                                  |            |    |     |    |
| zk001-1  | 4                            | 30   | 60   | 0.0498                           | 0.3316     | 0.0297                           | 0.0487            | 0.0014                           | 187        | 244                              | 291        | 23 | 306 | 9  |
| zk001-2  | 5                            | 40   | 85   | 0.0559                           | 0.3636     | 0.0288                           | 0.0475            | 0.0011                           | 450        | 207                              | 315        | 21 | 299 | 7  |
| zk001-3  | 5                            | 47   | 72   | 0.0584                           | 0.3712     | 0.0311                           | 0.0482            | 0.0015                           | 543        | 222                              | 321        | 23 | 304 | 9  |
| zk001-4  | 7                            | 72   | 108  | 0.055                            | 0.3695     | 0.0304                           | 0.048             | 0.0011                           | 413        | 196                              | 319        | 23 | 302 | 6  |
| zk001-5  | 8                            | 79   | 128  | 0.052                            | 0.3458     | 0.0274                           | 0.0481            | 0.001                            | 283        | 199                              | 302        | 21 | 303 | 6  |
| zk001-6  | 6                            | 69   | 93   | 0.0604                           | 0.3636     | 0.0356                           | 0.0471            | 0.0013                           | 617        | 275                              | 315        | 26 | 296 | 8  |
| zk001-7  | 9                            | 85   | 133  | 0.0502                           | 0.3193     | 0.0181                           | 0.0474            | 0.001                            | 206        | 168                              | 281        | 14 | 299 | 6  |
| zk001-8  | 8                            | 72   | 128  | 0.0499                           | 0.3111     | 0.0249                           | 0.0476            | 0.0012                           | 191        | 230                              | 275        | 19 | 300 | 7  |
| zk001-9  | 5                            | 49   | 87   | 0.0568                           | 0.3463     | 0.026                            | 0.0466            | 0.0012                           | 483        | 213                              | 302        | 20 | 294 | 7  |
| zk001-10 | 4                            | 28   | 58   | 0.0597                           | 0.3772     | 0.0304                           | 0.047             | 0.0012                           | 591        | 222                              | 325        | 22 | 296 | 7  |
| zk001-11 | 5                            | 47   | 69   | 0.0506                           | 0.3367     | 0.0377                           | 0.048             | 0.0019                           | 233        | 224                              | 295        | 29 | 303 | 11 |
| zk001-12 | 10                           | 91   | 149  | 0.0481                           | 0.3198     | 0.0212                           | 0.0487            | 0.0011                           | 106        | 181                              | 282        | 16 | 306 | 7  |
| zk001-13 | 8                            | 85   | 118  | 0.0581                           | 0.3758     | 0.0265                           | 0.0469            | 0.001                            | 600        | 170                              | 324        | 20 | 296 | 6  |



The calculated results of zircon  $\text{Ce}^{4+}/\text{Ce}^{3+}$  and Ti-in-zircon thermometer have been used to estimate the magma temperatures and oxidation states [17], with the detailed calculation procedures being presented by [17]. In this study, the zircon  $\text{Ce}^{4+}/\text{Ce}^{3+}$  values of the monzonitic granite, diorite, and granite were calculated to be ~6–248 (avg. 60), 11–182 (avg. 54), and 6–241 (avg. 85), respectively (Table 3). Ti-in-zircon temperatures were calculated to be 590–954 °C (avg. 744 °C) for the monzonitic granite, 698–775 °C (avg. 728 °C), for the diorite and 653–917 °C (avg. 712 °C) for the granite (Table 3). The zircon REE patterns are commonly featured by HREE enrichments with positive Ce anomalies and negative Eu anomalies (Figure 7).



**Figure 7.** Chondrite-normalized REE patterns for zircon grains from the Yuhai intrusions. Chondrite values are from [20].

Table 3. Trace element abundance (in ppm), Eu anomalies, and Ce<sup>4+</sup>/Ce<sup>3+</sup> in zircon and Ti-in-zircon temperature.

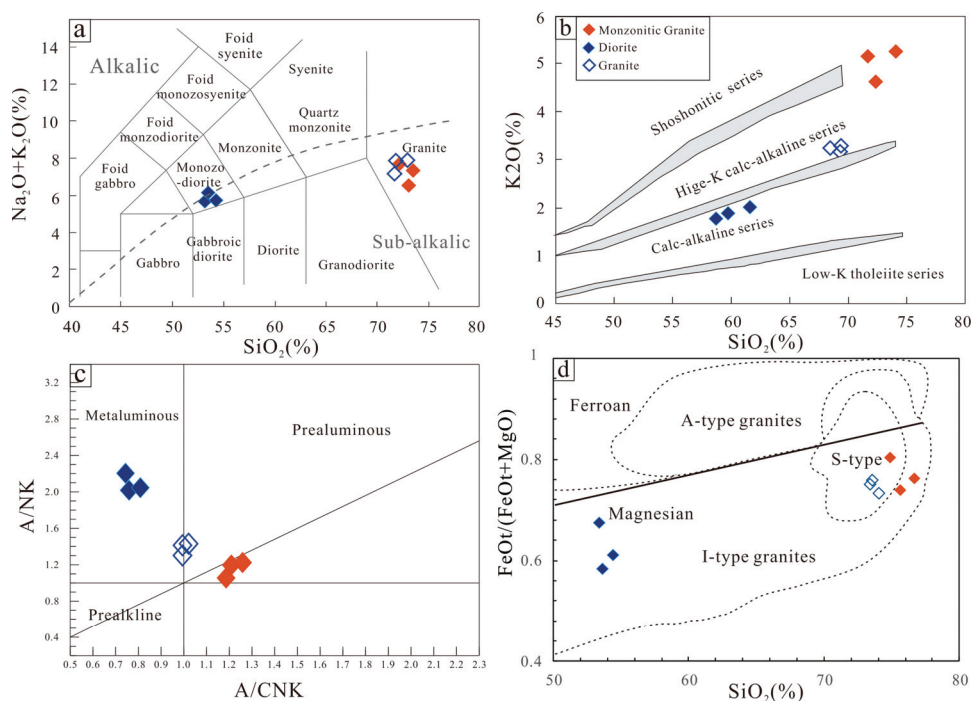
| Analysis     | Ti  | Y    | La   | Ce   | Pr  | Nd   | Sm   | Eu   | Gd  | Tb   | Dy  | Ho   | Er   | Tm   | Yb   | Lu  | Eu/Eu* T |
|--------------|-----|------|------|------|-----|------|------|------|-----|------|-----|------|------|------|------|-----|----------|
| YHX-ZK-1     | 38  | 1860 | 9.55 | 101  | 11  | 63.5 | 34.9 | 7.57 | 63  | 15.5 | 154 | 56.7 | 257  | 55   | 525  | 114 | 0.52 732 |
| YHX-ZK-2     | 8.1 | 3041 | 3.15 | 99.1 | 3.4 | 25.5 | 15.3 | 4.62 | 70  | 22.1 | 261 | 108  | 466  | 105  | 918  | 200 | 0.56 745 |
| YHX-ZK-3     | 5.2 | 2093 | 0.04 | 32.2 | 0.3 | 2.73 | 7.59 | 2.57 | 39  | 12.6 | 159 | 65.3 | 298  | 64.9 | 606  | 130 | 0.45 747 |
| YHX-ZK-4     | 5.9 | 1501 | 0.2  | 33.4 | 0.4 | 3.21 | 5.53 | 1.82 | 23  | 8.64 | 112 | 49.2 | 245  | 54.7 | 521  | 125 | 0.41 748 |
| YHX-ZK-5     | 27  | 3836 | 12.5 | 137  | 15  | 88.1 | 57.1 | 11.1 | 118 | 33.3 | 356 | 138  | 601  | 128  | 1137 | 252 | 0.49 677 |
| YHX-ZK-6     | 6.1 | 1496 | 0.35 | 32.9 | 0.4 | 3.96 | 6.36 | 1.77 | 29  | 10.4 | 128 | 50.8 | 236  | 52.5 | 526  | 108 | 0.47 715 |
| YHX-ZK-7     | 6.2 | 1879 | 0.24 | 28.6 | 0.4 | 5.12 | 9.43 | 2.32 | 41  | 13.2 | 167 | 64   | 299  | 63.8 | 597  | 135 | 0.35 631 |
| YHX-ZK-8     | 13  | 2846 | 1.38 | 136  | 1.4 | 11.6 | 15.8 | 3.42 | 59  | 20.4 | 257 | 97.9 | 431  | 90.9 | 824  | 187 | 0.37 815 |
| YHX-ZK-9     | 12  | 2797 | 0.69 | 65.9 | 1   | 6.91 | 8.41 | 2    | 43  | 17.2 | 232 | 94.2 | 452  | 97.8 | 925  | 206 | 0.41 745 |
| YHX-ZK-10    | 6   | 1867 | 0.14 | 43   | 0.1 | 1.15 | 4.61 | 1.29 | 26  | 11   | 138 | 62.7 | 310  | 68.3 | 629  | 148 | 0.36 637 |
| YHX-ZK-11    | 17  | 2089 | 2.31 | 53.1 | 0.8 | 6.62 | 11.9 | 3.34 | 53  | 15.7 | 175 | 74.6 | 350  | 72.1 | 694  | 151 | 0.70 731 |
| YHX-ZK-12    | 1.6 | 1329 | 0.02 | 22.7 | 0   | 0.98 | 3.79 | 0.95 | 22  | 8.39 | 111 | 44.5 | 223  | 50.2 | 473  | 103 | 0.52 884 |
| YHX-ZK-13    | 22  | 2186 | 0.92 | 46.7 | 1.1 | 8.24 | 9.48 | 2.81 | 38  | 12.9 | 160 | 65.9 | 305  | 68.2 | 674  | 140 | 0.42 955 |
| YHX-ZK-14    | 24  | 1112 | 0.54 | 28.1 | 0.2 | 2.7  | 3.87 | 1.32 | 22  | 6.98 | 98  | 40.1 | 178  | 38.9 | 357  | 83  | 0.48 693 |
| YHX-ZK-15    | 17  | 5436 | 17.6 | 178  | 20  | 124  | 76.3 | 16.8 | 177 | 49.1 | 527 | 185  | 800  | 168  | 1441 | 298 | 0.41 692 |
| YHX-ZK-16    | 3.3 | 2710 | 0.51 | 38   | 0.7 | 7.62 | 11.2 | 3.02 | 58  | 19.3 | 227 | 85.2 | 377  | 81.3 | 747  | 159 | 0.64 626 |
| zk001-412-1  | 9.1 | 956  | 0.02 | 9.89 | 0.1 | 3.49 | 5.43 | 1.25 | 26  | 7.73 | 87  | 31.7 | 146  | 30.8 | 277  | 57  | 0.47 799 |
| zk001-412-2  | 8.4 | 515  | 0.11 | 8.09 | 0   | 1.22 | 1.07 | 0.34 | 7.6 | 3.4  | 41  | 16.8 | 76.2 | 18.7 | 182  | 38  | 0.43 741 |
| zk001-412-3  | 6.2 | 820  | 0.01 | 12.3 | 0   | 0.85 | 2.37 | 0.57 | 17  | 5.93 | 69  | 27.9 | 124  | 27.9 | 259  | 54  | 0.40 799 |
| zk001-412-4  | 6.7 | 907  | 0.01 | 11.5 | 0.1 | 1.83 | 4.09 | 0.6  | 19  | 6.5  | 78  | 30.1 | 132  | 29.2 | 275  | 60  | 0.35 787 |
| zk001-412-5  | 5.9 | 809  | 0.04 | 12.1 | 0   | 0.75 | 2.68 | 0.4  | 13  | 5.12 | 66  | 25.9 | 123  | 26.4 | 256  | 56  | 0.40 778 |
| zk001-412-6  | 8.8 | 574  | 0.01 | 10.1 | 0   | 0.71 | 1.9  | 0.52 | 12  | 4.17 | 51  | 18.8 | 85.9 | 18.9 | 177  | 37  | 0.30 749 |
| zk001-412-7  | 9.4 | 446  | 0.01 | 7.37 | 0   | 0.53 | 1.01 | 0.36 | 7.9 | 2.86 | 34  | 14.3 | 66.8 | 15.7 | 149  | 33  | 0.30 782 |
| zk001-412-8  | 9.8 | 658  | 0.01 | 7.69 | 0   | 1.61 | 3.52 | 0.74 | 16  | 5.21 | 58  | 21.9 | 96.2 | 20.4 | 189  | 39  | 0.23 757 |
| zk001-412-9  | 8.7 | 1111 | 0    | 12.1 | 0.3 | 4.6  | 6.9  | 1.26 | 31  | 9.23 | 101 | 36.7 | 163  | 34.3 | 308  | 63  | 0.22 745 |
| zk001-412-10 | 14  | 1237 | 0.01 | 11.2 | 0.2 | 3.91 | 7.2  | 1.52 | 31  | 10.1 | 112 | 40.9 | 182  | 37.6 | 336  | 69  | 0.37 783 |
| zk001-412-11 | 8.6 | 649  | 0.01 | 8.97 | 0   | 0.98 | 2.79 | 0.43 | 12  | 4.38 | 52  | 21.5 | 98.7 | 22.1 | 216  | 48  | 0.42 790 |
| zk001-412-12 | 11  | 1265 | 0    | 12.5 | 0.3 | 4.06 | 6.62 | 1.42 | 31  | 9.51 | 110 | 42   | 191  | 41.8 | 354  | 77  | 0.32 794 |
| zk001-412-13 | 5.8 | 552  | 0.01 | 8.09 | 0   | 0.29 | 1.13 | 0.24 | 9.1 | 3.27 | 42  | 17.5 | 82.8 | 19.2 | 189  | 41  | 0.28 766 |
| zk001-412-14 | 6.7 | 1109 | 0.02 | 11.7 | 0.1 | 3.15 | 5.28 | 1.16 | 29  | 8.81 | 103 | 37.7 | 161  | 36   | 324  | 65  | 0.26 766 |
| 7216-1       | 6.4 | 1636 | 0.05 | 26.9 | 0.2 | 3.83 | 6.68 | 3.07 | 36  | 11.3 | 134 | 52.8 | 256  | 56.2 | 555  | 131 | 0.55 752 |
| 7216-2       | 9.3 | 3942 | 0.51 | 95   | 0.6 | 6.55 | 11.3 | 5.1  | 77  | 26.8 | 330 | 131  | 610  | 129  | 1234 | 276 | 0.48 789 |
| 7216-3       | 6.3 | 3785 | 1.19 | 58.2 | 1.1 | 7.02 | 9.66 | 3.63 | 58  | 22.6 | 299 | 125  | 600  | 130  | 1255 | 272 | 0.46 733 |
| 7216-4       | 5.3 | 3706 | 0.16 | 46.2 | 0.3 | 3.23 | 8.03 | 3.7  | 61  | 22.6 | 297 | 121  | 577  | 127  | 1200 | 265 | 0.45 739 |
| 7216-5       | 5.6 | 3438 | 0    | 43.7 | 0.1 | 1.51 | 5.39 | 2.45 | 42  | 18   | 253 | 111  | 558  | 127  | 1250 | 279 | 0.44 666 |
| 7216-6       | 2.4 | 3024 | 0    | 17.6 | 0   | 1.5  | 4.7  | 2.16 | 39  | 16.2 | 224 | 97.3 | 495  | 112  | 1110 | 252 | 0.45 776 |
| 7216-7       | 8.2 | 2765 | 0.02 | 57   | 0.1 | 2.48 | 6.69 | 2.97 | 49  | 17.3 | 223 | 90.1 | 431  | 94.1 | 890  | 208 | 0.50 771 |
| 7216-8       | 9.4 | 3352 | 1.86 | 77.4 | 1.9 | 13   | 13.1 | 5.35 | 64  | 22.6 | 273 | 109  | 517  | 113  | 1072 | 241 | 0.45 747 |
| 7216-9       | 11  | 3309 | 3.84 | 77.9 | 3.6 | 23.4 | 20.8 | 8.18 | 76  | 25   | 285 | 109  | 489  | 103  | 973  | 215 | 0.56 772 |
| 7216-10      | 48  | 7715 | 23.6 | 227  | 21  | 141  | 95.1 | 37.6 | 228 | 69.6 | 704 | 248  | 1096 | 220  | 2021 | 419 | 0.63 695 |
| 7216-11      | 6.1 | 1957 | 0.02 | 42   | 0.2 | 2.01 | 5.07 | 2.16 | 35  | 12.2 | 155 | 64.5 | 308  | 68.6 | 672  | 156 | 0.57 742 |
| 7216-12      | 11  | 3451 | 22.8 | 111  | 8.8 | 49.4 | 25.3 | 8.75 | 79  | 25.3 | 291 | 111  | 506  | 110  | 1044 | 235 | 0.49 712 |
| 7216-13      | 7.9 | 1906 | 0.08 | 37.7 | 0.2 | 2.07 | 5.13 | 2.62 | 33  | 11.5 | 148 | 62.1 | 301  | 69.1 | 693  | 158 | 0.51 730 |
| 7216-14      | 3.4 | 720  | 0    | 11.6 | 0.1 | 1.63 | 2.86 | 1.43 | 14  | 4.39 | 55  | 22.6 | 113  | 27   | 300  | 77  | 0.46 753 |
| 7216-15      | 5.8 | 1816 | 0.02 | 34.9 | 0.1 | 1.93 | 4.62 | 2.52 | 32  | 11.4 | 143 | 59.5 | 281  | 64   | 620  | 144 | 0.48 731 |

<sup>1</sup> (Eu/Eu\*) = Eu/(Sm + Gd)<sup>1/2</sup> [18]. <sup>2</sup> Ti-in-zircon temperatures are calculated using the equation proposed by [22]: log (ppm Ti-in-zircon) = (5.711 ± 0.072) − (4800 ± 86)/T(K) − logαSiO<sub>2</sub> + logαTiO<sub>2</sub>, where αSiO<sub>2</sub> = 1, αTiO<sub>2</sub> = 0.6 are used in the calculation.

4.2. Whole-Rock Major and Trace Elements

The representative whole-rock geochemical data for the Yuhaixi intrusive samples are presented in Table 1. The Yuhaixi monzonitic granite, granite and diorite samples plot inside the granite, granite and monzodiorite fields, respectively on the Na<sub>2</sub>O + K<sub>2</sub>O vs. SiO<sub>2</sub> diagram (Figure 8a; [37]). The Yuhaixi monzonitic granites are characterized by high SiO<sub>2</sub> (74.20–76.57 wt.%) and total alkali contents (K<sub>2</sub>O + Na<sub>2</sub>O = 7.14–8.30 wt.%), but low MgO (0.23–0.36 wt.%), TiO<sub>2</sub> (0.14–0.17 wt.%), and P<sub>2</sub>O<sub>5</sub> (0.04–0.05 wt.%), with low Mg<sup>#</sup> = 28–32 [100 × molecular Mg<sup>2+</sup> / (Mg<sup>2+</sup> + Fe<sup>2+</sup>)], which belong to the high-K calc-alkaline series (Figure 8b). The Yuhaixi post-ore granite exhibited similar major element compositions, but they show relatively high Na<sub>2</sub>O and low K<sub>2</sub>O contents relative to the monzonitic granites. These rocks are characterized by high SiO<sub>2</sub> and K<sub>2</sub>O + Na<sub>2</sub>O (7.11–7.37 wt.%) contents, which suggests that they are high-K calc-alkaline series rocks (Figure 8b). The Yuhaixi diorite is chemically different from the Yuhaixi monzonitic granite and granite,

and has  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{TFe}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{P}_2\text{O}_5$  contents of 53.55–54.58 wt.%, 17.33–17.98 wt.%, 3.86–4.11 wt.%, 0.90–1.15 wt.%, 7.90–8.69 wt.%, 0.80–0.95 wt.%, and 0.16–0.25 wt.%, respectively. The Yuhaixi diorite belongs to the calc-alkaline series (Figure 8b). In the A/NK vs. A/CNK diagram, the Yuhaixi monzonitic granite and granite samples are metaluminous to weak peraluminous (Figure 8c), with an aluminum saturation index ( $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$ ) ranging from 0.66–1.07.



**Figure 8.** Classification and series diagrams of intrusions in the Yuhaixi porphyry Mo(Cu) deposit. (a)  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  vs.  $\text{SiO}_2$  plot diagram [43]. (b)  $\text{K}_2\text{O}$  vs.  $\text{SiO}_2$  diagram [44]. (c) A/NK vs. A/CNK plot diagram [45]. (d)  $\text{FeOt}/(\text{FeOt} + \text{MgO})$  vs.  $\text{SiO}_2$  diagram.

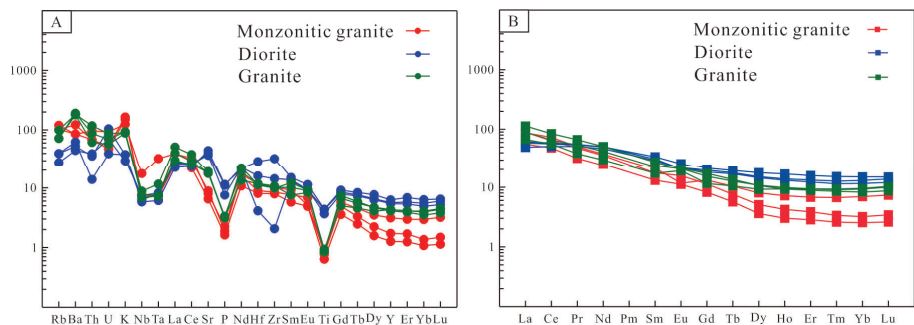
As for the chondrite-normalized REE patterns, the Yuhaixi diorite samples are moderately fractionated ( $(\text{La}/\text{Yb})_{\text{N}} = 4.19\text{--}7.64$ ), with light rare earth element (LREE) enrichment and heavy rare earth element (HREE) depletion in the absence of clear Eu anomalies ( $\text{Eu}/\text{Eu}^* = 0.92\text{--}1.27$ ) (Figure 9A). The overall rare earth content is low ( $\Sigma\text{REE} = 32.1\text{--}162.16$ ) in Yuhaixi, among which the rare earth content of granite is the lowest ( $\Sigma\text{REE} = 32.1\text{--}78.49$ ). The granite samples show a slight positive Eu anomaly ( $\delta\text{Eu} = 0.94\text{--}1.33$ ). The diorite samples show weaker negative Eu anomalies ( $\delta\text{Eu} = 0.84\text{--}0.94$ ) (Figure 9A). In the primitive mantle-normalized trace element spider diagram (Figure 9A; [30]), different magmatic rocks show different characteristics, which are generally characterized by enrichment of large-ion lithophile elements (LILE: Rb, Ba, K, U) and relative depletion of high-field-strength elements (HFSE: Nb, Ta, Zr). The monzonite granite is enriched in Rb, Ba, U, K, Pb, and depleted of Nb, Ta, Sr, Ti, P. Compared with granite, the LILE enrichment and the HFSE depletion in monzonitic granite and diorite are more significant (Figure 9A).

#### 4.3. Zircon Hf Isotopes

Zircon Hf isotope analysis results are listed in Table 4. The monzonitic granite, diorite, and granite yielded  $\varepsilon\text{Hf}(t)$  values of 11.37–17.59, 11.59–13.46, and 11.73–14.76, respectively. The zircon Hf single- and two-stage model ages are 280–538 Ma and 240–637 Ma for the



monzonitic granite, 399–472 Ma and 458–578 Ma for the diorite, and 354–478 Ma and 377–572 Ma for the granite, respectively (Table 4).



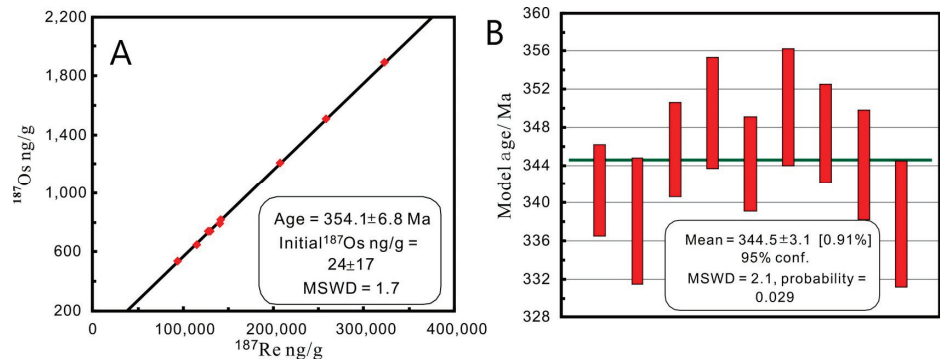
**Figure 9.** (A) primitive mantle-normalized trace element abundance spider diagram and (B) chondrite-normalized REE of the intrusions in the Yuhaxi porphyry Mo(Cu) deposit. (normalization values are from [20]). The N-MORB, E-MORB, and OIB patterns are from [20].

4.4. Whole-Rock Sr-Nd Isotopes

The initial  $^{87}\text{Sr}/^{86}\text{Sr}$  (Isr) isotope ratios and  $\epsilon\text{Nd}(t)$  were calculated using the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, Nd values, and zircon U-Pb ages analyzed in this study (Table 5). All rock samples from the Yuhaxi Mo(Cu) deposit (e.g., monzonitic granite, diorite and granite) are characterized by low  $(^{87}\text{Sr}/^{86}\text{Sr})_i$  values with obviously varied ranges (e.g., 0.7043–0.7128, 0.7037–0.7041, and 0.7042–0.7043, respectively). They show positive and narrow ranges of  $\epsilon\text{Nd}(t)$  (1.36–3.4, 5.16–7.75, and 4.62–6.44, respectively), corresponding to  $T_{\text{DM2}}$  ages of 832–1002 Ma, 430–642 Ma, and 545–693 Ma, respectively (Table 5).

4.5. Re-Os Isotopic Ages

The Re-Os isotopic data for nine molybdenite samples from the Yuhaxi porphyry Mo deposit are listed in Table 6 and are plotted in an isochron diagram in Figure 10. The concentrations of  $^{187}\text{Re}$  and  $^{187}\text{Os}$  ranged from 93.9 to 322.9  $\mu\text{g/g}$  and from 539.5 to 1889.2 ng/g, respectively. Nine samples yielded model ages ranging from  $337.9 \pm 6.7$  to  $350.2 \pm 6.1$  Ma and a well-constrained  $^{187}\text{Re}$ – $^{187}\text{Os}$  isochron age of  $354.1 \pm 6.8$  Ma, with  $\text{MSWD} = 1.7$  and an initial  $^{187}\text{Os}$  of  $24 \pm 17$  ng/g (Figure 10A). The data also yields a weighted average age of  $344.5 \pm 3.1$  Ma ( $\text{MSWD} = 2.1$ ) (Figure 10B). These ages are concordant within the errors, indicating that the Yuhaxi Mo(Cu) deposit was formed in the Carboniferous.



**Figure 10.** Re-Os isochron diagram and weighted average model age diagram for four molybdenite samples in the Yuhaxi porphyry Mo(Cu) deposit.

Table 4. In situ zircon Hf isotopic data on the studied intrusive rocks in the Yuhaixi Mo(Cu) deposit.

| Sample No.   | Age (Ma) | <sup>176</sup> Hf/ <sup>177</sup> Hf | 1σ       | <sup>176</sup> Lu/ <sup>177</sup> Hf | 1σ       | <sup>176</sup> Yb/ <sup>177</sup> Hf | 1σ       | eHf (0) | eHf (T) | T <sub>DM</sub> | T <sub>DMC</sub> | fs    |
|--------------|----------|--------------------------------------|----------|--------------------------------------|----------|--------------------------------------|----------|---------|---------|-----------------|------------------|-------|
| YHX-ZK-1     | 364.07   | 0.283072                             | 0.000014 | 0.004346                             | 0.000038 | 0.125695                             | 0.000845 | 10.61   | 17.59   | 279.05          | 240.34           | −0.87 |
| YHX-ZK-2     | 364.28   | 0.282921                             | 0.000016 | 0.002443                             | 0.000049 | 0.068981                             | 0.001428 | 5.27    | 12.71   | 487.64          | 553.83           | −0.93 |
| YHX-ZK-3     | 362.36   | 0.282939                             | 0.000013 | 0.002261                             | 0.000021 | 0.062658                             | 0.000663 | 5.91    | 13.34   | 458.91          | 511.47           | −0.93 |
| YHX-ZK-4     | 352.34   | 0.282972                             | 0.000017 | 0.002645                             | 0.000092 | 0.076706                             | 0.002935 | 7.09    | 14.23   | 414.25          | 446.94           | −0.92 |
| YHX-ZK-5     | 362.89   | 0.282947                             | 0.000014 | 0.001811                             | 0.000013 | 0.051511                             | 0.000516 | 6.18    | 13.74   | 442.01          | 486.6            | −0.95 |
| YHX-ZK-6     | 363.7    | 0.282929                             | 0.000015 | 0.002913                             | 0.000044 | 0.085132                             | 0.001176 | 5.56    | 12.87   | 481.81          | 542.82           | −0.91 |
| YHX-ZK-7     | 358.97   | 0.282965                             | 0.000014 | 0.001719                             | 0.000046 | 0.048263                             | 0.001292 | 6.83    | 14.32   | 414.48          | 445.98           | −0.95 |
| YHX-ZK-8     | 354.4    | 0.282978                             | 0.000016 | 0.003775                             | 0.000091 | 0.106083                             | 0.002773 | 7.3     | 14.22   | 418.43          | 449.15           | −0.89 |
| YHX-ZK-9     | 361      | 0.282947                             | 0.000013 | 0.001313                             | 0.000006 | 0.035821                             | 0.000127 | 6.21    | 13.84   | 435.14          | 478.51           | −0.96 |
| YHX-ZK-10    | 361.26   | 0.282985                             | 0.000016 | 0.003241                             | 0.000026 | 0.088301                             | 0.000827 | 7.54    | 14.72   | 401.89          | 472.3            | −0.9  |
| YHX-ZK-11    | 358.08   | 0.282945                             | 0.000016 | 0.002979                             | 0.000054 | 0.083992                             | 0.001507 | 6.12    | 13.3    | 459.23          | 511.2            | −0.91 |
| YHX-ZK-12    | 358.06   | 0.282903                             | 0.000013 | 0.002089                             | 0.000038 | 0.056193                             | 0.001068 | 4.62    | 12.01   | 509.8           | 593.52           | −0.94 |
| YHX-ZK-13    | 361.99   | 0.28288                              | 0.000014 | 0.001761                             | 0.000034 | 0.046745                             | 0.000888 | 3.82    | 11.37   | 538.24          | 637.96           | −0.95 |
| YHX-ZK-14    | 359.72   | 0.282956                             | 0.000014 | 0.001655                             | 0.000009 | 0.046342                             | 0.000231 | 6.52    | 14.05   | 426.25          | 464.2            | −0.95 |
| YHX-ZK-15    | 358.69   | 0.282968                             | 0.000016 | 0.003117                             | 0.000047 | 0.087435                             | 0.001308 | 6.93    | 14.08   | 426.66          | 461.17           | −0.91 |
| YHX-ZK-16    | 360.35   | 0.282957                             | 0.000016 | 0.001848                             | 0.000006 | 0.048001                             | 0.000285 | 6.53    | 14.03   | 427.98          | 466              | −0.94 |
| YHX-ZK-17    | 356.41   | 0.283007                             | 0.000014 | 0.003289                             | 0.000063 | 0.097506                             | 0.001856 | 8.3     | 15.37   | 369.99          | 376.79           | −0.9  |
| YHX-ZK-18    | 356.81   | 0.282927                             | 0.000018 | 0.003289                             | 0.000045 | 0.096394                             | 0.001396 | 5.49    | 12.57   | 490.31          | 557.13           | −0.9  |
| Diorite      |          |                                      |          |                                      |          |                                      |          |         |         |                 |                  |       |
| zk001-412-1  | 306.4    | 0.282943                             | 0.000014 | 0.000731                             | 0.00001  | 0.02065                              | 0.000259 | 6.04    | 12.64   | 434.94          | 513.32           | −0.98 |
| zk001-412-2  | 298.94   | 0.282967                             | 0.000014 | 0.000688                             | 0.00001  | 0.01916                              | 0.000048 | 6.9     | 13.34   | 400.38          | 462.42           | −0.98 |
| zk001-412-3  | 303.67   | 0.282969                             | 0.000016 | 0.000888                             | 0.00002  | 0.026311                             | 0.000066 | 6.95    | 13.46   | 400.35          | 458.66           | −0.97 |
| zk001-412-4  | 302.43   | 0.282938                             | 0.000016 | 0.001176                             | 0.000012 | 0.033611                             | 0.000286 | 5.87    | 12.29   | 447.19          | 532.71           | −0.96 |
| zk001-412-6  | 303.05   | 0.282944                             | 0.000012 | 0.000827                             | 0.000005 | 0.023606                             | 0.00012  | 6.09    | 12.59   | 434.22          | 513.67           | −0.98 |
| zk001-412-7  | 296.45   | 0.282927                             | 0.000012 | 0.000631                             | 0.000004 | 0.018343                             | 0.000149 | 5.5     | 11.9    | 455.47          | 553.11           | −0.98 |
| zk001-412-8  | 298.79   | 0.282937                             | 0.000014 | 0.000837                             | 0.000016 | 0.024897                             | 0.000592 | 5.85    | 12.26   | 443.87          | 531.68           | −0.97 |
| zk001-412-9  | 299.82   | 0.282946                             | 0.000014 | 0.000701                             | 0.000003 | 0.020066                             | 0.000103 | 6.16    | 12.62   | 430.05          | 509.63           | −0.98 |
| zk001-412-10 | 293.73   | 0.282967                             | 0.000011 | 0.000607                             | 0.000005 | 0.017496                             | 0.000137 | 6.91    | 13.26   | 398.9           | 463.59           | −0.98 |
| zk001-412-11 | 295.9    | 0.282925                             | 0.000013 | 0.000574                             | 0.000001 | 0.016515                             | 0.000039 | 5.41    | 11.81   | 458.27          | 558.37           | −0.98 |
| zk001-412-12 | 302.54   | 0.282914                             | 0.000015 | 0.000449                             | 0.000011 | 0.012607                             | 0.000408 | 5.02    | 11.59   | 472.15          | 577.62           | −0.99 |
| zk001-412-13 | 306.43   | 0.28294                              | 0.000013 | 0.00094                              | 0.000005 | 0.027755                             | 0.000198 | 5.95    | 12.51   | 440.87          | 521.65           | −0.97 |
| zk001-412-14 | 295.58   | 0.282937                             | 0.000012 | 0.00096                              | 0.000001 | 0.02861                              | 0.000066 | 5.83    | 12.14   | 446.22          | 536.6            | −0.97 |
| zk001-412-15 | 297.65   | 0.282955                             | 0.000012 | 0.000885                             | 0.000003 | 0.025982                             | 0.000121 | 6.48    | 12.86   | 419.08          | 492.32           | −0.97 |
| zk001-412-16 | 296.55   | 0.282953                             | 0.000013 | 0.000649                             | 0.000003 | 0.018522                             | 0.000146 | 6.41    | 12.81   | 419.37          | 494.69           | −0.98 |
| zk001-412-17 | 296.48   | 0.282952                             | 0.000014 | 0.001076                             | 0.000004 | 0.032282                             | 0.000155 | 6.38    | 12.69   | 425.56          | 502.38           | −0.97 |
| zk001-412-18 | 293.48   | 0.282934                             | 0.000013 | 0.000679                             | 0.000002 | 0.019199                             | 0.000088 | 5.73    | 12.05   | 446.96          | 540.9            | −0.98 |
| zk001-412-19 | 301.64   | 0.282966                             | 0.000017 | 0.000677                             | 0.000003 | 0.018615                             | 0.000083 | 6.87    | 13.38   | 401.16          | 462.08           | −0.98 |
| zk001-412-20 | 295.72   | 0.282931                             | 0.000011 | 0.000607                             | 0.000005 | 0.016322                             | 0.000143 | 5.62    | 12.01   | 450.39          | 545.54           | −0.98 |
| zk001-412-21 | 303.2    | 0.282938                             | 0.000015 | 0.000835                             | 0.000009 | 0.024164                             | 0.000315 | 5.87    | 12.38   | 442.95          | 527.54           | −0.97 |

Table 4. Cont.

| Sample No. | Age (Ma) | $^{176}\text{Hf}/^{177}\text{Hf}$ | 1 $\sigma$ | $^{176}\text{Lu}/^{177}\text{Hf}$ | 1 $\sigma$ | $^{176}\text{Yb}/^{177}\text{Hf}$ | 1 $\sigma$ | eHf (0) | eHf (1) | T <sub>DM</sub> | T <sub>DMC</sub> | fs    |
|------------|----------|-----------------------------------|------------|-----------------------------------|------------|-----------------------------------|------------|---------|---------|-----------------|------------------|-------|
| 7216-1     | 306.63   | 0.282925                          | 0.000034   | 0.00212                           | 0.000015   | Granite                           | 0.000742   | 5.41    | 11.73   | 477.66          | 571.8            | −0.94 |
| 7216-2     | 307.95   | 0.28298                           | 0.000027   | 0.004211                          | 0.000022   | 0.052126                          | 0.000672   | 7.36    | 13.28   | 421.22          | 473.44           | −0.87 |
| 7216-3     | 305.7    | 0.283025                          | 0.000023   | 0.004513                          | 0.000057   | 0.114445                          | 0.001314   | 8.94    | 14.76   | 354.81          | 376.83           | −0.86 |
| 7216-4     | 306.15   | 0.282992                          | 0.000019   | 0.004137                          | 0.000074   | 0.16852                           | 0.002601   | 7.78    | 13.68   | 401.84          | 446.26           | −0.88 |
| 7216-5     | 308.54   | 0.282968                          | 0.000014   | 0.003326                          | 0.000032   | 0.088744                          | 0.001145   | 6.94    | 13.06   | 428.42          | 488.23           | −0.9  |
| 7216-6     | 307.07   | 0.282947                          | 0.000021   | 0.002676                          | 0.000013   | 0.07104                           | 0.000482   | 6.19    | 12.41   | 452.27          | 528.74           | −0.92 |
| 7216-7     | 306.32   | 0.282989                          | 0.000019   | 0.004237                          | 0.000041   | 0.110844                          | 0.001475   | 7.69    | 13.58   | 452.88          | 453.14           | −0.87 |
| 7216-8     | 308.07   | 0.282945                          | 0.000019   | 0.0022                            | 0.000039   | 0.05607                           | 0.001128   | 6.11    | 12.44   | 449.83          | 527.37           | −0.93 |
| 7216-9     | 307.16   | 0.282962                          | 0.00002    | 0.001427                          | 0.000076   | 0.033621                          | 0.001796   | 6.71    | 13.18   | 416.07          | 479.25           | −0.96 |

Note:  $e\text{Hf}(0) = [(^{176}\text{Hf}/^{177}\text{Hf})_s / (^{176}\text{Hf}/^{177}\text{Hf})_{\text{CHUR0}} - 1] \cdot 10,000$ ;  $e\text{Hf}(1) = \{[(^{176}\text{Hf}/^{177}\text{Hf})_s - (^{176}\text{Lu}/^{177}\text{Hf})_s - (^{176}\text{Lu}/^{177}\text{Hf})_{\text{DM1}}] / [(^{176}\text{Lu}/^{177}\text{Hf})_{\text{DM1}}] - 1\} \cdot 10,000$ ;  $T_{\text{DM1}} = 1/\lambda \cdot \ln[1 + ((^{176}\text{Hf}/^{177}\text{Hf})_s - (^{176}\text{Lu}/^{177}\text{Hf})_{\text{DM1}}) / ((^{176}\text{Lu}/^{177}\text{Hf})_{\text{DM1}})]$ ;  $T_{\text{DM2}} = T_{\text{DM1}} - t$ ;  $(f_{\text{Ce}} - f_s) \cdot (f_{\text{Ce}} - f_{\text{DM}}) / f_{\text{Lu}} / \text{Hf} = [(^{176}\text{Lu}/^{177}\text{Hf})_s / (^{176}\text{Lu}/^{177}\text{Hf})_{\text{CHUR0}}] - 1$ , where  $(^{176}\text{Hf}/^{177}\text{Hf})_s$  and  $(^{176}\text{Lu}/^{177}\text{Hf})_s$  are the measured values of the samples;  $s$  = sample, and  $t$  = crystallization time of zircon;  $(^{176}\text{Lu}/^{177}\text{Hf})_{\text{CHUR0}} = 0.0332$  and  $(^{176}\text{Hf}/^{177}\text{Hf})_{\text{CHUR0}} = 0.282772$  [23];  $(^{176}\text{Lu}/^{177}\text{Hf})_{\text{DM}} = 0.0384$  and  $(^{176}\text{Hf}/^{177}\text{Hf})_{\text{DM}} = 0.28325$  [24];  $f_{\text{Ce}} = -0.55$  and  $f_{\text{DM}} = 0.16$ ; and  $\lambda = 1.867 \times 10^{-12} / \text{yr}^{-1}$  [46] were used in the calculation.

Table 5. Sr–Nd isotopic compositions of the studied intrusive rocks in the Yuhai Mo(Cu) deposit.

| Sample No. | Rock Type | Age (Ma) | Rb      | Sr    | $^{87}\text{Rb}/^{86}\text{Sr}$ | $^{87}\text{Sr}/^{86}\text{Sr}$ | $\text{I}_{\text{Sr}}$ | Sm    | Nd    | $^{147}\text{Sm}/^{144}\text{Nd}$ | $^{143}\text{Nd}/^{144}\text{Nd}$ | Sm/Nd | $\text{I}_{\text{Nd}}$ | $\epsilon\text{Nd}(0)$ | $\epsilon\text{Nd}(t)$ | T <sub>DM</sub> |
|------------|-----------|----------|---------|-------|---------------------------------|---------------------------------|------------------------|-------|-------|-----------------------------------|-----------------------------------|-------|------------------------|------------------------|------------------------|-----------------|
| YHX-ZK-1   | MG        | 359.4    | 30.9563 | 107   | 0.8371                          | 0.711                           | 0.7062                 | 4.545 | 13.95 | 0.197                             | 0.5127                            | 0.326 | 0.5122                 | 1.3655                 | 1.3597                 | 3992            |
| YHX-ZK-2   | MG        | 359.4    | 28.9275 | 68.65 | 1.2193                          | 0.711                           | 0.7043                 | 1.948 | 6.905 | 0.171                             | 0.5127                            | 0.282 | 0.5123                 | 1.4045                 | 2.6103                 | 1555            |
| S3201-20   | GNG       | 364      | 58.6    | 289   | 0.5866                          | 0.706                           | 0.7032                 | 1.64  | 10.4  | 0.095                             | 0.5126                            |       |                        | −0.68                  | 4.03                   | 705             |
| S3201-26   | GNG       | 364      | 69.9    | 203   | 0.9964                          | 0.709                           | 0.7037                 | 2.56  | 14.9  | 0.104                             | 0.5126                            |       |                        | −0.76                  | 3.56                   | 765             |
| ZK001-25   | DI        | 298.8    | 11.6175 | 657.9 | 0.0511                          | 0.704                           | 0.7037                 | 1.996 | 17.47 | 0.069                             | 0.5128                            | 0.114 | 0.5127                 | 2.887                  | 7.7512                 | 386             |
| ZK001-350  | DI        | 298.8    | 8.715   | 648.6 | 0.0389                          | 0.704                           | 0.7037                 | 1.968 | 19.86 | 0.06                              | 0.5128                            | 0.099 | 0.5126                 | 2.4969                 | 7.7096                 | 382             |
| ZK001-396  | DI        | 298.8    | 11.9025 | 749.4 | 0.046                           | 0.704                           | 0.7041                 | 3.966 | 17.23 | 0.139                             | 0.5128                            | 0.23  | 0.5125                 | 2.9651                 | 5.1618                 | 739             |
| 721-1      | GR        | 307      | 14.9663 | 212.8 | 0.2035                          | 0.705                           | 0.7043                 | 1.443 | 9.591 | 0.091                             | 0.5128                            | 0.151 | 0.5126                 | 2.2823                 | 6.435                  | 493             |
| 721-3      | GR        | 307      | 14.2313 | 194.2 | 0.212                           | 0.705                           | 0.7043                 | 2.673 | 12.85 | 0.126                             | 0.5128                            | 0.208 | 0.5125                 | 1.8337                 | 4.6214                 | 727             |
| 721-5      | GR        | 307      | 14.5125 | 209   | 0.2009                          | 0.705                           | 0.7043                 | 1.739 | 12.24 | 0.086                             | 0.5127                            | 0.142 | 0.5126                 | 1.9307                 | 6.3017                 | 493             |

Abbreviation: MG, monzonitic granite; GNG, gneissic granite; DI, diorite; GR, granite.  $(^{87}\text{Sr}/^{86}\text{Sr})_s = (^{87}\text{Sr}/^{86}\text{Sr})_0 \times (e^{\lambda t} - 1)$ ;  $^{87}\text{Sr}/^{86}\text{Sr} = (\text{Rb}/\text{Sr}) \times 2.8956$ ;  $\lambda_{\text{Rb-Sr}} = 1.42 \times 10^{-11} / \text{a}$ ;  $(^{143}\text{Nd}/^{144}\text{Nd})_s = (^{143}\text{Nd}/^{144}\text{Nd})_0 - 1$ ;  $(^{147}\text{Sm}/^{144}\text{Nd})_s = (\text{Sm}/\text{Nd}) \times 0.60456$ ;  $\lambda_{\text{Sm-Nd}} = 6.54 \times 10^{-12} / \text{a}$ ;  $\epsilon\text{Nd}(t) = 10,000 [(^{143}\text{Nd}/^{144}\text{Nd})_s / (^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}(t)} - 1]$ ;  $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}(t)} = (^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}(0)} - 1$ ;  $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}(0)} = (^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}} \times (e^{\lambda t} - 1)$ ;  $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}(0)} = 0.512638$ ;  $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}} = 0.1967$ ;  $T_{\text{DM}} = 1/\lambda \times \ln[1 + ((^{143}\text{Nd}/^{144}\text{Nd})_s - (^{143}\text{Nd}/^{144}\text{Nd})_{\text{DM}}) / ((^{147}\text{Sm}/^{144}\text{Nd})_{\text{DM}})]$ ;  $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{DM}} = 0.21357$ ;  $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{DM}} = 0.51315$ ;  $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{crust}} = 0.118$ .

Table 6. Molybdenite Re-Os isotopic data for the Yuhaixi Mo(Cu) deposit.

| Sample No. | Weight (g) | Ores Type         | Occurrence    | Re/ $\mu\text{g g}^{-1}$ |            | Os/ $\text{ng g}^{-1}$ |            | $^{187}\text{Re}/\mu\text{g g}^{-1}$ |            | $^{187}\text{Os}/\text{ng g}^{-1}$ |            | Model Age (Ma) |            |
|------------|------------|-------------------|---------------|--------------------------|------------|------------------------|------------|--------------------------------------|------------|------------------------------------|------------|----------------|------------|
|            |            |                   |               | Measured                 | 2 $\sigma$ | Measured               | 2 $\sigma$ | Measured                             | 2 $\sigma$ | Measured                           | 2 $\sigma$ | Measured       | 2 $\sigma$ |
| Mo-01      | 0.00306    | Mo mineralized MG | Dissemination | 206.7                    | 1.8        | 0.0072                 | 0.2        | 129.9                                | 1.1        | 741                                | 4.2        | 341.4          | 4.9        |
| Mo-02      | 0.00516    | Mo mineralized MG | Dissemination | 223.4                    | 3.4        | 0.0022                 | 0.1        | 140.4                                | 2.2        | 793.4                              | 5.8        | 338.2          | 6.7        |
| Mo-03      | 0.00141    | Mo mineralized MG | Dissemination | 226                      | 1.8        | 0.008                  | 0.1        | 142.1                                | 1.2        | 820.5                              | 5.7        | 345.7          | 5.0        |
| Mo-04      | 0.00311    | Mo mineralized MG | Dissemination | 411.5                    | 5.0        | 0.0071                 | 0.2        | 258.6                                | 3.1        | 1510.8                             | 9.3        | 349.6          | 5.9        |
| Mo-05      | 0.00205    | Mo mineralized MG | Dissemination | 204.1                    | 1.8        | 0.0087                 | 0.3        | 128.3                                | 1.1        | 737.7                              | 4.5        | 344.2          | 5.0        |
| Mo-06      | 0.00051    | Mo mineralized MG | Dissemination | 513.7                    | 5.4        | 0.0087                 | 0.4        | 322.9                                | 3.4        | 1889.2                             | 18.7       | 350.2          | 6.1        |
| Mo-07      | 0.0031     | Ccp-Mo-Qz veinlet | Veinlet       | 330.7                    | 3.2        | 0.0072                 | 0.2        | 207.8                                | 2.0        | 1206.3                             | 7.2        | 347.4          | 5.2        |
| Mo-08      | 0.00509    | Ccp-Mo-Qz veinlet | Veinlet       | 149.3                    | 1.9        | 0.0023                 | 0.1        | 93.9                                 | 1.2        | 539.5                              | 3.3        | 344.1          | 5.8        |
| Mo-09      | 0.00511    | Ccp-Mo-Qz veinlet | Veinlet       | 182.6                    | 2.9        | 0.0021                 | 0.1        | 114.8                                | 1.8        | 648                                | 4.0        | 337.9          | 6.7        |

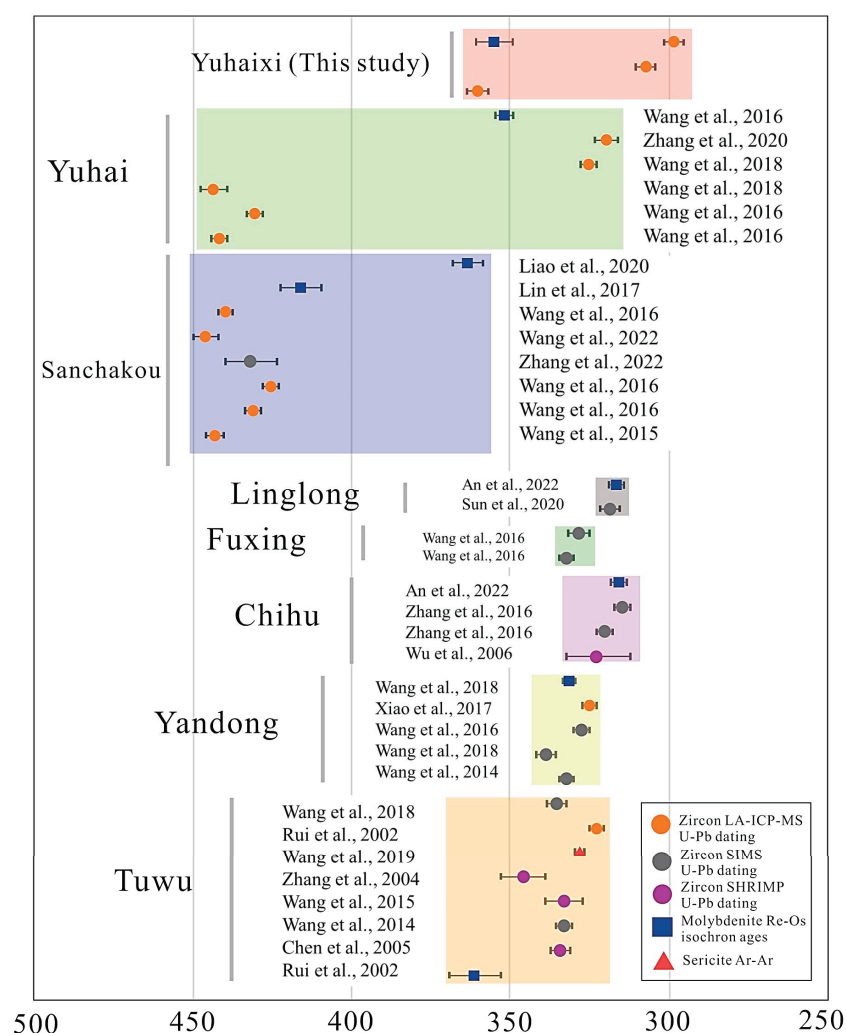
Abbreviation: MG, monzonitic granite. Decay constant:  $\lambda^{187}\text{Re} = 1.666 \times 10^{-11} \text{ year}^{-1}$  [46]. Uncertainty in the Re and Os concentrations includes errors associated with the weighing of the sample and diluent, the calibration error of the diluent, the mass spectrometry analytical error, and the measurement error of the isotope ratios for the test sample; the confidence level is 95%. Uncertainty in the Re-Os model ages includes the uncertainty of the  $^{187}\text{Re}$  decay constant, with a confidence level of 95%. Uncertainties for ages are absolute (2 $\sigma$ ).

## 5. Discussion

### 5.1. Timing of Magmatism and Mineralization of Yuhaixi Mo(Cu) Deposit

Multiple magmatic activities were documented in the eastern segment of the Dananhu-Tousuquan island arc belt [25–29]. Our study reveals that at least two stages (~359 Ma and ~307–299 Ma) of magmatic activities occurred in the Yuhaixi area. Zircon U-Pb dating showed that Yuhaixi monzonitic granite, granite, and diorite were emplaced at ~359 Ma, ~307 Ma, and ~299 Ma, respectively. However, other intrusive rocks near the Yuhaixi orefield were reported to form at ~443–430 Ma, earlier than that of Yuhaixi intrusive rocks. For example, Wang et al. (2016) obtained the age of the rocks in the Yuhai Mo(Cu) deposit to be  $441.6 \pm 2.5$  Ma,  $430.3 \pm 2.6$  Ma for the diorite and granodiorite, respectively [5]; Wang et al. (2015) obtained the age of the Sanchakou pluton to be 443 Ma; Wang et al. (2016a) obtained the age of the felsic intrusion in the Sanchakou mining area to be 440–426 Ma [30]; and Wang et al. (2018) obtained the age of the Yuhai quartz diorite to be  $443.5 \pm 4.1$  Ma [12]. Overall, at least three stages of magmatic activities were identified and recorded in the eastern segment of the Dananhu-Tousuquan island arc belt, namely ~430–443 Ma, ~359 Ma, and ~307–299 Ma.

The molybdenite Re-Os dating shows that the Yuhaixi Mo(Cu) deposit was formed at  $354 \pm 6.8$  Ma (Figure 10), which is approximately coeval with the emplaced ages of the Yuhaixi monzonitic granite ( $359.4 \pm 1.6$  Ma). Previous studies have shown that the Yuhai molybdenite age [5] and the Sanchakou molybdenite age are concentrated in 370–350 Ma (Figure 11 [30]), which are consistent with the molybdenite Re-Os age of Yuhaixi Mo(Cu) deposit. So, the Yuhaixi Mo(Cu) deposit is suggested to form at ~354–360 Ma. The Yuhaixi granite and diorite rocks are post-ore intrusive plutons. Field investigations revealed that Yuhaixi Mo(Cu) deposits are characterized by disseminated or veinlet ores, and Mo mineralization mainly occurs in the potassic alteration zone (Figure 4I). It is highly likely that the monzonitic granite contributed to the generation of the Yuhaixi deposit.



**Figure 11.** Summary of geochronological data of major porphyry Cu deposits in the Eastern-Tianshan. Error bars are  $2\sigma$  [5–7,9,12,47–58].

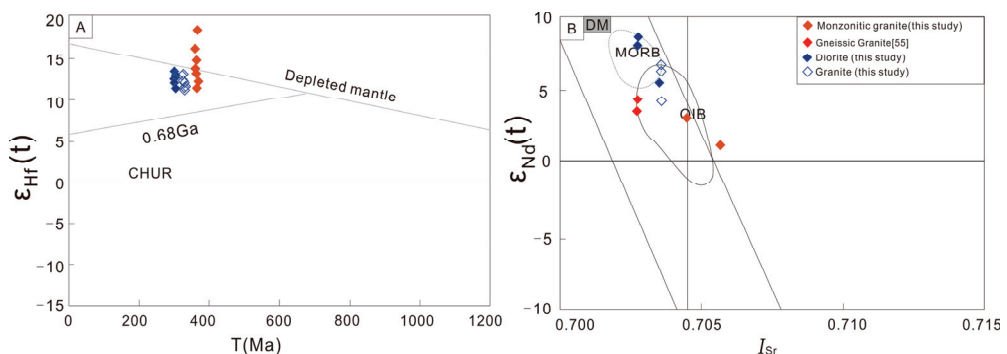
## 5.2. Petrogenesis

The Yuhaixi monzonitic granite is characterized by high  $\text{SiO}_2$  and  $\text{K}_2\text{O} + \text{Na}_2\text{O}$  contents, low  $\text{Al}_2\text{O}_3$  content, and the depletion of aluminum-rich minerals (e.g., muscovite, tourmaline, and garnet). They have a weak peraluminous character ( $1 < \text{A}/\text{CNK} < 1.1$ ), and they exhibit low Sr (<188 ppm) and Y contents with relatively low Sr/Y ratios (<25). These features suggest that the Yuhaixi intrusion can be classified as the I- or A-type granite [21]. In addition, the Yuhaixi monzonitic granite shows low  $\text{FeOt}/(\text{FeOt} + \text{MgO})$  ratios, Zr content, and  $10^4 \times \text{Ga}/\text{Al}$  ratios (2.1–2.4), excluding the possibility of A-type granite (Figure 8d). Therefore, the Yuhaixi monzonitic granite likely belongs to I-type granites [59]. The Yuhaixi post-ore granite is a high silica granite and exhibits similar geochemical signatures to the causative monzonitic granite. The Yuhaixi post-ore granite also has relatively low  $\text{A}/\text{CNK}$  (<1.1) and  $\text{Ga}/\text{Al}$  ratios, which is consistent with the features of I-type granites.



Generally, the  $Mg^\#$  values of magmatic rocks formed by the partial melting of the basaltic lower crust are less than 40 regardless of the degree of melting [43,44,60]. If mantle material was involved in the origin of ore-forming felsic rocks,  $Mg^\#$  values of these rocks will be higher than 40 [60]. Thus, the  $Mg^\#$  values can be used as an important indicator to track the addition of mantle-derived magma. Overall, the Yuhaixi felsic rocks both show high silica and low  $MgO$ ,  $Cr$ ,  $Ni$  contents, which is in favor of the crust origin. They both are enriched in LREE and LILE and depleted in HFSE elements (e.g.,  $Nb$ ,  $Ta$ ) in the primitive mantle-normalized diagram (Figure 9). The Yuhaixi monzonitic granite samples have significant variable  $^{87}Sr/^{86}Sr$  ratios, ranging from 0.7041–0.7127, and high  $\epsilon_{Hf}(t)$  (11.37–17.59) and  $\epsilon_{Nd}(t)$  (1.36–3.4) values, suggesting that it may have formed by melting the juvenile crust with the involvement of crustal components [43–45,60]. In addition, the Yuhaixi monzonitic granite is high silica granite and is lithologically homogeneous, arguing against the significant upper crustal contamination and fractional crystallization of basaltic magmas [40]. The studied monzonitic granite is characterized by high  $K_2O$  (3.8–5.0 wt.%) and  $K_2O/Na_2O$  (1.1–1.6) ratios and shows relatively low  $Rb/Sr$  (0.34–0.47) and high  $K/Rb$  (396–615) ratios without obvious  $Eu$ -negative anomaly, indicating that it is less evolved than high- $K$  granites. Thus, we proposed that Yuhaixi monzonitic granite likely originated from the partial melting of the juvenile lower crust with the involvement of hydrous melts or fluids sourced from continental crustal components (e.g., subducting sediments). However, Yuhaixi post-ore granite shows high  $Na_2O$  (4.5–4.6 wt.%) contents and low  $K_2O/Na_2O$  ( $\sim 0.6$ ) ratios and it has low initial  $^{87}Sr/^{86}Sr$  ratios (0.7042–0.7043) but high  $\epsilon_{Hf}(t)$  (11.7–14.8) and  $\epsilon_{Nd}(t)$  (4.6–6.4) values, which suggests that Yuhaixi granite likely originated from the partial melting of the juvenile crust with the addition of ocean crustal components (e.g., subducting oceanic slab) [45].

Compared to the Yuhaixi felsic rocks, Yuhaixi diorites have relatively low silica (53–54 wt.%) and high  $MgO$  (4.1–5.1 wt.%),  $Na_2O$  (3.9–4.1 wt.%), and  $Al_2O_3$  (17.3–18 wt.%) contents with high  $Cr$ ,  $V$ , and  $Ni$  contents. Their high  $MgO$  ( $Mg^\# > 45$ ) and high transition metal (e.g.,  $Cr$ ,  $Ni$ ,  $V$ ) contents suggest the Yuhaixi high- $Al$  diorites may be derived from the depleted lithospheric mantle source [20,23,25]. They have relatively low initial  $^{87}Sr/^{86}Sr$  ratios, and high  $\epsilon_{Nd}(t)$  (5.16–7.75) and  $\epsilon_{Hf}(t)$  values (11.59–13.46), further supporting the depleted mantle origin. However, the Yuhaixi diorite samples are enriched in LREEs and LILEs, depleted in HREEs and HFSEs, and exhibit high  $Sr$  contents (785–941 ppm),  $Ba/La$ ,  $Ba/Th$  ratios, but low  $Th/Yb$ , and  $Th/Nb$  ratios. Plank and Langmuir (1998) pointed out that the magma formed from the source area metasomatized by the slab dehydration fluid usually has high  $Sr$ ,  $Ba$  content and  $Ba/Th$  ratio ( $>170$ ) [45]. Therefore, the Yuhaixi diorite is likely derived from partial melting of the metasomatized mantle wedge (Figure 12) [31].

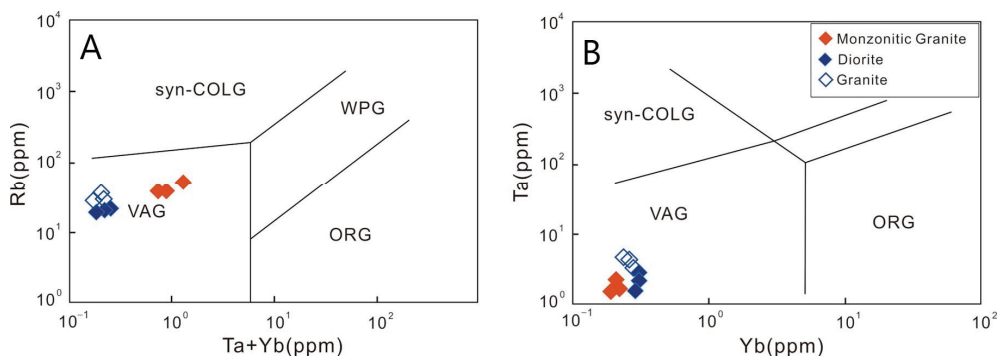


**Figure 12.** (A) Zircon  $\epsilon_{Hf}(t)$  vs. U-Pb ages ( $T$ ) diagram for the Yuhaixi intrusions. (B)  $\epsilon_{Nd}(t)$  vs.  $I_{Sr}$  diagram for the Yuhaixi intrusions.

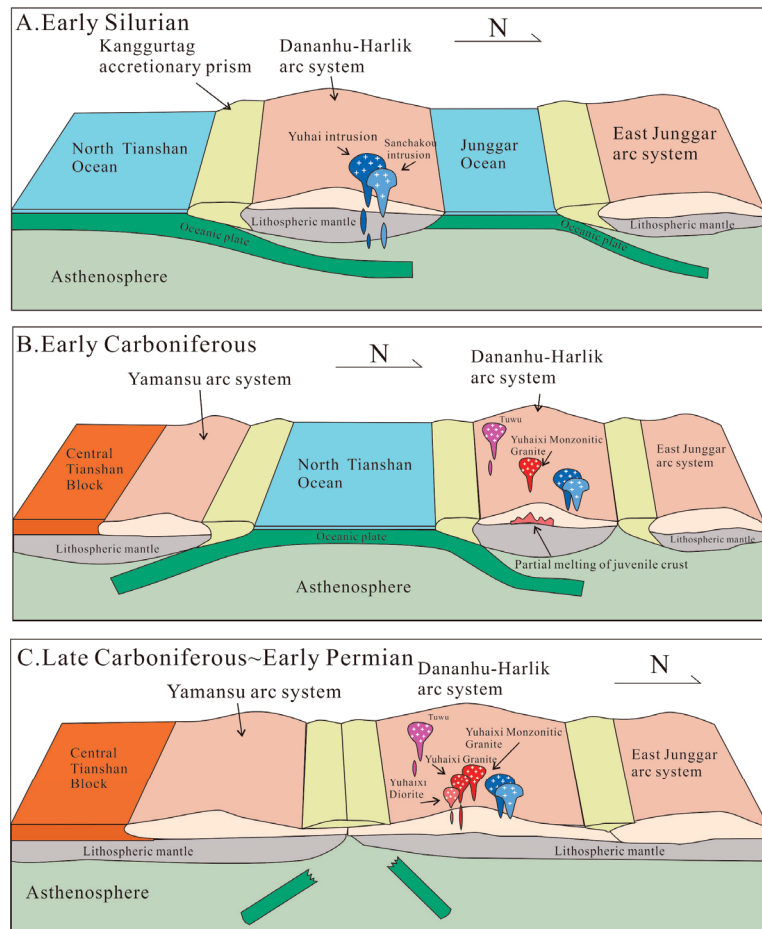
In a word, the Yuhaixi felsic intrusive rocks are high silica ( $\text{SiO}_2 > 70 \text{ wt.}\%$ ) and are characterized by high total alkali and low MgO, Cr, Ni contents and high  $\epsilon\text{Nd}(t)$  and  $\epsilon\text{Hf}(t)$  values. These characteristics suggest that their melts are mainly derived from the partial melting of the juvenile lower crust. However, the post-ore diorite has a feature of high  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$  contents with depleted isotopic signatures, indicating that diorite melts likely originated from the partial melting of depleted lithospheric mantle metasomatized by fluids or hydrous melts from the subducting slabs [5,9,12,21,23].

### 5.3. Implication for Tectonic Evolution and Porphyry Mineralization in Eastern Tianshan

The tectonic evolution of the Dananhu-Tousuquan arc belt has been widely addressed in previous studies [5,12,27–29], and a growing number of Paleozoic arc-related magmatic rocks have been reported in the Dananhu-Tousuquan island arc belt [11–16,25–30]. As reflected by the tectonic discrimination diagrams (Figure 13), Yuhaixi intrusive rocks including felsic and intermediate rocks all fall within the volcanic arc granitoid field, suggesting that they were formed in a subduction tectonic setting during Paleozoic era. Stratigraphic [29] and tectonic [30] studies indicated that the early Paleozoic Dananhu-Tousuquan island arcs were formed by the N-dipping subduction of the North Tianshan oceanic plate [5,12,27,29]. In the early Paleozoic, the partial melting of the low-angle, young subducted North Tianshan oceanic slab probably generated the Sanchakou adakite rocks (ca. 443 Ma–430 Ma; Unpublished data) (Figure 14A). The Carboniferous bipolar subduction of the North Tianshan Ocean formed the major Dananhu-Tousuquan island arc belt to the north and the Aqishan-Yamansu arc belt to the south (Figure 14B; [9,27,34–36,40]). During this period, asthenosphere upwelling triggered by the roll back or retraction of the subduction plate resulted in the partial melting of the juvenile lower crust to generate the Yuhaixi monzonitic granite (~360 Ma; Figure 14B). Meanwhile, with the emplacement of these magmas, the arc-related porphyry Mo mineralization was formed in the Dananhu-Tousuquan island arc belt (Figure 14B). The Eastern Tianshan bimodal magmatism, e.g., the Baiyanggou gabbro ( $295.8 \pm 2.8 \text{ Ma}$ ) and rhyolite ( $293 \pm 1.7 \text{ Ma}$ ) [61,62], the Cheguluquan rhyolite ( $294.5 \pm 3.6 \text{ Ma}$ ) and basalt ( $293.6 \pm 2.3 \text{ Ma}$ ) [63], and the youngest Hongshishan ophiolite in this belt (~310 Ma), suggest that the Eastern Tianshan tectonic setting was dominated by extension, which implies that the collision between the Dananhu-Tousuquan and Aqishan-Yamansu belts likely occurred during the late Carboniferous to early Permian periods [38,41]. This idea is also favored by the occurrence of diorite ( $298.0 \pm 1.8 \text{ Ma}$ ) and granite ( $307.0 \pm 2.3 \text{ Ma}$ ) in the Yuhaixi area. Moreover, many extension-related magmatic Cu–Ni sulfide deposits that occurred in the post-collisional setting were documented and reported in ca. 300–275 Ma [64], which also support the view of the collision between the Dananhu-Tousuquan and Aqishan-Yamansu belts [65–67].



**Figure 13.** Tectonic discrimination diagrams for the Yuhaixi intrusions. (A) Rb vs. Ta + Yb diagram [33]; (B) Ta vs. Yb diagram [33]. Syn-COLG = Syn-collision granites; WPG = Within plate granites; ORG = Ocean ridge granites; VAG = Volcanic arc granites.



**Figure 14.** Schematic cartoons illustrating the tectono–magmatic–metallogenic evolution model of the Yuhaixi porphyry Mo(Cu) deposit in eastern Tianshan. (A) N-dipping subduction of the North Tianshan oceanic plate gave rise to the Bogeda-Haerlike and Dananhu-Tousuquan island arcs in the early Paleozoic period. (B) Bipolar subduction of the North Tianshan oceanic plate gave rise to the Dananhu-Tousuquan and Aqishan-Yamansu arcs in the Carboniferous period, forming Yuhaixi monzonitic granite and granite. (C) The Permian period post-collisional extension forming Yuhaixi diorite.

## 6. Conclusions

- (1) Zircon LA-ICP-MS U-Pb dating suggests that the emplaced ages of the Yuhaixi monzonitic granite, diorite, and granite are  $359.4 \pm 1.6$  Ma,  $298.8 \pm 1.8$  Ma, and  $307.0 \pm 2.3$  Ma, respectively.
- (2) The Re-Os dating of molybdenite hosted by Yuhaixi monzonitic granite yields a well-constrained  $^{187}\text{Re}$ – $^{187}\text{Os}$  isochron age of  $354.1 \pm 6.8$  Ma (MSWD = 1.7).
- (3) Whole-rock geochemical characteristics and Sr-Nd-Hf isotopic compositions indicate that the Yuhaixi monzonitic granite and granite were formed via the partial melting of the juvenile crust. The post-ore diorite was formed via the partial melting of the metasomatized mantle wedge.
- (4) The eastern section of the Dananhu-Tousuquan island arc is a promising target for late Paleozoic porphyry Mo(Cu) deposits.

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## Article

# Early Permian Post-Collision Extensional Setting in the Southern Beishan Orogenic Belt: Evidence from the Zhangfangshan Granodiorite and the Baishantang Bimodal Volcanic Rocks

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**Abstract:** Outcrops of late Paleozoic magmatic rocks are common in the Southern Beishan Orogenic Belt (SBOB), Southern Central Asian Orogenic Belt (CAOB), which is a key object for the understanding of regional tectonism and defining the final closure time of the Paleo-Asian Ocean (PAO). We present zircon U-Pb chronology and whole-rock geochemistry data for late Paleozoic granodiorites and bimodal volcanic rocks from the Shuangyingshan-Huaniushan unit in the north Huitongshan-Zhangfangshan ophiolitic belt in the SBOB. The Zhangfangshan granodiorites (LA-ICP-MS, Ca. 288 Ma) are A2-type granite enriched in Rb, Th, Pb and LREEs and depleted in Nb, Ta, Ti, Sr, Ba and HREEs. They have varying MgO and <sup>T</sup>Fe<sub>2</sub>O<sub>3</sub> contents with high Mg<sup>#</sup> (38.56–48.97) values; the Lu/Yb ratios (0.14–0.15) of these granodiorites are similar to mantle-derived magma. A clear plagioclase zoning structure and acicular apatite occur in mineral assemblages derived from magma mixing between mafic and felsic magmas. The Baishantang bimodal volcanic rocks (272 Ma) consist of rhyolite and basaltic andesite. Baishantang rhyolites are A2-type felsic rock enriched in Rb, Th, Pb and LREEs and depleted in Nb, Ta, Ti, Sr, Ba and HREEs, with negative  $\epsilon_{Nd}(t)$  and  $\epsilon_{Hf}(t)$  (−5.2–−4.8 and −2.2–−1.9, respectively). Rhyolites originated from the partial melting of the crust, influenced by mantle material. Basaltic andesites belong to calc-alkaline series and have an enrichment of Rb, Ba, Th, U, Pb and LREEs, are weakly enriched in Zr-Hf, and are depleted in Nb, Ta, Ti and HREEs. The Nd-Hf isotopes of these basaltic andesites are not coupled with negative  $\epsilon_{Nd}(t)$  (−2.8–−0.4) and positive  $\epsilon_{Hf}(t)$  (1.8–5.5) values. These characteristics indicate that they originated from the partial melting of the mantle mixed with sediment-derived melts. In combination with previous studies, our findings show that the early Permian Zhangfangshan granodiorites and Baishantang bimodal volcanic rocks formed in a post-collision extensional setting, and the Huitongshan-Zhangfangshan ocean had been closed before early Permian.

**Keywords:** early Permian; post-collisional extension environment; granodiorite; bimodal volcanic rocks; Beishan Orogenic Belt

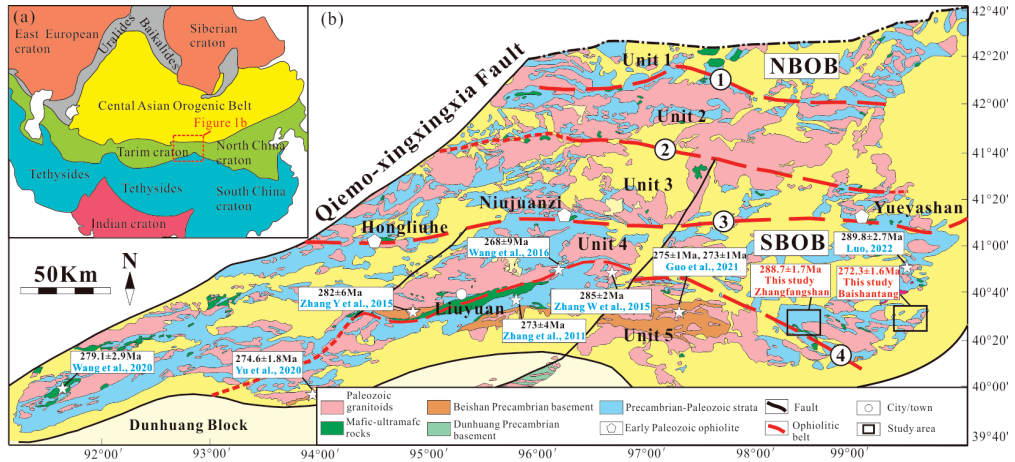
## 1. Introduction

The Central Asian Orogenic Belt (CAOB), is the largest Phanerozoic accretionary orogenic belt in the world, situated between the European, Sibrian, Tarim and North China cratons (Figure 1a) [1–5]. The CAOB evolved from the Neoproterozoic to the late Paleozoic–early Mesozoic through multiple accretion of arc/back-arc systems, ophiolites and microcontinental fragments during the closure of the Paleo-Asian Ocean (PAO) [5–8].

Voluminous magmatic and metamorphic rocks are widely exposed in CAO and associated with accretionary, intra-continental, collisional and post-collisional processes [9–14], and the reference therein. These magmatic and metamorphic rocks provide good clues for the study of the closure time of PAO and evolution process of orogenic belt.

The Beishan Orogenic Belt (BOB), located in the southern margin of the CAO, is an important part of the CAO (Figure 1). It is a key area in the study of the tectonic evolution of the southern CAO and the closure time of the PAO [15]. Four magmatic events occurred in the BOB [16]: Mesoproterozoic magmatic events representing the formation of an ancient basement in the Southern Beishan Orogenic Belt (SBOB) [17,18]; Neoproterozoic magmatism which represents the reworked ancient crust during the evolution of the Rodinia supercontinent [19,20]; Cambrian–Silurian arc magmatism related to the subduction of the Beishan ocean/PAO [21–23]; Ordovician–early late Paleozoic magmatic events correlating with the opening and closure of the branch of PAO [16,24], and the reference therein. Although a large number of late Paleozoic igneous rocks are distributed in the SBOB (Figure 1b), the formation environment of these magmatic rocks is still controversial (subduction, syn-collision or post collision) [12–14,25–30], which hampers the understanding of the final closure time of the PAO [12–14,25–30] and the tectonic evolution of the SBOB. The study of Carboniferous–Permian magmatism, especially magmatic rocks intruded into the ophiolites, provides an ideal target to investigate the late Paleozoic tectonic evolution of the SBOB and the final closure time of the PAO.

In this paper, we focus on the early Permian Zhangfangshan granodiorite intruded into the Zhangfangshan ophiolites and Baishantang bimodal volcanic rocks in the SBOB (Figure 1b) using zircon U–Pb isotopic dating, whole-rock major oxides, trace elements and Nd–Hf isotopic analysis in order to discuss their petrogenesis and the implications for the closure time of PAO and the tectonic evolution of the SBOB.



**Figure 1.** (a) Simplified tectonic map of the Central Asian Orogenic Belt showing the location of the Beishan Orogenic Belt (BOB) (modified after [31]). (b) Simplified geological map of the BOB (modified after [17]). (b) Early Permian magmatism in the SBOB (age data are taken from [13,26,32–37]). (1): Hongshishan ophiolitic belt; (2): Jijitazi–Xiaohuangshan ophiolitic belt; (3): Hongliuhe–Niujuanzi–Yueyashan ophiolitic belt; (4): Huitongshan–Zhangfangshan ophiolitic belt; Unit 1: Queershan unit; Unit 2: Heiyingshan–Hanshan unit; Unit 3: Mazongshan unit; Unit 4: Shuangyingshan–Huaniushan unit; Unit 5: Shibanshan unit.

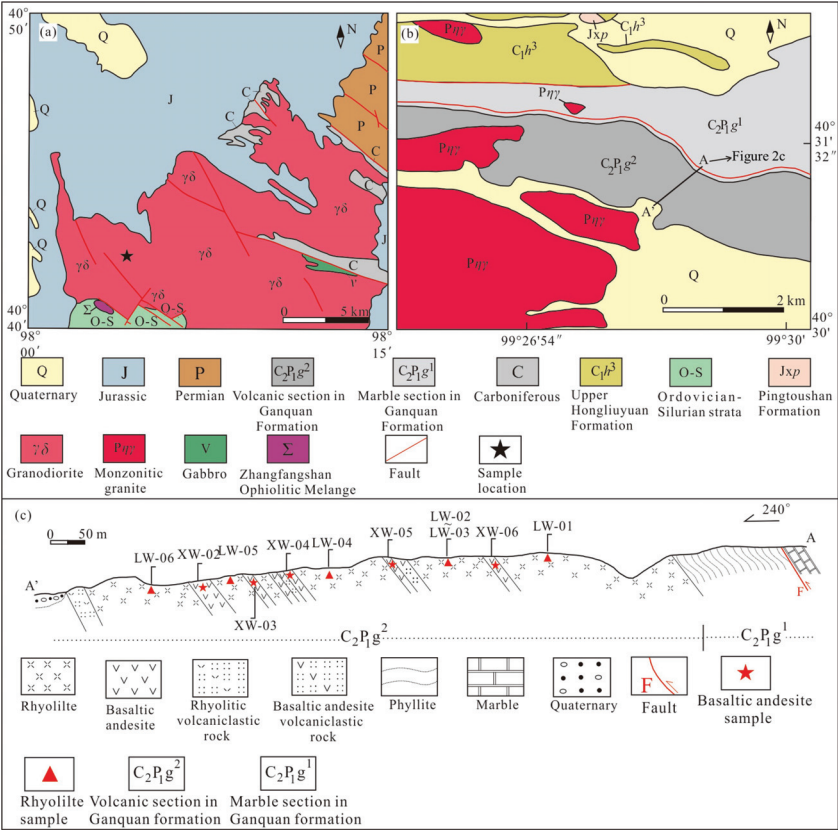
## 2. Geological Setting

The BOB is located at the southern margin of the CAO and juxtaposed against the Dunhuang block to the south [15,17,30]. From north to south, there are four important ophi-

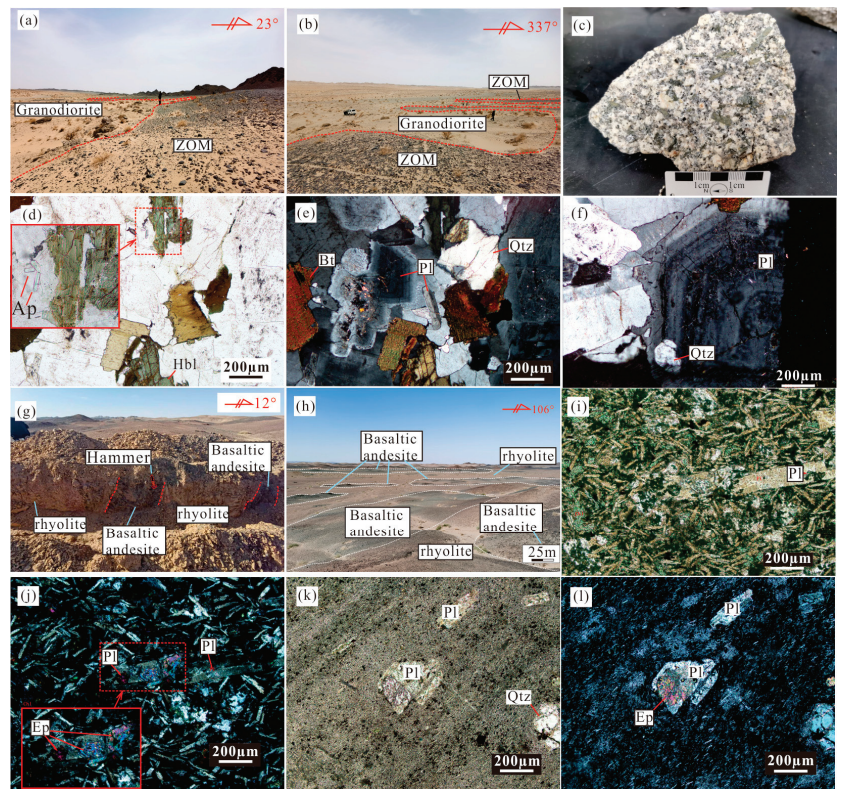
olite belts in the BOB, namely, Hongshishan, Jijitaizi-Xiaohuangshan, Hongliuhe-Niujuanzi-Yueyashan (HNY) and Huitongshan-Zhangfangshan (HZ) ophiolitic belts (Figure 1b) [30,38–41]. The BOB is sub-divided into Queershan, Heiyingshan-Hanshan, Mazongshan, Shuangyingshan-Huaniushan (SH) and Shibanshan units from north to south by these ophiolitic belts (Figure 1b) [15].

The study regions are located at the SH unit bounded by the HNY ophiolitic belt to the north and the HZ ophiolitic belt to the south. Neoproterozoic–late Paleozoic strata and intrusive rocks are widely exposed in this unit. Neoproterozoic–Cambrian strata are mainly composed of metasedimentary–sedimentary rocks [42]. Ordovician–Devonian strata are characterized by volcano–sedimentary formations. Carboniferous clastic and carbonate strata are sparsely distributed in this unit. Permian clastic and volcanic rocks are mainly exposed on the southern margin of the SH unit [43,44].

The Zhangfangshan granodiorite and the Baishantang bimodal volcanic rocks crop out in the east of the SH unit. The Zhangfangshan granodiorite is located in the north of the Zhangfangshan ophiolitic belt and west of the Baishantang area, intruded into the Ordovician–Silurian strata, ophiolites and Carboniferous strata while making unconformable contact with Jurassic strata (Figures 2a and 3a,b).



**Figure 2.** Geological maps of (a) the Zhangfangshan granodiorite and (b) the Baishantang bimodal volcanic rocks (after [45,46]); (c) profile of the Baishantang bimodal volcanic rocks.



**Figure 3.** Field photos and photomicrographs of the Zhangfangshan granodiorite and Baishantang bimodal volcanic rocks. (a,b) Zhangfangshan granodiorite intruded into Zhangfangshan ophiolitic mélange (ZOM); (c) Photo of the Zhangfangshan granodiorite sample. Hornblende can be clearly seen in the rock; (d–f) Photomicrographs of the Zhangfangshan granodiorite. Tiny acicular apatite and zonal structure of plagioclase are detected (d,f). The mineral assemblages of granodiorite (e). Quartz crystal as inclusions occur in plagioclase (f); (g,h) Field photos of the Baishantang bimodal volcanic rocks. Rhyolite and basaltic andesite are interbedded (g), and the distribution area of rhyolite is larger than that of basaltic andesite (h); (i) Plane-polarized photograph of basaltic andesite; (j) Cross-polarized photograph of basaltic andesite, where epidotization occurs in plagioclase; (k) Plane-polarized photograph of rhyolite; (l) Cross-polarized photograph of rhyolite, where epidotization occurs in plagioclase. Ap: apatite; Hbl: hornblende; Bt: biotite; Pl: plagioclase; Qtz: quartz; Chl: chlorite; Ep: Epidote.

The Baishantang bimodal volcanic rocks are exposed in the volcanic section in Ganquan Formation. The Ganquan Formation is exposed in the south of the Hongliuyuan Formation and separated from it by faults (Figure 2b). The Ganquan Formation can be divided into marble and volcanic sections. The marble section is mainly composed of marble with rhyolite, phyllite, mica quartz schist and metabasaltic and is separated from the volcanic section by a fault to the south. The volcanic section is mainly composed of rhyolite and basaltic andesite, with a small amount of rhyolitic and basaltic andesite pyroclastic rocks. Rhyolites have larger distribution areas than the basaltic andesites, and they are interbedded to form bimodal volcanic rocks (Figures 2c and 3g,h). Due to intense weathering, only few complete rhyolite and basaltic andesite outcrops can be seen in the study area.



### 3. Sample Description

#### 3.1. Zhangfangshan Granodiorite

The granodiorite is grayish white, medium- to coarse-grained and massive structure. Its mineral composition includes plagioclase (40~45 vol%), quartz (35~40 vol%), biotite (10~15 vol%) and hornblende (5~10 vol%). Accessory minerals include apatite, zircon and others (Figure 3d–f). One sample was collected for zircon U–Pb dating, and six samples were collected for the whole-rock major oxides and trace elements study.

#### 3.2. Baishantang Bimodal Volcanic Rocks

The rhyolite is light red to light pink in color, massive and porphyritic in texture, with up to 20 vol% phenocrysts, mainly comprising plagioclase and a minor amount of quartz (Figure 3k,l). The directional arrangement of phenocrysts can be observed in Figure 3k,l. The groundmass is usually a fine-grained assemblage of feldspar, quartz and minor Fe–Ti oxides. Plagioclase has a certain degree of kaolinization and epidotization.

The basaltic andesite is dark grey with a typical porphyritic texture (Figure 3i,j). The phenocrysts are mainly plagioclase (~15 vol%), while the matrix consists of plagioclase microcrystals and accessory minerals. Plagioclase has a certain degree of kaolinization and epidotization. One rhyolite was collected for zircon U–Pb dating; six rhyolite samples and five basaltic andesite samples were collected for whole-rock major oxides and trace elements study. Three rhyolite samples and three basaltic andesite samples were collected for the whole rock Nd–Hf isotopes analysis.

### 4. Analytical Methods

#### 4.1. Zircon U–Pb Dating

Zircon cathodoluminescence (CL) images of the Zhangfangshan granodiorite and the Baishantang rhyolite were taken at the Key Laboratory of Mineral Resources of Western China, Lanzhou University, Lanzhou, China, and Langfang Chenxin Geological Service Co., Hebei, China, respectively. After separation using the conventional heavy liquid and magnetic techniques, zircon grains were purified through hand-picking under a binocular microscope, embedded in an epoxy and then polished to expose half of the zircon grains [47]. The zircon grains with internal ring structures, no clear inclusions and few fractures in the CL were chosen for U–Pb dating. Zircon LA–ICP–MS U–Pb isotope analyses were performed at the Key Laboratory of Mineral Resources of Western China, Lanzhou University, using ICP–MS Agilent 7500a (Agilent, Santa Clara, CA, USA). The zircon standard 91500 [48] was used as the age reference. The glass NIST 610 and Si were used as an internal standard for Pb, Th and U [49]. The Glitter (ver. 4.0) [50] and Isoplot R [51] programs were employed to process the data. The analytical procedures are described in detail by Yuan et al. [52].

#### 4.2. Whole-Rock Major Oxides and Trace Elements Analyses

All analyses of major oxides and trace elements for the Zhangfangshan granodiorite and Baishantang bimodal volcanic rocks were carried out at the Key Laboratory of Mineral Resources of Western China, Lanzhou University. Major oxides were determined through ICP optical emission spectroscopy (ICP–OES) (manufactured by Agilent, Santa Clara, CA, USA) using a Leeman Prodigy system with analytical precision greater than 2%. Loss on ignition (LOI) was obtained by heating approximately 0.5 g of the dried-sample powder at 1000 °C for 2 h. Trace elements were determined through inductively coupled plasma mass spectrometry (ICP–MS) using an Agilent 7700× system. The relative standard deviation was less than 10% for the determination of trace elements, including rare earth elements (REEs). The US Geological Survey reference materials AGV-2 and BCR-2 were used as standards. Analytical procedures of major oxides and trace elements have been described by Li et al. [53] and Gao et al. [54], respectively.

4.3. Whole-Rock Nd-Hf Isotope Analyses

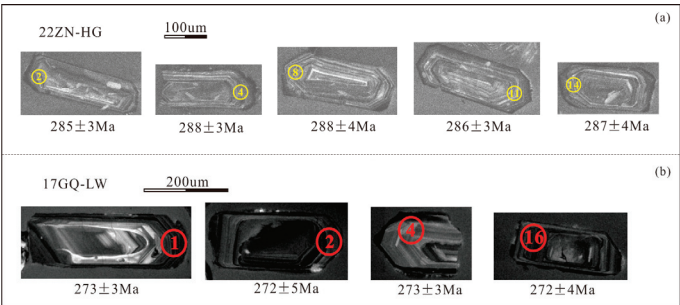
Sm-Nd and Lu-Hf isotopic analyses were performed on Nu Instruments Nu Plasma II MC-ICP-MS (Nu Instrument, Wrexham, Wales, UK) at the Key Laboratory of Mineral Resources of Western China, Lanzhou University. The US Geological Survey reference materials BCR-2 and AGV-2 were used as standards. JNDI and Alfa Hf standard solution were periodically analyzed to correct instrumental drift. Mass fractionation corrections for Nd and Hf isotopic ratios were based on 0.7219 for  $^{146}\text{Nd}/^{144}\text{Nd}$  and 0.7325 for  $^{179}\text{Hf}/^{177}\text{Hf}$ , respectively. Standard BCR-2 yielded average values of  $0.512642 \pm 0.00003$  ( $2\sigma$ ,  $n = 5$ ) for  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $0.282871 \pm 0.00004$  ( $2\sigma$ ,  $n = 2$ ) for  $^{176}\text{Hf}/^{177}\text{Hf}$ . Standard AGV-2 yielded  $0.512742 \pm 0.00003$  ( $2\sigma$ ,  $n = 5$ ) for  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $0.282950 \pm 0.00004$  ( $2\sigma$ ,  $n = 1$ ) for  $^{176}\text{Hf}/^{177}\text{Hf}$ . Analytical procedures were described by Bao et al. [55].

5. Analytical Results

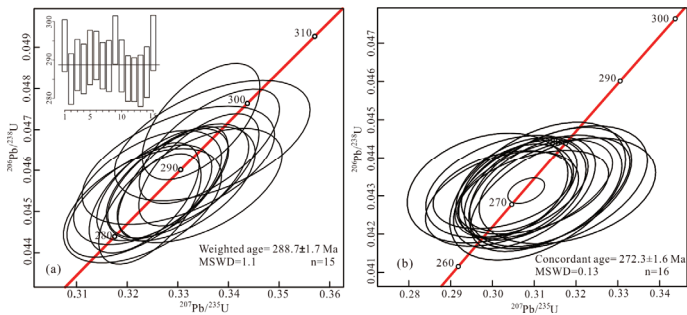
The zircon U-Pb isotopic data, whole-rock major oxides, trace element data and Nd-Hf isotopic data are listed in Supplementary Table S1, Table S2 and Table S3, respectively.

5.1. Zircon U-Pb Geochronology

Fifteen zircons from the granodiorite samples are euhedral to subhedral and columnar in shape, with length-to-width ratios of 2:1~3:1. The zircons display well-preserved concentric oscillatory zoning (Figure 4a) and high Th/U ratios (0.44~0.65) (Table S1), indicating a typical magmatic origin [56]. All fifteen analyses yielded similar apparent  $^{206}\text{Pb}/^{238}\text{U}$  ages of 297~284 Ma, with a weighted mean age of  $288.7 \pm 1.7$  Ma (MSWD = 1.1,  $n = 15$ ) (Figure 5a).



**Figure 4.** Representative zircons cathodoluminescence images for zircons in the Zhangfangshan granodiorite (a) and the Baishantang rhyolite (b). Yellow and red numbers represent the U-Pb analytical sites of the Zhangfangshan granodiorite and the Baishantang rhyolite, respectively.



**Figure 5.** U-Pb dating results of zircons for the Zhangfangshan granodiorite (a) and the Baishantang rhyolite (b).

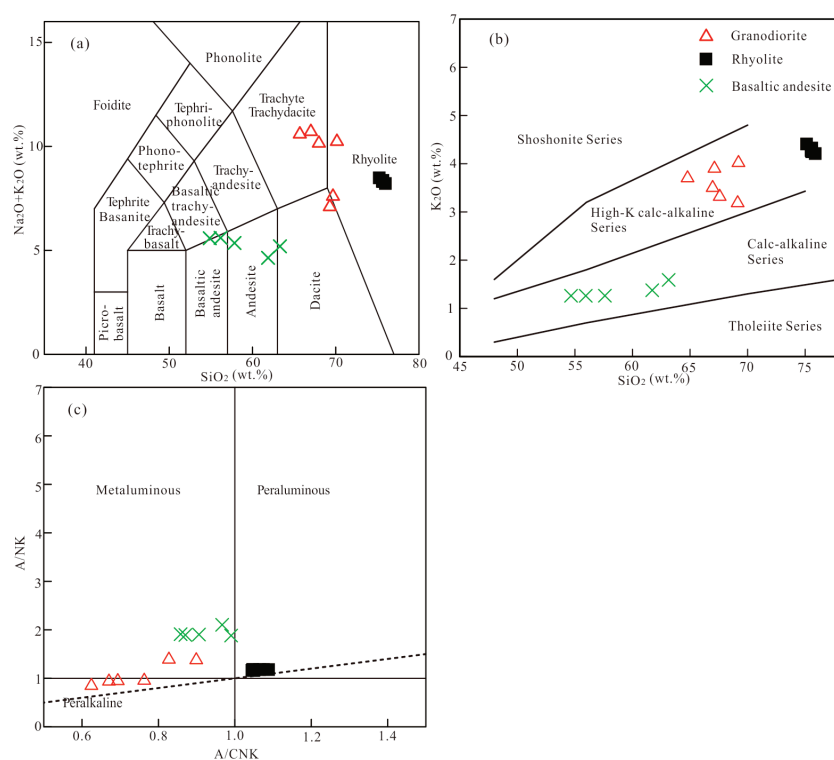


Eighteen zircons from the Baishantang rhyolite are euhedral to subhedral and display well-preserved concentric oscillatory zoning (Figure 4b). Their Th/U ratios are 0.46–1.30 (Table S1), indicating a typical magmatic origin. Sixteen analyses yield close apparent  $^{206}\text{Pb}/^{238}\text{U}$  ages of 271–273 Ma and a concordant age of  $272.3 \pm 1.6$  Ma (MSWD = 0.13,  $n = 16$ ) (Figure 5b). The other two analyses yield old  $^{206}\text{Pb}/^{238}\text{U}$  ages (both of GQ-LW-03 and GQ-LW-07 are 395 Ma) (Table S1).

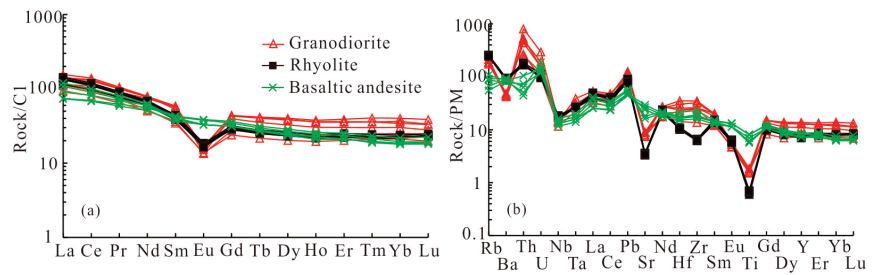
## 5.2. Whole-Rock Major Oxides and Trace Elements

### 5.2.1. The Zhangfangshan Granodiorite

The composition of major oxides is as follows:  $\text{SiO}_2$  (64.78–69.21 wt.%),  $\text{Al}_2\text{O}_3$  (13.55–14.58 wt.%),  $^{\text{T}}\text{Fe}_2\text{O}_3$  (2.04–3.47 wt.%),  $\text{MgO}$  (0.65–1.68 wt.%),  $\text{Na}_2\text{O}$  (3.92–7.22 wt.%),  $\text{K}_2\text{O}$  (3.20–4.03 wt.%) and  $\text{TiO}_2$  (0.33–0.40 wt.%). The  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  values are 7.12–10.74 wt.%,  $\text{Mg}^\#$  values are 38.56–48.97 and A/CNK ratios are less than 1 (0.62–0.90). The samples' plots are in the granite field and are high-K calc-alkaline series and metaluminous (Figure 6). Chondrite-normalized REE patterns of Zhangfangshan granodiorites (Figure 7a) show a weakly fractionated REE pattern ( $(\text{La}/\text{Yb})_{\text{N}} = 3.39\text{--}5.27$ ), enrichments of LREEs ( $\text{LREE}/\text{HREE} = 4.08\text{--}6.14$ ) and negative Eu anomalies ( $\delta\text{Eu} = 0.27\text{--}0.48$ ). Primitive mantle-normalized trace elements' patterns (Figure 7b) show enrichments of Rb, Th and Pb; weak enrichments of Zr and Hf; and a depletion of Nb, Ta, Ti, Sr and Ba.



**Figure 6.** Geochemical classification diagrams for the Zhangfangshan granodiorites and Baishantang bimodal volcanic rocks. (a) TAS diagram [57], (b)  $\text{K}_2\text{O}$  versus  $\text{SiO}_2$  diagram [58], (c) A/NK versus A/CNK diagram [59].



**Figure 7.** Chondrite (C1)-normalized REE patterns (a) and Primitive Mantle (PM)-normalized multi-element diagrams (b) for the Zhangfangshan granodiorites and Baishantang bimodal volcanic rocks. C1 and PM values are from Sun and McDonough [60].

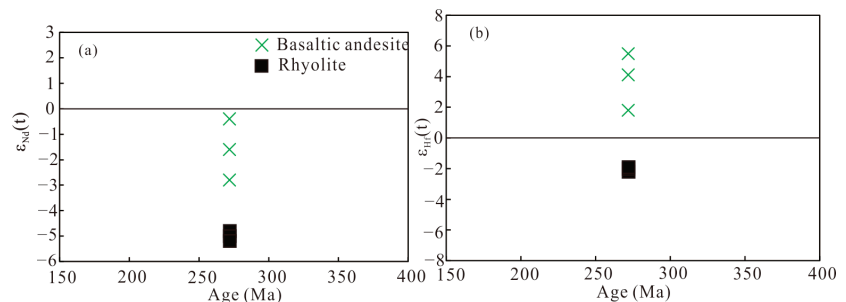
### 5.2.2. Baishantang Bimodal Volcanic Rocks

Baishantang rhyolites have high  $\text{SiO}_2$  (75.12–75.87 wt.%),  $\text{Na}_2\text{O}$  (4.00–4.07 wt.%),  $\text{K}_2\text{O}$  (4.21–4.41 wt.%) and  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  (8.21–8.48 wt.%) contents; moderate  $\text{Al}_2\text{O}_3$  (13.14–13.53 wt.%) contents; and low  $^{\text{T}}\text{Fe}_2\text{O}_3$  (1.41–1.74 wt.%),  $\text{MgO}$  (0.26–0.37 wt.%) and  $\text{TiO}_2$  (0.13–0.14 wt.%) contents; their  $\text{Mg}^\#$  values are 23.72–33.58. In the TAS diagram (Figure 6a), all samples are plotted in the rhyolite field in the TAS diagram (Figure 6a) and belong to the high-K calc-alkaline series in the  $\text{K}_2\text{O}$ - $\text{SiO}_2$  diagram (Figure 6b). The A/CNK ratios of all rhyolites are 1.04–1.09 and plotted in the peraluminous (Figure 6c). Rhyolite samples display LREE-enriched REE patterns ( $(\text{La}/\text{Yb})_{\text{N}} = 5.18\text{--}6.28$ ,  $\text{LREEs}/\text{HREEs} = 5.71\text{--}6.55$ ) and have obvious negative Eu anomalies ( $\delta\text{Eu} = 0.48\text{--}0.52$ ) (Figure 7a). They are enriched in Rb, Th and Pb; depleted in HREEs and Ba, Nb, Ta, Ti and Sr; and weakly depleted in Zr and Hf (Figure 7b).

Baishantang basaltic andesites have moderate  $\text{SiO}_2$  (54.66–63.14 wt.%) contents; high  $\text{Al}_2\text{O}_3$  (14.36–16.13 wt.%),  $\text{MgO}$  (3.47–4.26 wt.%),  $\text{Na}_2\text{O}$  (3.25–4.32 wt.%),  $^{\text{T}}\text{Fe}_2\text{O}_3$  (7.97–10.71 wt.%) and  $\text{TiO}_2$  (1.28–1.87 wt.%) contents; and low  $\text{P}_2\text{O}_5$  (0.40–0.55 wt.%) and  $\text{K}_2\text{O}$  (1.26–1.59 wt.%) contents. The  $\text{Mg}^\#$  values are 44.08–46.30, and the  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  values are 4.63–5.58 wt.%. The samples belong to calc-alkaline series (Figure 6b). Basaltic andesite samples display LREE-enriched REE patterns ( $(\text{La}/\text{Yb})_{\text{N}} = 3.85\text{--}6.49$ ,  $\text{LREEs}/\text{HREEs} = 4.09\text{--}6.06$ ) and have no obvious negative Eu anomalies ( $\delta\text{Eu} = 0.92\text{--}0.99$ ) (Figure 7a). They are enriched in Rb, Ba, Th, U and Pb; weakly enriched in Zr and Hf; and depleted in Nb, Ta and Ti (Figure 7b).

### 5.3. Whole-Rock Nd-Hf Isotope of the Baishantang Bimodal Volcanic Rocks

Whole-rock Nd-Hf isotopic compositions of Baishantang rocks are plotted in Figure 8. The initial Nd and Hf isotope ratios were calculated using the zircon U-Pb ages (272 Ma). The  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios of 0.282674–0.282682 and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of 0.512252–0.512264 were measured for three rhyolite samples, which correspond to initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios of 0.282542–0.282549 and initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of 0.512023–0.512041. They had negative  $\varepsilon_{\text{Hf}}(\text{t})$  (−2.2–−1.9) and  $\varepsilon_{\text{Nd}}(\text{t})$  (−5.2–−4.8) values, with two-stage Hf and Nd model ages ( $T_{\text{DM}2}$ ) between 1427–1411 Ma and 1460–1433 Ma, respectively. The  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios of 0.282721–0.282831 and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of 0.512381–0.512522 were measured for three basaltic andesite samples, which correspond to initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios of 0.282655–0.282760 and initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of 0.512146–0.512205. Basaltic andesites have a negative  $\varepsilon_{\text{Nd}}(\text{t})$  (−2.8–−0.4) but positive  $\varepsilon_{\text{Hf}}(\text{t})$  (1.8–5.5).



**Figure 8.** (a)  $\epsilon_{Nd}(t)$  values of the Baishantang bimodal volcanic rocks; (b)  $\epsilon_{Hf}(t)$  values of the Baishantang bimodal volcanic rocks.

## 6. Discussion

### 6.1. Early Permian Magmatism in the SBOB

In this research, we studied granodiorite and obtained new zircon U-Pb ages of  $288.7 \pm 1.7$  Ma. Zircon grains from this pluton are euhedral-subhedral with clear concentric oscillatory patterns, without overgrowth rim and inherited cores (Figure 4a). Meanwhile, these zircons have relatively high Th/U ratios (0.44–0.65), indicative of a magmatic origin. In the field, the Zhangfangshan granodiorite intruded the Zhangfangshan ophiolite (362 Ma) [61], suggesting that the Zhangfangshan granodiorite was formed in the early Permian.

The Baishantang basaltic andesite and rhyolite are spatially associated with each other, and their  $\text{SiO}_2$  contents have obvious discontinuity, which clearly suggests that they are likely coeval and, thus, constitute a bimodal volcanic suit. The timing of the Baishantang bimodal volcanic magmatism can be determined by the eruption age of the rhyolite [62]. The basaltic andesite and rhyolite outcrops are in the volcanic section of the Ganquan Formation. The Ganquan Formation is widely distributed in the SBOB and consists of marble and volcanic sections. Through studies, it has been determined that the Ganquan Formation is in contact with the Upper Carboniferous Shibanshan and Lower Permian Shuangbaotang Formations [63]. The fossils in the marble section and the zircon U-Pb isotopic age in the volcanic section indicate that the Ganquan Formation was formed in the late Carboniferous–early Permian while the volcanic section was formed in the early Permian [63]. All the dated zircons in this study exhibit well-developed zoning and have relatively high Th/U ratios (0.46–1.30), indicative of a magmatic origin. Sixteen analyses yielded a concordant age of  $272.3 \pm 1.6$  Ma; this result is consistent with the previous study and is interpreted as the crystallization age of the Baishantang rhyolite.  $^{206}\text{Pb}/^{207}\text{Pb}$  ages of 395 Ma are yielded by GQ-LW-3 and GQ-LW-7, clearly older than other ages, and represent the captured zircon ages. Therefore, the Baishantang bimodal volcanic rocks were formed in early Permian.

There are other early Permian magmatisms in the SBOB. Granitic plutons with an age of 290–270 Ma were reported in the Shuwojing, Western Shuwojing, Bandaoshan, Wohushan, Liuyuan and Yinwaxia, including syenogranite, biotite monzogranite, biotite granite, monzogranite and granodiorite [13,27,33,35]. Meanwhile, the ultramafic-mafic rocks and mafic-felsic dykes are also widely distributed in the SBOB, such as Podong, Cihai, Yitiaoshan, Gubaoquan, Yinwaxia and Niujuanzi [26,31,32,34,64–66]. These mafic-felsic rocks, combined with the Zhangfangshan granodiorite and the Baishantang bimodal volcanic rocks studied in this paper, indicate that the early Permian magmatic activities are widespread in the SBOB.

## 6.2. Petrogenesis

### 6.2.1. The Zhangfangshan Granodiorite

Generally, granites are categorized into I-, S-, A- and M-type granite based on geochemical and mineralogical features [67–69]. Early Permian granodiorites (Ca. 288 Ma) have high  $K_2O$  contents (3.20–4.03 wt.%), unlike M-type granites with low  $K_2O$  contents (<1 wt.%). Zhangfangshan granodiorites are metaluminous ( $A/CNK < 1.1$ ), and Al-bearing minerals are lacking (e.g., garnet and andalusite), indicating that Zhangfangshan granodiorites are not S-type granites. Therefore, the Zhangfangshan granodiorites are I- or A-type granites. All granodiorite samples display high  $K_2O + Na_2O$  (7.12–10.74 wt.%) and  $FeO_t$  contents (2.04–3.47 wt.%), low Rb contents (109.56–134.60 ppm), high  $10,000 \times Ga/Al$  (2.8–3.3) and  $Zr + Nb + Ce + Y$  (368.17–544.83 ppm) values, demonstrating that the Zhangfangshan granodiorites show an affinity to A-type granites [69–74]. In the discrimination diagrams for I-S-A-type granite by Whalen et al. [70] (Figure 9a,b), all samples are plotted in the A-type granite field rather than the I and S-type field. A high calculated zircon saturation temperature is the most typical feature of A-type granite [59,75]. The calculated zircon saturation temperatures of Zhangfangshan granodiorite samples are 895–1004 °C [76], higher than the average temperatures of A- and I-type granites (Figure 9c). In summary, the studied granodiorites can be regarded as A-type granites. Based on different geochemical characteristics, A-type granites can be further divided into A1- and A2-type granites [77]. All samples have high Y/Nb (3.47–5.99), Rb/Nb (10.73–14.51) and Ce/Nb (5.99–8.36) ratios and are plotted within the A2 field in the Nb-Y-Ce diagram (Figure 9d). In conclusion, Zhangfangshan granodiorites are defined as A2-type granites.

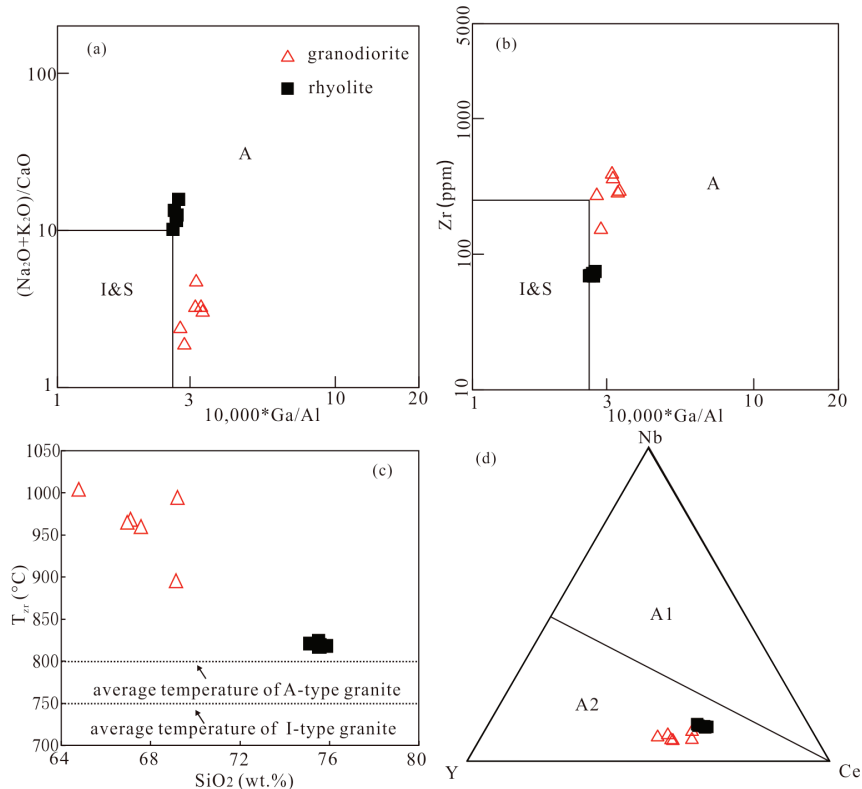
Various models have been proposed to illustrate the formation of A-type granites, including the fractionation-crystallization process of mantle-derived alkaline magma [78,79], magma mixing between mafic and felsic magma, and partial melting of the lower continental crust caused by mantle magma underplating [71].

The Zhangfangshan granodiorites have high  $SiO_2$  (64.78–69.21 wt.%) and  $K_2O$  (3.20–4.03 wt.%) contents, are enriched in LREEs and have a depletion of HFSEs as well as having negative Sr and Ti anomalies, indicating that the rocks are difficult to be formed by a high differentiation of mantle-derived magma [71]. The Y/Ho ratios (28.40–30.45) of granodiorites are close to those of chondrite (28), and the Zr/Hf ratios (34.7–38.9) of the samples belong to “CHARAC field (Zr/Hf ratios of 26–46)” [71], indicating that the fractional crystallization is limited. Meanwhile, if the felsic rocks were derived from the fractional crystallization of basaltic magma, voluminous mafic rocks should be exposed in the area [80]. However, there are no coeval intermediate-basic rocks exposed in the region. In conclusion, the Zhangfangshan granodiorites were not formed by the fractional crystallization of mantle-derived magmas.

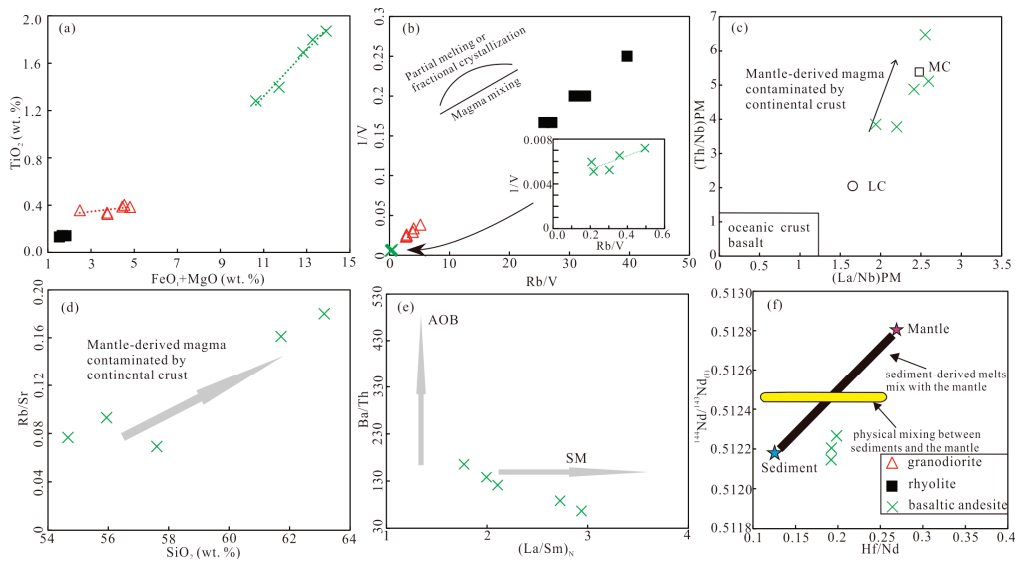
The Ce/Pb (2.56–4.53) and La/Nb (2.60–3.61) values of granodiorites were found to be close to those of the crust ( $Ce/Pb < 15$ ,  $La/Nb = 2.2$ ) [81], indicating that the granodiorite had crustal affinity. However, samples also have high MgO contents and  $Mg^\#$  values (>40, average 46.58), including  $Na_2O$  contents greater than or close to those of  $K_2O$ . These features are different from those of melts formed by the partial melting of the basaltic lower crust. Meanwhile, the Lu/Yb ratios (0.14–0.15) of these samples are similar to the ratio of the mantle-derived magma (0.15), suggesting a contribution from the mantle. Zhangfangshan granodiorite formation is not solely derived from the partial melting of the lower crust, and the addition of high-Mg mantle-derived mafic magma is required. Due to the strong Quaternary cover, no mafic enclaves have been found in the Zhangfangshan pluton, but we can still find evidence of magma mixing: (a) the obvious zonal structure of plagioclase, the existence of acicular apatite, and the presence of felsic inclusion in plagioclase crystals. These petrological features are special mineral phenomena in rocks formed from magma mixing [82]. (b) Previous studies have suggested that increasing Fe + Mg contents would be expected due to the basification of relatively felsic magma [71]. Zhangfangshan granodiorites display a positive correlation of  $FeO_t + MgO$  with  $TiO_2$  (Figure 10a). The samples also have variations in MgO and  $TFe_2O_3$  contents, which favors

magma mixing between mantle-derived mafic magma and crust-derived felsic melts [71,83]. (c) The Zhangfangshan granodiorite samples show magma-mixing trends in the 1/V-Rb/V diagram (Figure 10b). Therefore, potential magma mixing may occur in the Zhanfangshan granodiorite formation process.

Granodiorites have the characteristics of depletions of Ba, Eu, Sr, Ti, Nb and Ta and an obvious plagioclase ring structure, which indicate the crystallization differentiation of the granodiorite and fractionation of plagioclase and Ti-bearing phases.



**Figure 9.** (a)  $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{CaO}$  and (b) Zr vs.  $10,000 \cdot \text{Ga}/\text{Al}$  diagram [79]; (c)  $T_{\text{Zr}}$  (°C) vs.  $\text{SiO}_2$  diagram; (d) Nb-Y-Ce diagram [77]. I: I-type felsic rock; S: S-type felsic rock; A: A-type felsic rock; A1: A1-type felsic rock; A2: A2-type felsic rock;  $T_{\text{Zr}}$  (°C): zircon saturation temperature; average temperature of A and I-type granite after [73,84].



**Figure 10.** (a)  $\text{TiO}_2$  vs.  $\text{FeO}_t + \text{MgO}$  diagram [82]; (b)  $1/V$  vs.  $\text{Rb}/V$  diagram [85]; (c)  $(\text{Th}/\text{Nb})_{\text{PM}}$  vs.  $(\text{La}/\text{Nb})_{\text{PM}}$  diagram [86]; (d)  $\text{Rb}/\text{Sr}$  vs.  $\text{SiO}_2$  diagram [87]; (e)  $\text{Ba}/\text{Th}$  vs.  $(\text{La}/\text{Sm})_{\text{N}}$  diagram [88]; (f)  $^{144}\text{Nd}/^{143}\text{Nd}$  vs.  $\text{Hf}/\text{Nd}$  diagram [88]. C: crust; M: mantle; Cm: crust-mantle mixed; LC: lower crust; MC: middle crust; AOB: altered oceanic basalt; SM: sediment metasomatism.

### 6.2.2. The Baishantang Bimodal Volcanic Rocks

The Baishantang rhyolites have the characteristics of being weakly peraluminous ( $A/\text{CNK}$  are 1.04–1.09) and having no aluminum-rich minerals, indicating that the rhyolites are I- or A-type granites rather than S-type granites. Further, characteristics such as high  $10,000 \times \text{Ga}/\text{Al}$  and  $\text{FeO}_t/\text{MgO}$  values (2.60–2.73 and 3.53–5.73); low contents of  $\text{MgO}$  (0.26–0.37 wt.%) and  $\text{CaO}$  (0.53–0.82 wt.%); enrichment of  $\text{Rb}$ ,  $\text{Th}$  and  $\text{Pb}$ ; and depletion of  $\text{Nb}$ ,  $\text{Ta}$ ,  $\text{Ti}$ ,  $\text{Sr}$  and  $\text{Ba}$  pertain to an A-type signature. Although the  $\text{Zr} + \text{Nb} + \text{Ce} + \text{Y}$  values (173.40–356.60 ppm and most of them are less than 350 ppm) are different from values of typical A-type granite ( $\text{Zr} + \text{Nb} + \text{Ce} + \text{Y} > 350$  ppm), Baishantang rhyolites also have low  $\text{Rb}$  contents (154.00–163.50 ppm), high  $\text{FeO}_t$  contents (1.27–1.57 wt.%) and zircon saturation temperatures (817–824 °C) (Figure 9c), which are different from I-type but similar to A-type felsic rocks. Meanwhile, the almost constant  $\text{Rb}/\text{Sr}$  values of rhyolites (2.13–2.26) show that the Baishantang rhyolites do not belong to highly fractionated felsic rock [89]. In the discrimination diagrams of I-S-A-type granite (Figure 9a,b), all samples are plotted in the A-type field. Therefore, Baishantang rhyolites are A-type felsic rocks. All of these samples have relatively high  $\text{Y}/\text{Nb}$  (2.58–2.69),  $\text{Ce}/\text{Nb}$  (4.87–5.59) and  $\text{Rb}/\text{Nb}$  (11.88–13.69) ratios [71], plotting into the A2 field in the  $\text{Nb}$ - $\text{Y}$ - $\text{Ce}$  diagram (Figure 9d). In conclusion, the Baishantang rhyolites are defined as A2-type felsic rocks.

As A2-type felsic rocks, the Baishantang rhyolites have high  $\text{SiO}_2$  and  $\text{K}_2\text{O}$  contents, have low  $\text{MgO}$  contents and  $\text{Mg}^\#$  values, are enriched in LREEs, and are depleted in HFSEs,  $\text{Sr}$  and  $\text{P}$ . These characteristics indicate that rhyolites are difficult to form through the high differentiation of mantle-derived magma. The  $\text{Y}/\text{Ho}$  ratios (25.51–26.69) of the samples are close to those of chondrite, indicating that their fractional crystallization is limited [71]. Meanwhile, the exposed area of the rhyolite is much larger than that of the basaltic andesite. Therefore, the Baishantang rhyolite is probably derived from the partial melting of crustal or magma mixing rather than the crystallization differentiation of mantle-derived magma. A-type felsic rocks formed through magma mixing between crust- and mantle-derived magma generally exhibit a wide range of geochemical and



isotopic compositions [83]. However, the samples have stable and high  $\text{SiO}_2$  contents and low  $\text{MgO}$  contents and  $\text{Mg}^\#$  values; the Cr (1.00–8.00 ppm) and Ni (1.20–4.40 ppm) contents are also obviously lower than those of mantle-derived magma (Cr = 300–500 ppm, Ni = 300–400 ppm) [60]. These features illustrate that the Baishantang rhyolite could not be formed through magma mixing. Although the samples show a positive correlation in the  $1/\text{V-Rb}/\text{V}$  diagram (Figure 10b), the rhyolites have homogeneous and negative  $\epsilon_{\text{Nd}}(t)$  and  $\epsilon_{\text{Hf}}(t)$  values (Figure 8), and no special mineral phenomenon can be observed in the photomicrographs, implying that magma mixing is not the genesis of the rhyolites. The Ce/Pb (4.01–4.99), Lu/Yb (0.15–0.16), Nd/Th (1.94–2.14) and Nb/U (5.46–6.30) ratios of Baishantang rhyolites are different from those of mantle-derived magma but close to the average ratios of the crust (Ce/Pb < 15,  $0.16 < \text{Lu/Yb} < 0.18$ , Nd/Th = 3, Nb/U = 9.7) [60,81], indicating that the rhyolite has crustal affinity. The Baishantang rhyolites have negative  $\epsilon_{\text{Nd}}(t)$  and  $\epsilon_{\text{Hf}}(t)$  values, and the two-stage model ages ( $T_{\text{DM2}}$ ) of Nd and Hf are 1460–1433 Ma and 1411–1427 Ma, which are larger than the crystallization age of rhyolites. Studies have shown that if the  $\epsilon_{\text{Nd}}(t)$  ( $\epsilon_{\text{Hf}}(t)$ ) of intermediate-felsic rocks is negative, and the two-stage model age is much larger than its crystallization age, then the rocks originated from the partial melting of ancient crust, and the zircon age represents the reconstruction time of the crust [90–92]. There are Mesoproterozoic crustal materials in the SBOB, such as the Jiujing biotite plagioclase gneiss ( $1408 \pm 4$  Ma) [18] and the Gubaoquan paragneiss (detrital zircon age  $\sim 1.4$  Ga) [93]. The two-stage model ages of the rhyolites are consistent with the previous results, suggesting that the Baishantang rhyolite is related to the partial melting of ancient continental crust [94]. The rhyolite samples show depletions in Eu, Ba, Nb, Ta, Sr and Ti, which could be due to the fractionation of plagioclase and Ti-bearing phases [26].

The Baishantang basaltic andesite has high contents of  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ , has low contents of  $\text{P}_2\text{O}_5$  and  $\text{K}_2\text{O}$ , and belongs to the calc-alkaline series (Figure 6b). These high  $\text{Mg}^\#$  values (44.08–46.30) are in contrast to the magma produced through partial melting of the basic lower crust (in which the  $\text{Mg}^\#$  value is lower than 45). The Lu/Yb ratios (0.15) are similar to the mantle value (Lu/Yb = 0.15) [60], indicating the mantle's origin. However, these rocks display low Ce/Pb ratios (4.51–8.75) and Nd/Th ratios (3.33–6.95), which are close to the values of the continental crust (Ce/Pb < 15, Nd/Th  $\approx 3$ ) [95], and they are depleted in HFSEs (Nb, Ta, Ti) while being enriched in LILEs (Rb, Ba, Th, U and Pb), implying the influence of crustal material on magma. The Nb/Ta and high (Th/Nb) $_{\text{PM}}$  ratios are considered to be important parameters for crustal contamination [96,97]. The (Th/Nb) $_{\text{PM}}$  values of these samples are 3.78–6.47, larger than 1 [98], and the Nb/Ta values (14.15–14.56) for basaltic andesites are between those of the mantle ( $17.5 \pm 2.5$ ) and the crust (11.4) [60,92]. Meanwhile, all basaltic andesites have extremely heterogeneous isotopic signatures (Figure 8) and are plotted along the mantle-derived magma contaminated by the continental crust trend as shown in the (La/Nb) $_{\text{PM}}$ –(Th/Nb) $_{\text{PM}}$  and Rb/Sr– $\text{SiO}_2$  diagrams (Figure 10c,d). All these features indicate that the magmas were modified by crustal materials during magma emplacement. Baishantang basaltic andesites have negative  $\epsilon_{\text{Nd}}(t)$  but positive  $\epsilon_{\text{Hf}}(t)$  values, which seems to indicate an opposite mantle source region (enriched mantle for  $\epsilon_{\text{Nd}}(t)$  but depleted mantle for  $\epsilon_{\text{Hf}}(t)$ ). According to the formula for the crust Nd–Hf isotope ( $\epsilon_{\text{Hf}}(t) = 1.34 \times \epsilon_{\text{Nd}}(t) + 2.82$ ) [98], the actual  $\epsilon_{\text{Hf}}(t)$  values are obviously larger than the values coupled with the whole rock (−0.93–2.28), and Nd–Hf isotopes are decoupled. Several mechanisms that can lead to Nd–Hf isotopic decoupling: (1) deeply subducted oceanic basalt [99]; (2) the lower crust that has undergone an ancient anatexis with residual phases of garnet and zircon may be an optional reservoir [88,100,101]; (3) mixing of components with different geochemical features [88,102–104]. The magmatic rock formed by the melting of basaltic crust has lower  $\text{Mg}^\#$  ( $\text{Mg}^\# < 45$ ) values [105] and obvious differentiation between MREE and HREE during anatexis [102]. The features of Baishantang basaltic andesites, such as high  $\text{Mg}^\#$  values and weak differentiation between MREEs and HREEs ( $(\text{Dy/Yb})_{\text{N}} = 1.28\text{--}1.40$ ), contradict the idea that decoupling was caused by deeply subducted ocean basalt or the lower crust undergoing an ancient anatexis event.

Nd-Hf isotopic decoupling may result from the mixing of components with different geochemical features. As discussed above, the crustal material played an important role in the basaltic andesite formation (Figure 10c,d). Basaltic andesites have high  $(\text{La}/\text{Sm})_N$  ratios and low  $\text{Ba}/\text{Th}$  values (Figure 10e), which are thought to reflect sediment involvement. The influence of sediments on magma can be classified as sediment-derived melt mixing and physical mixing. The  $(^{143}\text{Nd}/^{144}\text{Nd})-(\text{Hf}/\text{Nd})$  diagram (Figure 10f) can distinguish between these two models [106]. All samples are distributed along an oblique line rather than a horizontal line (Figure 10f), indicating that sediment-derived melt mixing, rather than physical mixing between sediments, and mantle-derived magma play an important role in basaltic andesites formation. The partial melting of the mantle mixed with sediment-derived melts or bulk subducted sediments could generate magmas with Nd-Hf isotopic decoupling [88]. Therefore, the Nd-Hf isotopic decoupling of basaltic andesite is a result of the mixing of sediment-derived melts and mantle magma.

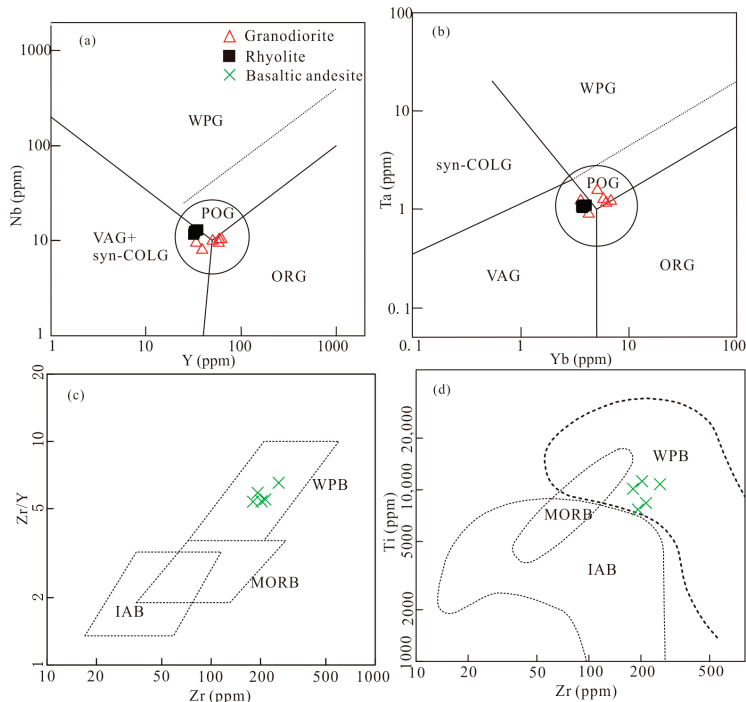
The  $\text{Dy}/\text{Yb}$  values of basaltic andesites are 1.92–2.09. These values are between the spinel lherzolite mantle melts ( $<1.5$ ) and garnet lherzolite mantle melts ( $>2.5$ ), indicating that the magma comes from the partial melting of the two [107]. The transformation depth of the spinel and garnet is 70–80 km [108], and it is speculated that the formation depth of basaltic andesite magma is about 70–80 km.

### 6.3. Tectonic Implications

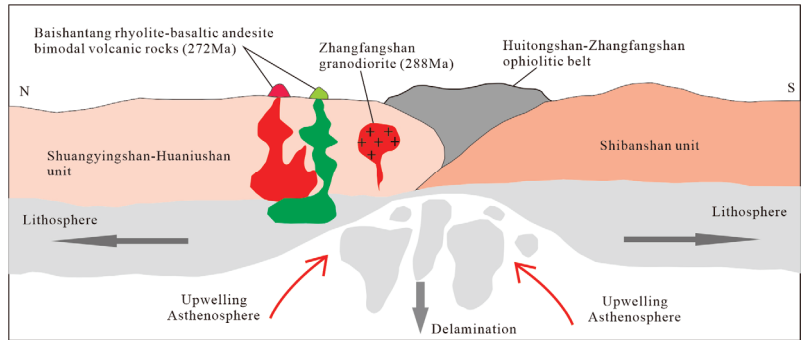
The late Paleozoic tectonic setting of the SBOB and the closure time of the PAO are the focus of this research. Paleozoic magmatic rocks are widely distributed in the SBOB, which record the subduction, closure and post-collision evolution history of the PAO. The Xiaoaquandong 395 Ma A-type granite and Hongliuhe 404 Ma A-type granite intruded into the Hongliuhe ophiolite in the SH unit, indicating that the HNY ocean closed before the early Devonian [44,109,110]. Magmatism in the SH and Shibanshan units after early Devonian indicate the evolution process of the back-arc basin represented by the HZ ophiolitic belt [44]. Late Devonian–early Carboniferous arc magmatism occurred in the Tanshanzidong, Huaniushan and Shuangfengshan in the SH unit [44], but it did not occur in the Shibanshan unit, indicating the northward subduction of the HZ ocean during this time [94].

Late Carboniferous to early Permian magmatic rocks are widely distributed in the Shibanshan and SH units, constituting the main magmatic events during the late Paleozoic. Qiaowan 304 Ma granite [27], Liuyuan and Shuwojing 285–275 Ma granite [12,13] and Yinwaxia 273 Ma rhyolite [111], and other acidic rocks, are the main types of late Carboniferous–early Permian magmatic rocks in the SBOB. These rocks have the geochemical characteristics of calc-alkaline to high K calc-alkaline and belong to highly differentiated I- or A-type felsic rocks. Except for these felsic rocks, the Podong, Cihai and Niujuanzi 282–280 Ma tholeiite-Calc-alkaline series diabase and other mafic rocks are also widely distributed in the SBOB [64–66]. These felsic and mafic rocks were formed in the extensional tectonic setting [12,13,64–66,111]. The A1-type felsic rocks were formed in the non-orogenic but the A2-type in syn-collision or post-collision tectonic environments [77]. The Zhangfangshan granodiorite and Baishantang rhyolite are A2-type felsic rocks, and all samples are plotted in the POG field in the Nb-Y and Ta-Yb diagrams (Figure 11a,b), suggesting the post-collision tectonic setting. Baishantang basaltic andesites have high Zr (180–258 ppm) concentrations and  $\text{Zr}/\text{Y}$  (5.37–6.53) ratios, similar to basalts formed in the within-plate extensional setting ( $\text{Zr} > 70$  ppm and  $\text{Zr}/\text{Y} > 3$ ) [112]. All basaltic andesite samples are plotted in the WPB field in the Zr/Y-Zr and Ti-Zr diagrams (Figure 11c,d), suggesting a within-plate extensional environment. The formation age and tectonic setting of the granodiorites and the bimodal volcanic rocks in this study are similar to late Carboniferous–early Permian magmatic rocks, showing that the late Carboniferous–early Permian magmatism in the SBOB were formed in the same tectonic environment. Meanwhile, intermediate-basic dikes in 282–280 Ma are widely distributed in the SBOB, indicating an extensional tectonic background caused by lithospheric delamination [25,26]. Based on the regional stratigraphic,

the late Carboniferous to early middle Permian in the SBOB is a continuous transgressive sedimentary sequence, and there is no unconformity interface reflecting the continental crust of the SBOB, which was further stretched on the basis of a post-collisional extension in the late Carboniferous [63,113–115]. Therefore, combined with magmatism and stratigraphic characteristics in the SBOB, the HZ ocean has been closed, and the SBOB was in a post-collisional extensional setting during early Permian (Figure 12).



**Figure 11.** Tectonic setting discrimination diagrams for the Zhangfangshan granodiorite and the Baishantang bimodal volcanic rocks: (a) Nb vs. Y diagram [116]; (b) Ta vs. Yb diagram [116]; (c) Zr/Y vs. Zr diagram [117]; (d) Ti vs. Zr diagram [117]. MORB: mid-ocean ridge basalt; IAB: island-arc basalt; WPB: within-plate basalt; VAG: volcanic arc granite; POG: post-orogenic granite; ORG: ocean ridge granite; WPG: within-plate granite; syn-COLG: syn-collisional granite.



**Figure 12.** Schematic illustration of the proposed genetic model for the early Permian in the Southern Beishan Orogenic Belt.

## 7. Conclusions

A petrographic, geochronological, whole-rock major-oxides, trace-element and Nd-Hf isotopic study of the Zhangfangshan granodiorite and the Baishantang bimodal volcanic rocks in the SBOB led to the following conclusions.

1. The Zhangfangshan granodiorites have  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $288.7 \pm 1.7$  Ma, and the Baishantang rhyolites have  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $272.3 \pm 1.6$  Ma.
2. The Zhangfangshan granodiorite belong to the A2-type granite and are generated from magma mixing between mafic and felsic magmas.
3. The Baishantang rhyolites belong to the A2-type granite and are generated from the partial melting of crust. The Baishantang basaltic andesites belong to the calc-alkaline series, which originated from the partial melting of the mantle and mixing via sediment-derived melts.
4. The Zhangfangshan granodiorites and the Baishantang bimodal volcanic rocks were formed in the post-collision extensional setting. The SBOB was in the post-collision period, and the HZ ocean was closed before the early Permian.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13121468/s1>, Table S1: Results of U-Pb dating using zircons from the Zhangfangshan granodiorites and the Baishantang bimodal volcanic rocks; Table S2: Whole-rock major (wt.%) and trace-element (ppm) analyses of the Zhangfangshan granodiorites and the Baishantang bimodal volcanic rocks; Table S3: Whole-rock Nd-Hf isotopic data of the Baishantang bimodal volcanic rocks.

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## Article

# Ocean–Continent Conversion in Beishan Orogenic Belt: Evidence from Geochemical and Zircon U–Pb–Hf Isotopic Data of Luotuoquan A-Type Granite

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**Abstract:** Devonian magmatism is one of the most important tectonothermal events in the Central Asian Orogenic Belt (CAOB). However, little is known regarding the petrogenesis and geodynamic setting of the widely distributed Devonian granitoids in the eastern Southern Beishan Orogenic Belt (SBOB). Early-Devonian granitic magmatism has been recognized from the Luotuoquan area, and the granites were emplaced between 404.9 Ma and 399.4 Ma according to LA-ICPMS zircon U–Pb dating. Geochemically, the granites exhibit high SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents and are enriched in light rare earth elements as well as Rb, Th, Nd, Zr, and Hf, while being depleted in heavy rare earth elements and Ba, U, Sr, and Ti, with distinct rare earth element fractionation and pronounced negative Eu anomalies. According to the comprehensive analysis, they closely resemble the features typically associated with A-type granites. The zircons  $\epsilon_{\text{Hf}}(t)$  values are within the range of +0.90–+5.19 (averaged 3.23) for the monzogranite and syenogranite, whereas their T<sub>DM2</sub> values fall between 1.05 and 1.34 Ga, suggesting that the magma source of the monzogranite–syenogranite originated from the partial melting of the Mesoproterozoic crust dominated by metagreywackes. Furthermore, the monzogranite and syenogranite exhibit high temperatures (average 782 °C), thin crustal thickness (average 30 km), and A-type characteristics, suggesting their formation in post-collision extensional settings. We propose the closure of the Beishan Ocean occurred before the early Devonian, followed by a transition in the Southern Beishan Orogenic Belt from a compressional to an extensional setting.

**Keywords:** zircon U–Pb dating; geochemistry; A-type granite; Luotuoquan complex; Beishan Orogenic Belt

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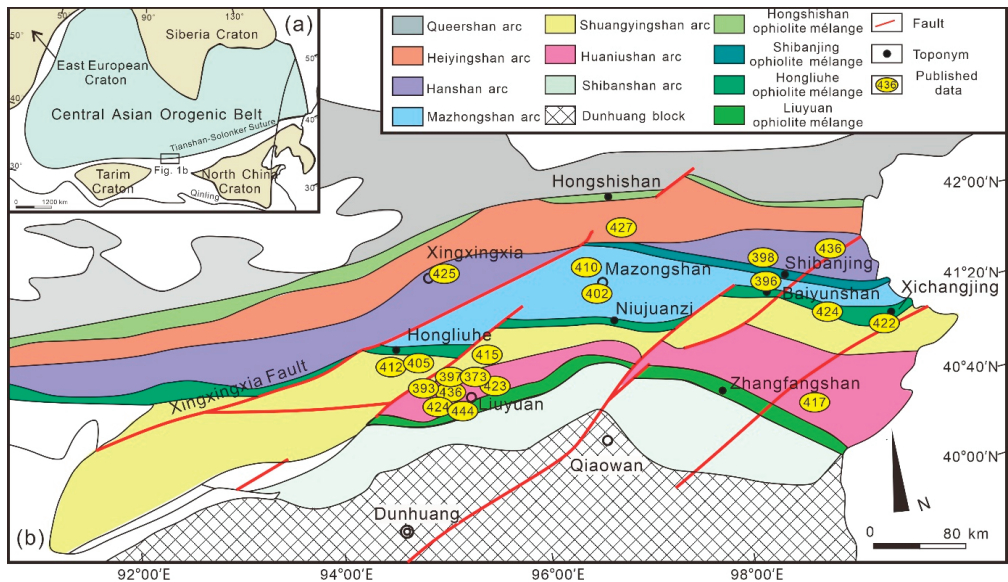


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## 1. Introduction

The Central Asian Orogenic Belt (CAOB) is formed by the sequential accretion of multiple microcontinents, island arcs, seamounts, oceanic plateaus, and accretionary complexes from the early Neoproterozoic to the late Paleozoic [1–3]. The Beishan Orogenic Belt (BOB) connects the Tarim, Kazakhstan, and North China cratons [4–6] (Figure 1a) and is considered a critical southern Central Asian Orogenic Belt segment, vital for understanding crustal growth and tectonic evolution [5–16]. The Southern Beishan Orogenic Belt (SBOB), primarily consisting of the Shuangyingshan and Huaniushan units (Figure 1), is thought to record the collision and subduction among ancient microcontinents with Mesoproterozoic to Neoproterozoic basements [17–21]. However, the tectonic and thermal evolution of the SBOB remains unclear, particularly the timing of the Beishan Ocean closure during the early Paleozoic. Current views suggest the closure occurred in the later Silurian–early Devonian [22–25], Carboniferous [25], early Permian [26], or after the late Permian [27–29]. Thus, the Paleozoic crustal growth and geodynamics of the SBOB are rather controversial

compared to those of the Mesozoic [11]. Further investigation of the tectonic and crustal development of the SBOB during the early–late Paleozoic is needed.



**Figure 1.** (a) Tectonic setting of the BOB (modified after [5]). (b) Simplified tectonic map of the Beishan orogenic collage and its adjacent area showing the tectonic subdivisions (modified after [5,13]). The zircon U–Pb age data of granitoids in (b) are from previous studies [4,6,10,30–35].

Herein, we present comprehensive whole-rock geochemical, in situ zircon U–Pb geochronology, and Hf isotopic data of A-type granites from the Luotuoquan complex. In addition to previously published findings, we discuss the genetic mechanism and tectonic settings of the early Paleozoic granitoids of the SBOB, elucidating their significant implications for understanding the tectonic evolution during this period in the BOB while also providing valuable insights into Beishan Ocean closure.

## 2. Geological Setting

The BOB comprises a complex assemblage of blocks, magmatic arcs, and ophiolitic mélanges that were formed through the subduction–accretion process of the Paleo–Asian Ocean [5]. Based on the spatial and temporal distributions of the ophiolitic mélanges and rock associations, the BOB is divided into several arcs [5], comprising (from north to south) the Queershan, Heiyingshan, Hanshan, Mazongshan, Shuangyingshan, Huaniushan, and Shibanshan arcs, which are separated by the Hongshishan, Shibanjing, Hongliuhe, and Liuyuan ophiolitic mélanges, respectively (Figure 1b).

The SBOB is situated within the Hongliuhe and Liuyuan ophiolitic mélanges [10] (Figure 1b) and comprises the Shuangyingshan and Huaniushan Units. In addition, the southern Beishan has recorded the subduction and collision of several microcontinental fragments and is characterized by early Paleozoic volcanic–sedimentary formations and intrusive plutons generated during early Paleozoic subduction [20,22,36,37]. Recent geochronological studies in the region reveal three stages of pluton emplacement in the Mid-Ordovician to late Silurian [6,23,38–40], early Devonian [4,6,40–42], and Late Devonian to early Carboniferous [6,38].

The Luotuoquan complex is situated in the eastern segment of the SBOB (Figure 1b) and intrudes into Silurian granitoids (Figure 2). It primarily consists of monzogranite, syenogranite, and minor basic rock. Field observations reveal that the syenogranite exhibits



weak mylonitization and has intruded into the monzogranite (Figure 2). The Devonian samples are derived from the Luotuoquan granite complex, comprising five monzogranite samples (PM03-2, PM03-26, PM03-41, PM12-20, and PM17-4 and three syenogranite samples (D5195, D8373, and PM06-34). The monzogranite samples display medium- to coarse-grained massive rocks, primarily composed of quartz (20–25 vol%), K-feldspar (35–40 vol%), plagioclase (30–35 vol%), and orientated biotite and/or muscovite (5 vol%) (Figure 3a,b). The syenogranite samples exhibit well-developed mylonitization and a granoblastic texture. They predominantly consist of K-feldspar (55–60 vol%), plagioclase (10–15 vol%), and quartz (20–25 vol%) with minor biotite (5 vol%) (Figure 3c,d).

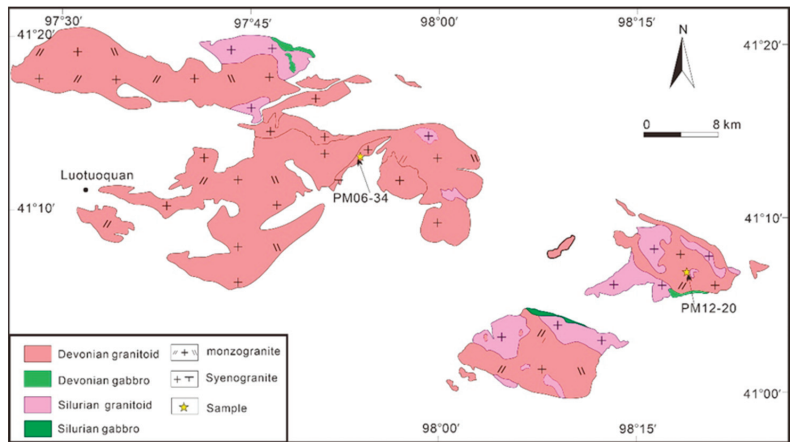


Figure 2. Geological map of the mafic-ultramafic intrusions and granite plutons in the Luotuoquan area.

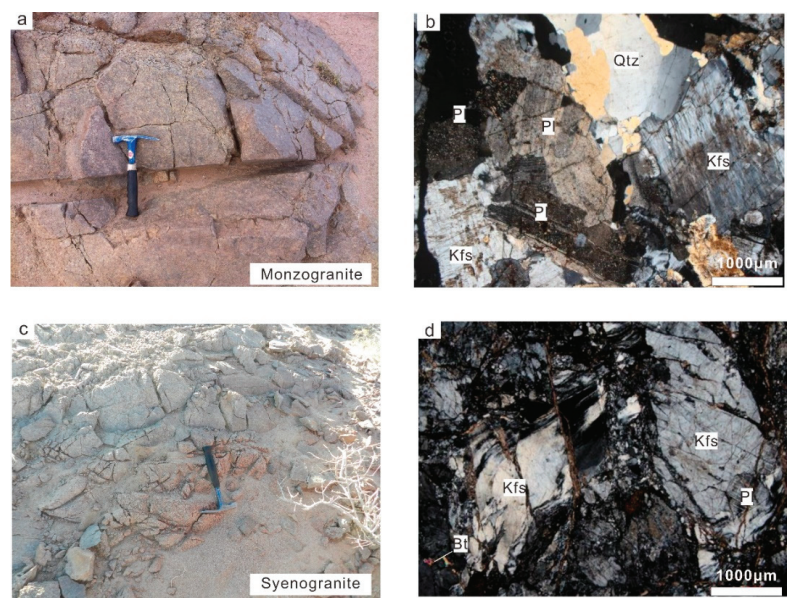


Figure 3. Field and microscopic photos of the Luotuoquan monzogranite (a,b) and syenogranite (c,d). Qtz-quartz; Pl-plagioclase; Kfs-potassium feldspar; Bt-biotite.



### 3. Analytic Methods

#### 3.1. Zircon Dating and CL Imaging

Zircons were separated from the granite samples PM06-34 and PM12-20 of the Luotuoquan complex for laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) U–Pb dating. Zircon grains were extracted using standard density and magnetic separation techniques. The selected zircon grains were handpicked under a stereoscopic microscope and mounted in epoxy resin before being polished to dissect the crystals in half for analysis. Cathodoluminescence (CL) and reflected-light photomicrographic analysis of the prepared sample targets were utilized to image the morphology and internal structure of the zircons to aid in selecting zircon grains for U–Pb dating. Zircon U–Pb dating analyses were conducted on a quadrupole inductively coupled plasma mass spectrometer (ICP-MS) (THERMO-ICAPRQ) coupled to a 193-nm ArF Excimer laser (Resolution-LR, Applied Spectra, West Sacramento, CA, USA) at Hebei Key Laboratory of Strategic Critical Mineral Resources. The laser spot size was set to 29  $\mu\text{m}$ , the laser energy density was 3 J/cm<sup>2</sup> and the repetition rate was 8 Hz. Each analysis comprised a 10 s blank, a 40 s sampling ablation, and a 20 s sample-chamber flushing after the ablation. The ablated material was carried into the ICP-MS by the high-purity helium gas stream with a flux of 0.4 L/min. The whole laser path was fluxed with argon (0.9 L/min) to increase energy stability. A zircon 91,500 standard was used for external age calibration, and a zircon GJ-1 standard was used as a secondary standard to supervise the deviation of age calculation. Calibrations for trace element concentration were carried out using NIST SRM610 as an external standard and Si as the internal standard. ICPMSDataCal (Ver. 4.6) [43] and Isoplot 3.0 [44] programs were used for data reduction.

#### 3.2. In Situ Lu–Hf Isotopes

In situ zircon Lu–Hf isotopic analyses were performed using a Neptune Plus MC–ICP–MS (Thermo Fisher Scientific, Brunswick, Germany) equipped with a Geolas 2005 excimer ArF laser ablation system (Lambda Physik, Göttingen, Germany). All data on zircon were acquired in a single-spot ablation mode at a spot size of 44  $\mu\text{m}$ . The energy density of laser ablation used in this study was  $\sim 7.0$  J/cm<sup>2</sup>. Each measurement consisted of a 20-s acquisition of the background signal, followed by a 50-s acquisition of ablation signals. Instrumental conditions and data acquisition were as described by Wu et al. (2006) [45]. Zircon 91,500 was used as the reference standard. The chondritic ratios of  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$  and  $^{176}\text{Lu}/^{177}\text{Hf} = 0.0332$  were used in our calculation of  $\varepsilon_{\text{Hf}}(t)$  values [46]. Single-stage model ages ( $T_{\text{DM1}}$ ) were calculated by reference to depleted mantle with a present day  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of 0.28325 and  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of 0.0384 [47]. The two-stage Hf model age ( $T_{\text{DM2}}$ ), also interpreted as crust formation age, was calculated by projecting the zircon  $^{176}\text{Hf}/^{177}\text{Hf}(t)$  back to the depleted mantle model growth curve, assuming a mean crustal value for Lu/Hf ( $^{176}\text{Lu}/^{177}\text{Hf} = 0.015$ ) [48].

#### 3.3. Whole-Rock Geochemical Analysis

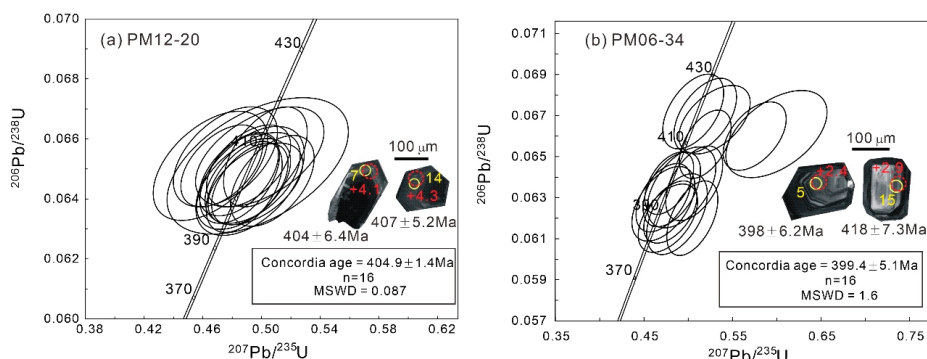
Whole-rock geochemical analyses were performed at the Institute of Regional Geology Survey of Hebei Province. Fresh chips of whole-rock samples were powdered to 200 mesh using a tungsten carbide ball mill. Major and trace elements were analyzed by X-ray fluorescence (Axios X; PANalytical B.V.) and inductively coupled plasma mass spectrometry (XSeries II; Thermo Fisher Scientific), respectively. The analytical precision is generally better than 2% for major elements. For trace element analyses, sample powders were digested using HF + HNO<sub>3</sub> mixture in high-pressure Teflon bombs at 190 °C for 48 h or longer. The analytical precision is generally better than 5% for trace elements.

### 4. Result

#### 4.1. Zircon U–Pb Dating and Lu–Hf Isotope Compositions

The zircons from monzogranite (PM12-20) and syenogranite (PM06-34) are similar in crystal morphology with sizes ranging from 80 to 200  $\mu\text{m}$  and aspects ratios of 2:1–3:1.

The CL images reveal oscillatory zoning and rare inherited cores (Figure 4). The Th/U ratios are  $>0.1$ , indicating magmatic origin (Table 1). Sixteen analyses from sample PM12-34 (monzogranite) were concordant and yielded a weighted mean age of  $404.9 \pm 1.4$  Ma (Figure 4a). Sixteen spots were analyzed for dating from sample PM06-12, apart from six spots (RZ7, RZ9-11, RZ13, and RZ15), which represent the age of the inherited core, the remaining ten analyses yielded a weighted mean age of  $399.4 \pm 5.1$  Ma (Figure 4b).



**Figure 4.** U–Pb concordia diagrams of zircons from Luotuoquan monzogranite (a) and syenogranite (b). The yellow line circle represents the spot of LA-ICP-MS analysis for U–Pb dating. The red dashed line circle represents the spot of LA-MC-ICP-MS analysis for Lu–Hf isotope compositions.

The analytical results are presented in Table 2, including  $\epsilon_{\text{Hf}}(t)$  values and model ages calculated using  $^{206}\text{Pb}/^{238}\text{U}$  ages. The 32 spots from the Luotuoquan granites exhibit initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios ranging from 0.282205 to 0.282415 and positive  $\epsilon_{\text{Hf}}(t)$  values of  $+0.90$ – $+5.19$ . Furthermore, the  $T_{\text{DM2}}$  model ages range from 1.05 to 1.34 Ga.

#### 4.2. Major and Trace Elements

The whole-rock major and trace element compositions of the five monzogranite samples and three syenogranite samples were analyzed, and the results are presented in Table 3.

##### 4.2.1. Major Elements

The samples possess high  $\text{SiO}_2$  (71.04–76.00 wt.%),  $\text{K}_2\text{O}$  (4.02–5.59 wt.%), and  $\text{K}_2\text{O} + \text{Na}_2\text{O}$  (7.04–8.62 wt.%); however, they possess low  $\text{Al}_2\text{O}_3$  (12.10–14.30 wt.%),  $\text{MgO}$  (0.07–0.63 wt.%), and  $\text{CaO}$  (0.76–2.53 wt.%). In the  $\text{SiO}_2$  versus  $\text{K}_2\text{O} + \text{Na}_2\text{O}$  diagram (Figure 5a), the samples are plotted within the granitoid fields, which is consistent with the petrographic observations. They further display low A/CNK values (molar  $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ ) ranging from 0.85 to 1.08 and exhibit peraluminous and high K characteristics (Figure 5).

##### 4.2.2. Trace Elements

In the chondrite-normalized rare earth element patterns, the samples exhibit relative enrichment of light rare earth elements (LREE) ( $[\text{La}/\text{Yb}]_{\text{N}} = 2.63$ – $16.87$ ) and significant negative Eu anomalies ( $\text{Eu}/\text{Eu}^* = 0.23$ – $0.45$ ), while the REE abundances range from 161.2 to 459.7 ppm (Figure 6a). All samples are depleted in Ba, U, Sr, P, and Ti and enriched in Rb, Th, Nd, Zr, and Hf relative to the primitive mantle (Figure 6b).

Table 1. LA-ICP-MS zircon U–Pb dating results of the Luotuoquan granites.

| No   | Pb                    | U   | Isotopic Ratios                   |            |                                  |            | Isotopic Age (Ma)                |            |                                  |            |                                  |            |     |     |
|------|-----------------------|-----|-----------------------------------|------------|----------------------------------|------------|----------------------------------|------------|----------------------------------|------------|----------------------------------|------------|-----|-----|
|      | (ppm)                 |     | $^{207}\text{Pb}/^{206}\text{Pb}$ | 1 $\sigma$ | $^{207}\text{Pb}/^{235}\text{U}$ | 1 $\sigma$ | $^{206}\text{Pb}/^{238}\text{U}$ | 1 $\sigma$ | $^{207}\text{Pb}/^{235}\text{U}$ | 1 $\sigma$ | $^{206}\text{Pb}/^{238}\text{U}$ | 1 $\sigma$ |     |     |
|      | PM12-20: monzogranite |     |                                   |            |                                  |            |                                  |            |                                  |            |                                  |            |     |     |
| RZ1  | 75                    | 294 | 0.0529                            | 0.0028     | 0.4754                           | 0.0234     | 0.0654                           | 0.0011     | 324                              | 120        | 395                              | 16.1       | 409 | 7.2 |
| RZ2  | 101                   | 457 | 0.0556                            | 0.0026     | 0.4958                           | 0.0213     | 0.0645                           | 0.0009     | 439                              | 104        | 409                              | 14.5       | 403 | 6.1 |
| RZ3  | 84                    | 420 | 0.0539                            | 0.0020     | 0.4851                           | 0.0179     | 0.0647                           | 0.0010     | 365                              | 88         | 402                              | 12.3       | 404 | 6.5 |
| RZ4  | 69                    | 360 | 0.0540                            | 0.0021     | 0.4845                           | 0.0178     | 0.0648                           | 0.0009     | 372                              | 87         | 401                              | 12.2       | 405 | 6.3 |
| RZ5  | 120                   | 529 | 0.0554                            | 0.0020     | 0.5026                           | 0.0188     | 0.0654                           | 0.0011     | 428                              | 81.5       | 413                              | 12.7       | 408 | 6.6 |
| RZ6  | 72                    | 296 | 0.0551                            | 0.0028     | 0.4922                           | 0.0244     | 0.0646                           | 0.0012     | 417                              | 115        | 406                              | 16.6       | 403 | 7.1 |
| RZ7  | 74                    | 300 | 0.0557                            | 0.0026     | 0.4939                           | 0.0214     | 0.0647                           | 0.0010     | 443                              | 99.1       | 408                              | 14.6       | 404 | 6.4 |
| RZ8  | 110                   | 486 | 0.0549                            | 0.0020     | 0.492                            | 0.0172     | 0.0645                           | 0.0009     | 406                              | 81.5       | 406                              | 11.7       | 403 | 6.2 |
| RZ9  | 60.6                  | 330 | 0.0510                            | 0.0028     | 0.4651                           | 0.0257     | 0.0651                           | 0.0012     | 239                              | 130        | 388                              | 17.8       | 406 | 7.1 |
| RZ10 | 233                   | 900 | 0.0559                            | 0.0022     | 0.5074                           | 0.0188     | 0.0646                           | 0.0010     | 456                              | 82.4       | 417                              | 12.7       | 403 | 6.3 |
| RZ11 | 56.3                  | 231 | 0.0548                            | 0.0026     | 0.4878                           | 0.0211     | 0.0645                           | 0.0010     | 467                              | 106        | 403                              | 14.4       | 403 | 6.4 |
| RZ12 | 34.4                  | 149 | 0.0551                            | 0.0048     | 0.4974                           | 0.0408     | 0.0651                           | 0.0015     | 413                              | 193        | 410                              | 27.7       | 406 | 9.4 |
| RZ13 | 127                   | 530 | 0.0544                            | 0.0019     | 0.4882                           | 0.0171     | 0.0644                           | 0.0010     | 387                              | 81.5       | 404                              | 11.7       | 402 | 6.8 |
| RZ14 | 86                    | 388 | 0.0545                            | 0.0022     | 0.4912                           | 0.0189     | 0.0651                           | 0.0009     | 391                              | 90.7       | 406                              | 12.8       | 407 | 5.2 |
| RZ15 | 76                    | 326 | 0.0550                            | 0.0032     | 0.4988                           | 0.0289     | 0.0654                           | 0.0011     | 413                              | 131        | 411                              | 19.6       | 408 | 7.3 |
| RZ16 | 82                    | 360 | 0.0524                            | 0.0021     | 0.4729                           | 0.0184     | 0.0651                           | 0.0009     | 306                              | 92.6       | 393                              | 12.7       | 407 | 6.1 |
|      | PM06-34: syenogranite |     |                                   |            |                                  |            |                                  |            |                                  |            |                                  |            |     |     |
| RZ1  | 48.3                  | 213 | 0.0554                            | 0.0025     | 0.4770                           | 0.0221     | 0.062                            | 0.0011     | 428                              | 104        | 396                              | 15.2       | 387 | 6.4 |
| RZ2  | 51.2                  | 227 | 0.0549                            | 0.0029     | 0.4719                           | 0.0234     | 0.0627                           | 0.0012     | 406                              | 117        | 392                              | 16.1       | 392 | 7.3 |
| RZ3  | 46.1                  | 192 | 0.0567                            | 0.0031     | 0.4925                           | 0.0255     | 0.0635                           | 0.0013     | 480                              | 114        | 407                              | 17.4       | 397 | 8.1 |
| RZ4  | 114                   | 422 | 0.0546                            | 0.0022     | 0.4798                           | 0.0198     | 0.0623                           | 0.0010     | 394                              | 90.7       | 398                              | 13.6       | 390 | 6.1 |
| RZ5  | 123                   | 585 | 0.0537                            | 0.0021     | 0.4785                           | 0.0182     | 0.0637                           | 0.0010     | 367                              | 88.9       | 397                              | 12.5       | 398 | 6.2 |
| RZ6  | 92                    | 305 | 0.0574                            | 0.0026     | 0.5068                           | 0.0212     | 0.0637                           | 0.0012     | 506                              | 100        | 416                              | 14.3       | 398 | 7.2 |
| RZ7  | 77                    | 337 | 0.0565                            | 0.0028     | 0.5297                           | 0.0266     | 0.0668                           | 0.0011     | 472                              | 105        | 432                              | 17.7       | 417 | 7.0 |
| RZ8  | 61.6                  | 384 | 0.0585                            | 0.0022     | 0.5046                           | 0.0190     | 0.0620                           | 0.0012     | 550                              | 83.3       | 415                              | 12.8       | 388 | 7.1 |
| RZ9  | 85                    | 398 | 0.0623                            | 0.0026     | 0.5750                           | 0.0235     | 0.0660                           | 0.0011     | 687                              | 88.9       | 461                              | 15.1       | 412 | 7.2 |
| RZ10 | 98                    | 447 | 0.0570                            | 0.0022     | 0.5192                           | 0.0193     | 0.0656                           | 0.0011     | 500                              | 83.3       | 425                              | 12.9       | 410 | 6.1 |
| RZ11 | 54.2                  | 278 | 0.0547                            | 0.0025     | 0.5056                           | 0.0227     | 0.0672                           | 0.0012     | 398                              | 99         | 415                              | 15.3       | 419 | 7.5 |
| RZ12 | 52.6                  | 241 | 0.0547                            | 0.0025     | 0.4720                           | 0.0204     | 0.0630                           | 0.0011     | 398                              | 102        | 393                              | 14.1       | 394 | 7.2 |
| RZ13 | 39.9                  | 168 | 0.0654                            | 0.0038     | 0.5996                           | 0.0377     | 0.0661                           | 0.0014     | 787                              | 122        | 477                              | 23.9       | 412 | 8.1 |
| RZ14 | 75                    | 267 | 0.0557                            | 0.0027     | 0.4814                           | 0.0214     | 0.0634                           | 0.0012     | 439                              | 107        | 399                              | 14.7       | 396 | 7.2 |
| RZ15 | 95                    | 424 | 0.0557                            | 0.0023     | 0.5192                           | 0.0233     | 0.0670                           | 0.0012     | 439                              | 94.4       | 425                              | 15.6       | 418 | 7.3 |
| RZ16 | 45.2                  | 220 | 0.0564                            | 0.0027     | 0.4873                           | 0.0226     | 0.0622                           | 0.0013     | 478                              | 103        | 403                              | 15.4       | 389 | 8.0 |

Table 2. In situ zircon Hf isotopic results of the Luotuoquan granites.

| No                    | Age (Ma) | <sup>176</sup> Yb/ <sup>177</sup> Hf | <sup>176</sup> Lu/ <sup>177</sup> Hf | <sup>176</sup> Hf/ <sup>177</sup> Hf | 2σ       | ε <sub>Hf(t)</sub> | 2σ   | TDM1 (Ma) | f(Lu/Hf) | TDM2 (Ma) |
|-----------------------|----------|--------------------------------------|--------------------------------------|--------------------------------------|----------|--------------------|------|-----------|----------|-----------|
| PM12-20: monzogranite |          |                                      |                                      |                                      |          |                    |      |           |          |           |
| RZ1                   | 409      | 0.014856                             | 0.000530                             | 0.282242                             | 0.000015 | −18.7              | 3.72 | 894       | −0.98    | 1160      |
| RZ2                   | 403      | 0.031534                             | 0.001173                             | 0.282400                             | 0.000017 | −13.2              | 2.96 | 927       | −0.96    | 1204      |
| RZ3                   | 404      | 0.025478                             | 0.000856                             | 0.28238                              | 0.000018 | −13.9              | 3.82 | 876       | −0.97    | 1150      |
| RZ4                   | 405      | 0.041885                             | 0.001418                             | 0.282381                             | 0.000014 | −13.8              | 3.39 | 895       | −0.96    | 1178      |
| RZ5                   | 408      | 0.030106                             | 0.001031                             | 0.282337                             | 0.000015 | −15.4              | 3.51 | 887       | −0.97    | 1173      |
| RZ6                   | 403      | 0.040490                             | 0.001374                             | 0.282318                             | 0.000015 | −16.1              | 3.71 | 873       | −0.96    | 1156      |
| RZ7                   | 404      | 0.048124                             | 0.001711                             | 0.282350                             | 0.000017 | −14.9              | 4.12 | 884       | −0.95    | 1131      |
| RZ8                   | 403      | 0.034757                             | 0.001174                             | 0.282334                             | 0.000014 | −15.5              | 2.32 | 934       | −0.96    | 1244      |
| RZ9                   | 406      | 0.028390                             | 0.000962                             | 0.282279                             | 0.000014 | −17.4              | 3.12 | 902       | −0.97    | 1196      |
| RZ10                  | 403      | 0.032415                             | 0.001107                             | 0.282360                             | 0.000015 | −14.6              | 2.66 | 914       | −0.97    | 1223      |
| RZ11                  | 403      | 0.033578                             | 0.001125                             | 0.282319                             | 0.000014 | −16.0              | 3.30 | 889       | −0.97    | 1182      |
| RZ12                  | 406      | 0.054288                             | 0.001987                             | 0.282317                             | 0.000014 | −16.1              | 3.88 | 879       | −0.94    | 1148      |
| RZ13                  | 402      | 0.008480                             | 0.000266                             | 0.282205                             | 0.000016 | −20.1              | 3.58 | 907       | −0.99    | 1164      |
| RZ14                  | 407      | 0.029075                             | 0.000976                             | 0.282415                             | 0.000014 | −12.6              | 4.34 | 873       | −0.97    | 1119      |
| RZ15                  | 408      | 0.054699                             | 0.001828                             | 0.282399                             | 0.000015 | −13.2              | 3.74 | 875       | −0.94    | 1158      |
| RZ16                  | 407      | 0.029610                             | 0.001011                             | 0.282348                             | 0.000016 | −15.0              | 4.57 | 847       | −0.97    | 1105      |
| PM06-34: syenogranite |          |                                      |                                      |                                      |          |                    |      |           |          |           |
| RZ1                   | 387      | 0.032029                             | 0.001097                             | 0.282317                             | 0.000018 | −16.1              | 2.96 | 890       | −0.97    | 1192      |
| RZ2                   | 392      | 0.011210                             | 0.000352                             | 0.282254                             | 0.000018 | −18.3              | 5.19 | 814       | −0.99    | 1054      |
| RZ3                   | 397      | 0.045344                             | 0.001502                             | 0.282343                             | 0.000015 | −15.2              | 2.52 | 914       | −0.95    | 1227      |
| RZ4                   | 390      | 0.028869                             | 0.000986                             | 0.282321                             | 0.000019 | −15.9              | 4.66 | 831       | −0.97    | 1086      |
| RZ5                   | 398      | 0.031534                             | 0.001173                             | 0.282400                             | 0.000015 | −13.2              | 2.39 | 922       | −0.96    | 1236      |
| RZ6                   | 398      | 0.025478                             | 0.000856                             | 0.282380                             | 0.000017 | −13.9              | 2.31 | 928       | −0.97    | 1241      |
| RZ7                   | 417      | 0.041885                             | 0.001418                             | 0.282381                             | 0.000016 | −13.8              | 0.95 | 998       | −0.96    | 1341      |
| RZ8                   | 388      | 0.030106                             | 0.001031                             | 0.282337                             | 0.000014 | −15.4              | 2.92 | 893       | −0.97    | 1195      |
| RZ9                   | 412      | 0.040490                             | 0.001374                             | 0.282318                             | 0.000014 | −16.1              | 1.81 | 958       | −0.96    | 1283      |
| RZ10                  | 410      | 0.048124                             | 0.001711                             | 0.282350                             | 0.000014 | −14.9              | 0.90 | 993       | −0.95    | 1339      |
| RZ11                  | 419      | 0.034757                             | 0.001174                             | 0.282334                             | 0.000014 | −15.5              | 4.30 | 862       | −0.96    | 1131      |
| RZ12                  | 394      | 0.028390                             | 0.000962                             | 0.282279                             | 0.000014 | −17.4              | 2.11 | 927       | −0.97    | 1250      |
| RZ13                  | 412      | 0.032415                             | 0.001107                             | 0.282360                             | 0.000013 | −14.6              | 2.98 | 910       | −0.97    | 1209      |
| RZ14                  | 396      | 0.033578                             | 0.001125                             | 0.282319                             | 0.000013 | −16.0              | 4.68 | 833       | −0.97    | 1090      |
| RZ15                  | 418      | 0.054288                             | 0.001987                             | 0.282317                             | 0.000017 | −16.1              | 2.91 | 922       | −0.94    | 1218      |
| RZ16                  | 389      | 0.008480                             | 0.000266                             | 0.282205                             | 0.000016 | −20.1              | 3.12 | 884       | −0.99    | 1183      |

Table 3. Major and trace element compositions of the Luotuoquan granites.

| Samples                         | Monzogranite |         |         |         |        | Syenogranite |       |         |
|---------------------------------|--------------|---------|---------|---------|--------|--------------|-------|---------|
|                                 | PM03-2       | PM03-26 | PM03-41 | PM12-20 | PM17-4 | D5195        | D8373 | PM06-34 |
| SiO <sub>2</sub>                | 71.04        | 71.80   | 74.95   | 72.80   | 74.10  | 71.60        | 76.00 | 72.30   |
| TiO <sub>2</sub>                | 0.29         | 0.32    | 0.14    | 0.29    | 0.12   | 0.49         | 0.18  | 0.17    |
| Al <sub>2</sub> O <sub>3</sub>  | 14.20        | 14.30   | 13.20   | 13.60   | 14.10  | 13.30        | 12.10 | 12.10   |
| TF <sub>e2</sub> O <sub>3</sub> | 2.41         | 2.61    | 1.11    | 2.57    | 1.08   | 3.63         | 1.70  | 1.86    |
| MnO                             | 0.06         | 0.06    | 0.01    | 0.05    | 0.01   | 0.03         | 0.01  | 0.03    |
| MgO                             | 0.55         | 0.63    | 0.27    | 0.41    | 0.30   | 0.62         | 0.07  | 0.63    |
| CaO                             | 2.16         | 1.98    | 0.76    | 1.33    | 1.29   | 2.00         | 1.03  | 2.53    |
| Na <sub>2</sub> O               | 3.45         | 3.49    | 3.03    | 3.10    | 3.51   | 3.01         | 2.46  | 2.69    |
| K <sub>2</sub> O                | 4.29         | 4.02    | 5.59    | 4.93    | 4.87   | 4.03         | 4.89  | 4.89    |
| P <sub>2</sub> O <sub>5</sub>   | 0.12         | 0.12    | 0.03    | 0.09    | 0.04   | 0.11         | 0.04  | 0.29    |
| LoI                             | 1.52         | 0.77    | 0.76    | 0.92    | 0.51   | 1.23         | 1.43  | 2.48    |
| Total                           | 100.07       | 100.07  | 99.85   | 100.03  | 99.99  | 100.06       | 99.93 | 99.99   |
| Rb                              | 211.0        | 132.0   | 167.0   | 177.0   | 215.0  | 112.0        | 114.0 | 134.0   |
| Ba                              | 406.0        | 444.0   | 398.0   | 345.0   | 466.0  | 556.0        | 499.0 | 755.0   |
| Th                              | 28.60        | 11.50   | 11.30   | 20.70   | 16.70  | 29.20        | 21.20 | 24.80   |
| U                               | 4.81         | 2.41    | 2.23    | 2.95    | 1.76   | 2.10         | 1.30  | 1.90    |
| Ta                              | 1.10         | 0.76    | 0.90    | 1.08    | 0.80   | 0.81         | 0.40  | 0.72    |
| Nb                              | 14.00        | 9.53    | 9.56    | 11.50   | 10.10  | 15.10        | 5.13  | 12.40   |
| Sr                              | 90.50        | 50.10   | 60.40   | 65.80   | 84.50  | 86.00        | 59.00 | 79.00   |
| Zr                              | 333.0        | 202.0   | 245.0   | 259.0   | 236.0  | 365.0        | 147.0 | 275.0   |
| Hf                              | 10.90        | 6.98    | 8.40    | 8.90    | 8.01   | 12.50        | 6.10  | 9.50    |
| Y                               | 55.52        | 57.88   | 58.64   | 43.61   | 44.51  | 47.40        | 43.40 | 37.70   |
| Ga                              | 19.10        | 18.20   | 14.30   | 17.00   | 20.60  | 25.40        | 21.70 | 17.20   |
| La                              | 40.28        | 25.93   | 19.75   | 47.56   | 42.23  | 93.60        | 48.60 | 68.20   |
| Ce                              | 93.30        | 56.65   | 45.19   | 108.9   | 83.71  | 189.0        | 89.60 | 140.0   |
| Pr                              | 10.97        | 7.51    | 5.87    | 14.30   | 11.20  | 25.60        | 12.90 | 19.20   |
| Nd                              | 43.77        | 31.14   | 24.06   | 55.80   | 44.47  | 94.90        | 50.90 | 74.00   |
| Sm                              | 9.62         | 7.69    | 6.25    | 11.46   | 9.12   | 17.20        | 11.50 | 14.10   |
| Eu                              | 1.13         | 0.96    | 0.86    | 1.37    | 1.00   | 1.22         | 1.18  | 1.20    |
| Gd                              | 7.84         | 6.18    | 5.11    | 9.07    | 7.45   | 15.10        | 9.35  | 11.50   |
| Tb                              | 1.61         | 1.44    | 1.33    | 1.62    | 1.42   | 2.11         | 1.53  | 1.80    |
| Dy                              | 9.84         | 9.66    | 9.57    | 8.49    | 8.51   | 9.62         | 8.13  | 9.20    |
| Ho                              | 1.87         | 1.89    | 1.89    | 1.50    | 1.53   | 1.64         | 1.50  | 1.70    |
| Er                              | 4.68         | 4.72    | 4.75    | 3.75    | 3.81   | 4.56         | 4.35  | 4.00    |
| Tm                              | 0.84         | 0.93    | 0.96    | 0.63    | 0.69   | 0.66         | 0.73  | 0.60    |
| Yb                              | 4.87         | 5.52    | 5.38    | 3.57    | 4.11   | 3.98         | 4.67  | 3.70    |
| Lu                              | 0.85         | 0.96    | 0.89    | 0.66    | 0.75   | 0.54         | 0.64  | 0.50    |
| ΣREE                            | 231.5        | 161.2   | 131.9   | 268.7   | 220.0  | 459.7        | 245.6 | 349.7   |
| LREE/HREE                       | 6.14         | 4.15    | 3.41    | 8.17    | 6.78   | 11.00        | 6.95  | 9.57    |
| δEu                             | 0.39         | 0.41    | 0.45    | 0.40    | 0.36   | 0.23         | 0.34  | 0.27    |

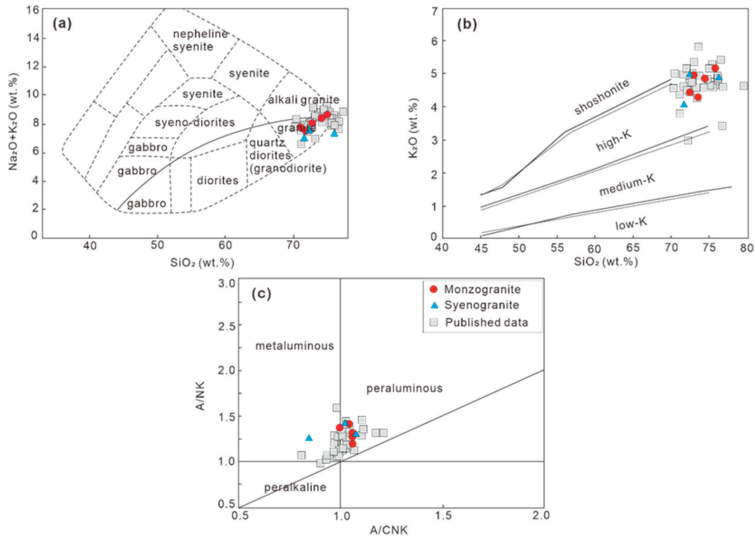
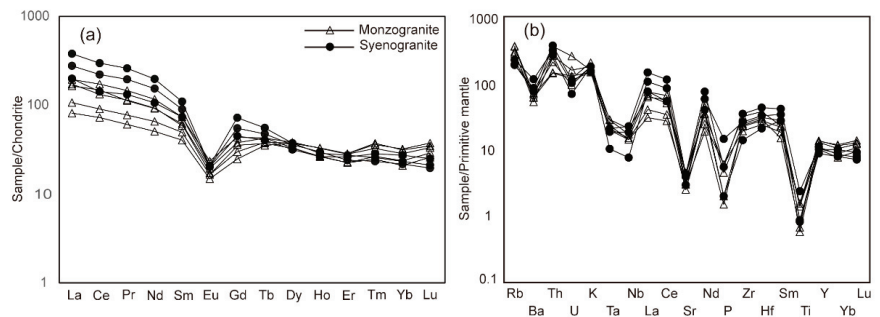


Figure 5. (a) Total alkalis (Na<sub>2</sub>O + K<sub>2</sub>O) vs. SiO<sub>2</sub> diagram [49]; (b) K<sub>2</sub>O vs. SiO<sub>2</sub> diagram [50]; (c) A/NK vs. A/CNK diagram [51]. Published data of the early Devonian granitoids in the Beishan area are from [4,6,30,31,42,52,53].



**Figure 6.** Chondrite-normalized REE element patterns (a) and primitive mantle-normalized trace element spider diagrams (b) for the Luotuoquan granites. Normalization values are from [54].

## 5. Discussion

### 5.1. Devonian Magmatism in the Southern Beishan Orogenic Belt

The LA-ICP-MS zircon U–Pb ages obtained in this study (404–399 Ma) are consistent with the timing of pluton emplacement in the SBOB, including the Liuyuan monzogranite ( $397 \pm 7$  Ma) [40], Shuangfengshan A-type granites ( $415 \pm 3$  Ma) [4], Huitongshan K-feldspar granite ( $397 \pm 3$  Ma) [42], and Shijinpo granitoid ( $404 \pm 2$  Ma) [53]. Previous studies have established that the Silurian–Devonian was a crucial period of magmatism in the BOB (Figure 1a), with age peaks of 440, 420, and 400 Ma. The Luotuoquan granites, as products of Devonian magmatism, offer valuable insights into the geodynamic evolution of the BOB during the mid-Paleozoic.

### 5.2. Petrogenesis and Magma Sources

The syenogranite samples in this study have undergone mylonitization, as evidenced by petrographic observation (Figure 2d). Therefore, it is imperative to evaluate the impact of alteration on both major and trace elements before discussing their petrogenesis [55]. Our samples demonstrate differentiated correlations between “immobile alteration” elements (e.g., Zr) and the other trace elements (Figure 7), where Nb, Ta, Th, and Hf display a stronger correlation with Zr than Rb and Ba, suggesting that this alteration has less effect on these elements. Consequently, the subsequent discussion will primarily focus on more immobile elements such as Nb, Ta, Zr, and REEs.

The Luotuoquan monzogranite and syenogranite exhibit similar geochemical characteristics and are discussed together. They have high  $\text{SiO}_2$  (71.04–76.00 wt.%) and  $\text{K}_2\text{O} + \text{Na}_2\text{O}$  (7.04–8.62 wt.%) but low  $\text{Al}_2\text{O}_3$  (mean of 13.36 wt.%), MgO (mean of 0.03 wt.%), and CaO (mean of 1.64 wt.%), indicating A-type granite geochemical characteristics. Nevertheless, highly fractionated I-type and S-type granites also share similarities with A-type granites. Highly fractionated S-type granites tend to exhibit higher  $\text{P}_2\text{O}_5$  (mean of 0.14 wt.%) and lower  $\text{Na}_2\text{O}$  (mean of 2.81 wt.%) than A-type granites [56]. The monzogranite–syenogranite displays low  $\text{P}_2\text{O}_5$  (mean of 0.11 wt.%) and high  $\text{Na}_2\text{O}$  (mean of 3.09 wt.%), indicating it does not belong to the highly fractionated S-type granite. Compared with highly fractionated I-type granite, A-type granite shows iron enrichment and magnesium depletion with higher  $\text{Fe}_2\text{O}_3^{\text{T}}/\text{MgO}$  ratios. The  $\text{Fe}_2\text{O}_3^{\text{T}}/\text{MgO}$  value of Luotuoquan granite ranges from 2.95 to 24.28 (mean of 6.95), which is significantly greater than that of highly fractionated I-type granite (2.27) and S-type granite (2.38) [57,58]. Additionally, typical A-type granites are enriched in trace elements such as Th, Nb, Ta, Zr, Hf, Ga, and Y while being depleted in Sr, Ti, P, Cr, Co, Ni, V, etc., with obvious negative Eu anomaly [57,59]. All samples exhibit high Th, Zr, K, Ga, Y, and Yb but low Sr, P, Eu, and Ti, which also implies that Luotuoquan granite had A-type geochemical features. Previous studies suggested that A-type granitoids share similar geochemistry characteristics of high  $10,000 \times \text{Ga}/\text{Al}$  values ( $>2.6$ ) and  $\text{Zr} + \text{Nb} + \text{Ce} + \text{Y}$  ( $>350$  ppm) [57]. The discrimination diagrams (Figure 8)



demonstrate that the majority, if not all, of the samples are plotted within the A-type granite field. We, therefore, conclude that the Luotuoquan monzogranite–syenogranite pluton are typical A-type intrusions.

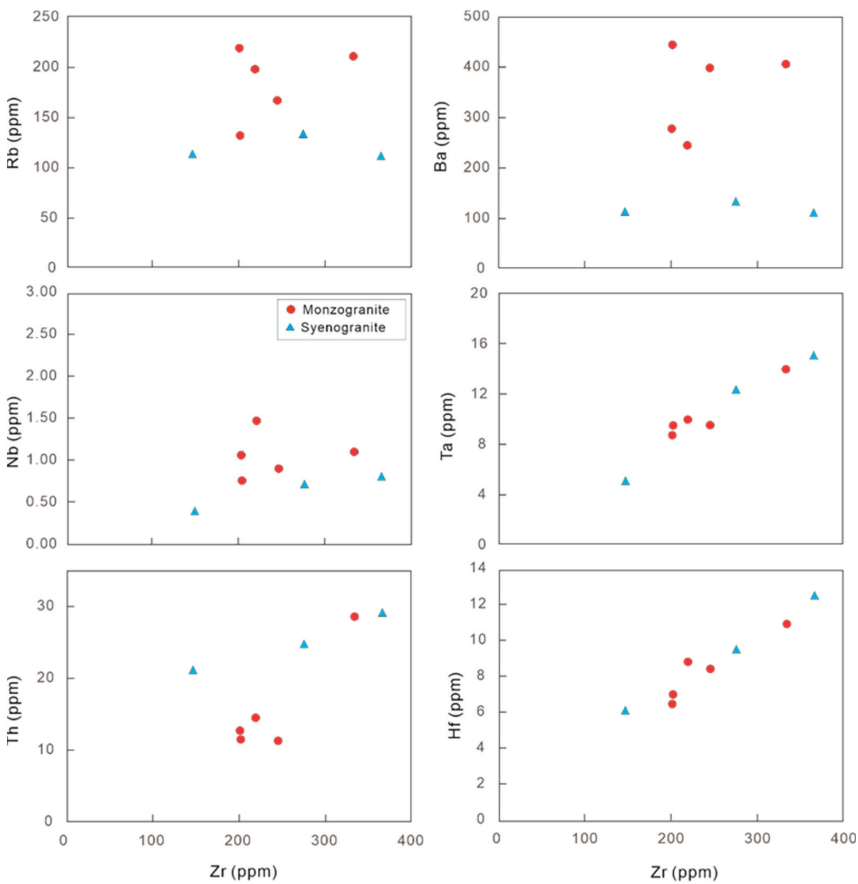


Figure 7. Trace elements vs. Zr for Luotuoquan A-type granites.

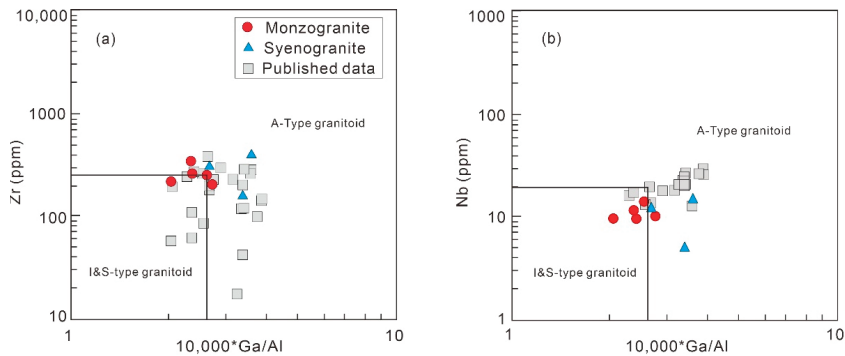
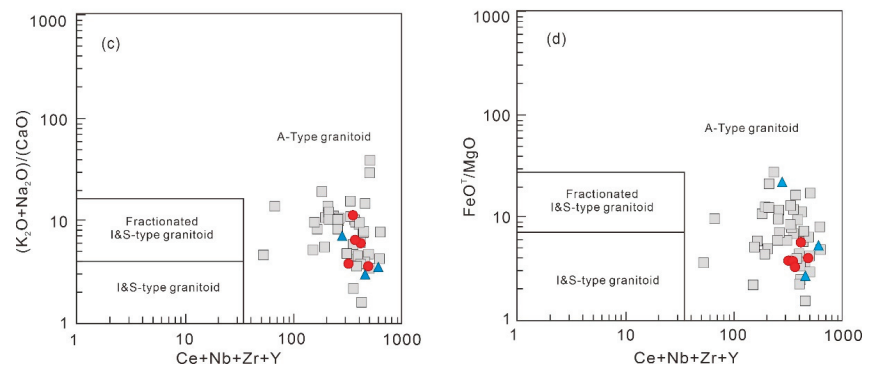


Figure 8. Cont.

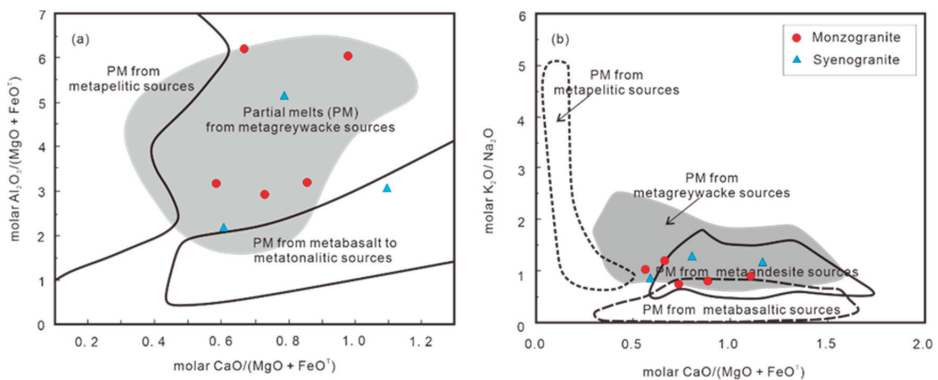


**Figure 8.** Discrimination diagrams for early Devonian granitoids from BOB. Zr (a) and Nb (b) vs.  $10,000 * Ga/Al$  and  $(K_2O + Na_2O)/CaO$  (c) and  $FeO^T/MgO$  (d) vs.  $Ce + Nb + Zr + Y$  diagrams [57]. Published data are from the same references as in Figure 5.

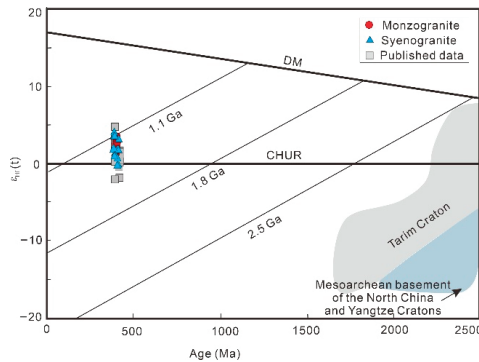
Various petrogenetic models have been proposed for A-type granites: (1) high crystallization differentiation of mantle-derived basaltic magma [60–63]; (2) mixing of mantle-derived and crustal materials [64–67]; (3) Partial melting of lower crustal material: partial melting of granulite facies remnants after granitic magma extraction [55,56,59,68], and partial melting of calc-alkaline tonalite-granodiorite [69]; (4) the melting of lower crustal rocks due to heating by mantle magma underplating [58,70,71]. Mafic rocks contemporaneous with A-type granite are rare in the study area, and no mafic microgranular enclaves are found in the granites, indicating little crust–mantle mixing. Experimental petrology shows residual granulite facies in the lower crust are low in K, Si and high in Ca, Al, and Mg [69], which cannot explain the production of Luotuoquan A-type granite rich in Si, alkali, low in Al and Mg by partial melting.

The  $CaO/Na_2O$  ratios distinguish between pelite-derived melts ( $CaO/Na_2O < 0.5$ ) and melts derived from greywackes or igneous sources ( $CaO/Na_2O = 0.3–1.5$ ) [72]. High-temperature melts generally exhibit lower  $Al_2O_3/TiO_2$  ratios than low-temperature melts [73]. The monzogranite–syenogranite is characterized by high  $CaO/Na_2O$  ratios (mean of 0.53) and low  $Al_2O_3/TiO_2$  ratios (mean of 63.73), suggesting a source of metagreywackes or metamorphic igneous rock. The samples are all plotted within the field of partial melts derived from metagreywackes in the molar  $Al_2O_3/(MgO + FeO^T)$  vs. molar  $CaO/(MgO + FeO^T)$  and molar  $K_2O/Na_2O$  vs. molar  $CaO/(MgO + FeO^T)$  diagrams (Figure 9). Therefore, the granitic magma source is likely related to partial melts from metagreywackes.

The Hf isotope analysis of U–Pb dated zircon grains can trace the original magma sources and distinguish between the reworking of continental crust and the remelting of juvenile crust [74,75]. In this study, the early Devonian Luotuoquan monzogranite–syenogranite has considerably positive zircon  $\epsilon_{Hf}(t)$  of  $+0.9–+5.2$  (Figure 10) and slightly young two-stage Hf model ages of 1.05–1.34 Ga (Figure 10). The SBOB is thought to have developed abundant Mesoproterozoic to Neoproterozoic basement complex, which is a suite of metamorphosed clastic rock [17,18,20,37]. The significantly positive  $\epsilon_{Hf}(t)$  values and relatively young two-stage Hf model ages suggest that the granitic rocks originated from either the depleted mantle or through partial melting of recently accreted juvenile crustal material within the depleted mantle. Relevant mafic rocks are rarely contemporaneous, and the absence of mafic microgranular enclaves suggests limited direct involvement of newly derived mantle magma in granite formation. Therefore, the early Devonian granitoids from the SBOB primarily originated from partial melting of the overlying Mesoproterozoic crust facilitated by the underplating of mantle-derived magma.



**Figure 9.** Discrimination diagrams of the source area of the Luotuoquan monzogranite and syenogranite. (a) molar  $\text{Al}_2\text{O}_3/(\text{MgO} + \text{FeO}^T)$  vs. molar  $\text{CaO}/(\text{MgO} + \text{FeO}^T)$  [76]; (b) molar  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  vs. molar  $\text{CaO}/(\text{MgO} + \text{FeO}^T)$  [77].



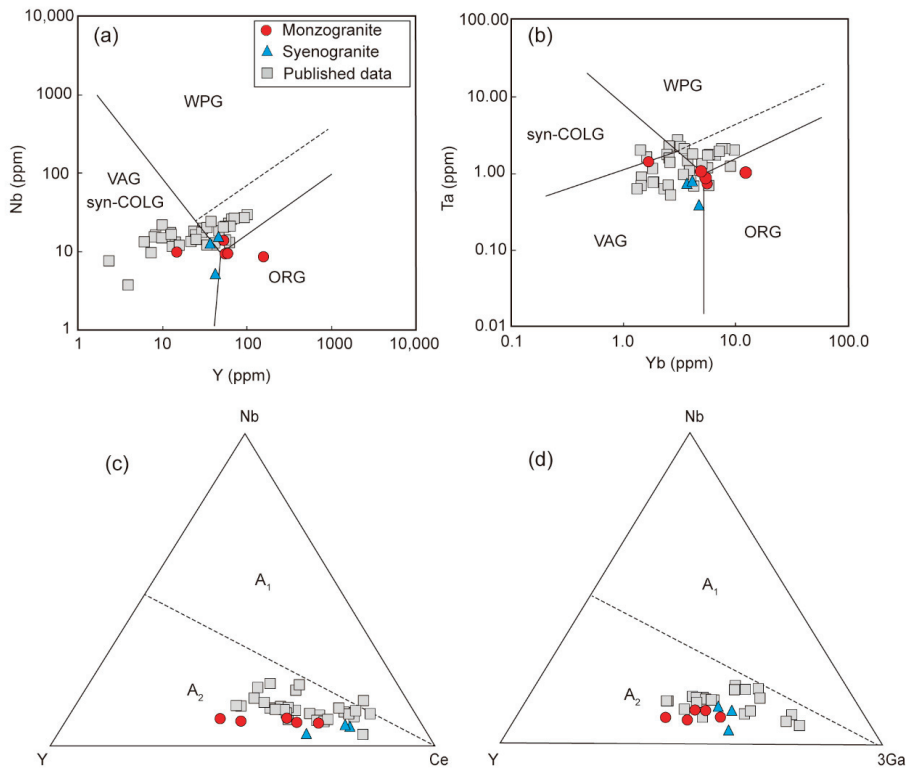
**Figure 10.** Zircon  $\epsilon_{\text{Hf}}(t)$  vs. Age (Ma) diagrams of granitoids from the SBOB (base map after [75]). Published data of granitoids from [6,42]. The data on Tarim, North China, and Yangtze blocks were from [78].

### 5.3. Geodynamic Evolution

Recent research suggests that the BOB is an accretionary orogen with multiple island arcs and mélangé belts that experienced subduction–collision during the Paleozoic [5,12, 28,30,37]. The zircon U–Pb age of the ophiolite complexes in the central part of the BOB is 536–519 Ma [7,79–81], and the lower Cambrian Shuangyingshan Formation unconformable overlies the Neoproterozoic Xichangjing Formation [38], indicating the Beishan Ocean was formed before the Cambrian. Previous studies have proposed that the magmatic effects of slab windows vary dramatically during ridge subduction, forming adakitic magmas due to slab melting and A-type magmas resulting from asthenosphere upwelling through the slab window [54,82]. Widespread early Paleozoic magmatic rocks (464–424 Ma) [6,10,16, 32,37,40,83,84] and ophiolitic mélangé (462–420 Ma) [9,13,39,85] in the BOB indicate slab subduction setting during the Ordovician to Devonian.

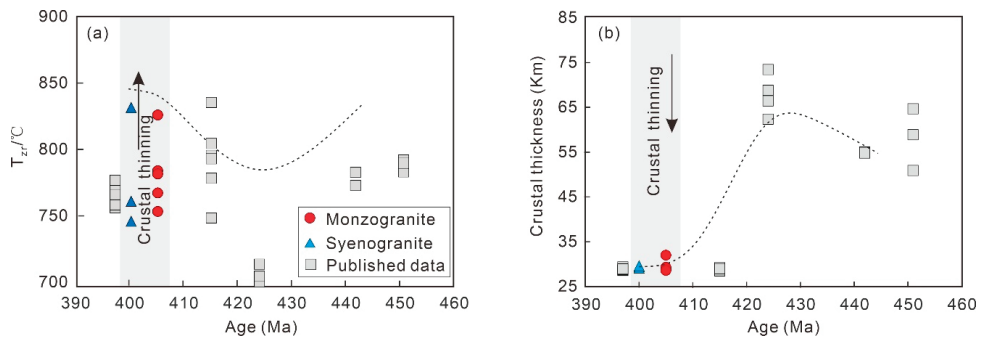
The A-type granite has garnered significant attention due to its distinctive tectonic background. The Luotuoquan A-type granites fall within the volcanic arc and within-plate granites on tectonic discrimination diagrams (Figure 11a,b) rather than pertaining to ocean ridge granites. The studied granites are generally plotted within the A2 field (Figure 11c,d). The A2-type granitoids represent magmas sourced from the underplated crust or continental crust that has experienced a cycle of island-arc magmatism or continent–continent collision [86]. We propose that their potential origins were associated with

island-arc magmatism. The monzogranite in the Hongliuhe ophiolite has a weighted age of  $412.4 \pm 2.9$  Ma, indicating that the closure of the oceanic basin was completed prior to this event [41]. The granites from the Liuyuan area, with ages ranging from 436–423 Ma [40], 415 Ma [42], and 397 Ma [4,40], represent post-collision background products that are possibly associated with subduction plate detachment. Moreover, recent discoveries have revealed the presence of early Devonian post-collision granites in the middle of BOB. U–Pb dating has determined that these granites range in age from 402 to 387 Ma [15,31,35,52]. The aforementioned evidence suggests that the formation of Luotuoquan A-type granites can be attributed to a post-collision tectonic setting.



**Figure 11.** Nb vs. Y (a), Ta vs. Yb (b), Nb–Y–Ce (c), Nb–Y–3Ga (d) tectonic discriminant diagrams of the early Devonian granitoids from BOB ((a,b) modified after [56], (c,d) modified after [86]). Syn-COLG–syn-collision granites; VAG–volcanic arc granites; WPG–within plate granites; ORG–ocean ridge granites; post-COLG–post collision granites. Published data are from the same references as in Figure 5.

Whole-rock geochemical data of 460–390 Ma granites from the SBOB were collected to calculate zircon saturation temperatures ( $\ln D_{Zr} = (10,108 \pm 32)/T(K) - (1.16 \pm 0.15)(M - 1) - (1.48 \pm 0.09)$ ) [87],  $M = (Na + K + 2Ca)/(Al \times Si)(mol)$  [88] and crustal thickness ( $H = [Sr/Y + (42.03 \pm 6.28)]/(1.49 \pm 0.15)$ ) [89,90]. During the early Paleozoic, a significant increase in crustal growth occurred due to the melting of subducting oceanic crust, resulting in the emplacement of large amounts of granitoids in the SBOB from 452 to 424 Ma [6]. This process was accompanied by a gradual decrease in zircon saturation temperatures and an increase in crustal thickness (Figure 11). The A-type granites, which were formed between 415 and 397 Ma [4,42], exhibit a higher Zr saturation temperature range of 755–831 °C and a thinner crust thickness ranging from 32 to 28 km (Figure 12). These findings suggest that the SBOB had already transitioned into an extensional setting during the early Devonian.



**Figure 12.**  $T_{zr}$  vs. Age (a) and Crustal thickness vs. Age (b) plots for Paleozoic granitoids in the SBOB. Published data from [4,6,42].

In summary, the Luotuoquan A-type granites yield U–Pb ages of approximately 404–399 Ma, indicating post-collision extensional setting during the early Devonian. This evidence indicates a post-collision extension setting in the early Devonian and implies the closure of the Beishan Ocean prior to this time.

## 6. Conclusions

- (1) The zircon U–Pb ages of the Luotuoquan monzogranite and syenogranite are  $399.4 \pm 5.1$  Ma and  $404.9 \pm 1.4$  Ma, respectively.
- (2) The petrographic and geochemical signatures of the Luotuoquan monzogranite and syenogranite indicate they are A-type granites and were emplaced in a post-collision extensional setting. Furthermore, these granites are the result of partial melting primarily from Mesoproterozoic crusts composed mainly of metagreywackes.
- (3) The occurrence of early Devonian granitoids suggests that SBOB had already undergone extensional tectonics following the closure of the Beishan Ocean during this period.

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## Article

# Petrogenesis and Tectonic Evolution of Huashigou Granitoids in the South Qilian Orogen, NW China: Constraints from Geochronology, Geochemistry, and Sr–Nd–Hf–O Isotopes

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**Abstract:** The origin of granitic rocks from the South Qilian orogenic belt is of great significance for understanding the continental tectonic framework of Western China. Currently, scholars have different opinions on the tectonic evolution of the South Qilian. Huashigou granite, which exhibits multiple intrusive episodes, is a suitable example for studying the tectonic evolution of the South Qilian. New zircon U–Pb ages and the whole-rock elemental and Sr–Nd–Hf–O isotopic compositions of Huashigou granitic rocks are presented here to investigate their petrogenesis and discuss the tectonic implications for the evolution of the South Qilian orogenic belt. LA-ICP-MS zircon U–Pb dating yielded crystallization ages of  $368.7 \pm 3.5$  Ma,  $261.5 \pm 0.63$  Ma, and  $262.2 \pm 1.4$  Ma for granodiorites from the Hua1 pluton, quartz diorites from the Hua2 pluton, and porphyritic tonalites from the Hua4 pluton, respectively. Late Devonian granodiorites from the Hua1 pluton belonged to the metaluminous calc-alkaline series and were characterized by an enrichment in LREEs, a depletion in HREEs, negative Eu anomalies, and Sr/Y ratios of 9.17 to 11.67. They showed ( $^{87}\text{Sr}/^{86}\text{Sr}$ )<sub>i</sub> ratios of 0.712356 to 0.711195,  $\epsilon_{\text{Nd}}(t)$  values of  $-6.56$  to  $-6.14$ , and an  $\epsilon_{\text{Hf}}(t)$  value of  $-2.06$ . Middle Permian granitic rocks mainly consisted of quartz diorites and porphyritic tonalites, which are part of the metaluminous tholeiitic series and weakly peraluminous tholeiitic series, respectively. Quartz diorites from the Hua2 pluton were characterized by an enrichment in LREEs, depletions in HREEs and HESEs, weak negative Eu anomalies, and Sr/Y ratios of 13.25 to 14.79. They showed ( $^{87}\text{Sr}/^{86}\text{Sr}$ )<sub>i</sub> ratios of 0.705905 to 0.705971,  $\epsilon_{\text{Nd}}(t)$  values of  $+0.78$  to  $+0.82$ , and a  $\delta^{18}\text{O}_{\text{V-SMOW}}$  value of 12.4‰. Porphyritic tonalites of the Hua4 pluton were characterized by an enrichment in LREEs, depletions in HREEs and HESEs, weak negative Eu anomalies, and Sr/Y ratios of 9.22 to 12.74. They showed ( $^{87}\text{Sr}/^{86}\text{Sr}$ )<sub>i</sub> ratios of 0.719528,  $\epsilon_{\text{Nd}}(t)$  values of  $-8.57$ , and a  $\delta^{18}\text{O}_{\text{V-SMOW}}$  value of 11.8‰. We can conclude that Late Devonian granodiorites were derived from the partial melting of enriched and shallow-depth crustal materials, whereas Middle Permian granitic rocks were formed by the delamination of a thickened lower crust after the closure of the Paleo-Tethys Ocean, which caused the underplating of mantle-derived basaltic magma, inducing the partial melting of the lower crust at different depths. Our results show that there were at least two important stages of compressional and extensional tectonic switches in the South Qilian orogenic belt during the Late Paleozoic Era, and the evolution of Altyn Tagh–Qilian–North Qaidam had evident stages.

**Keywords:** granitoids; geochemistry; Sr–Nd–Hf–O isotopes; tectonic evolution; Qilian orogenic belt

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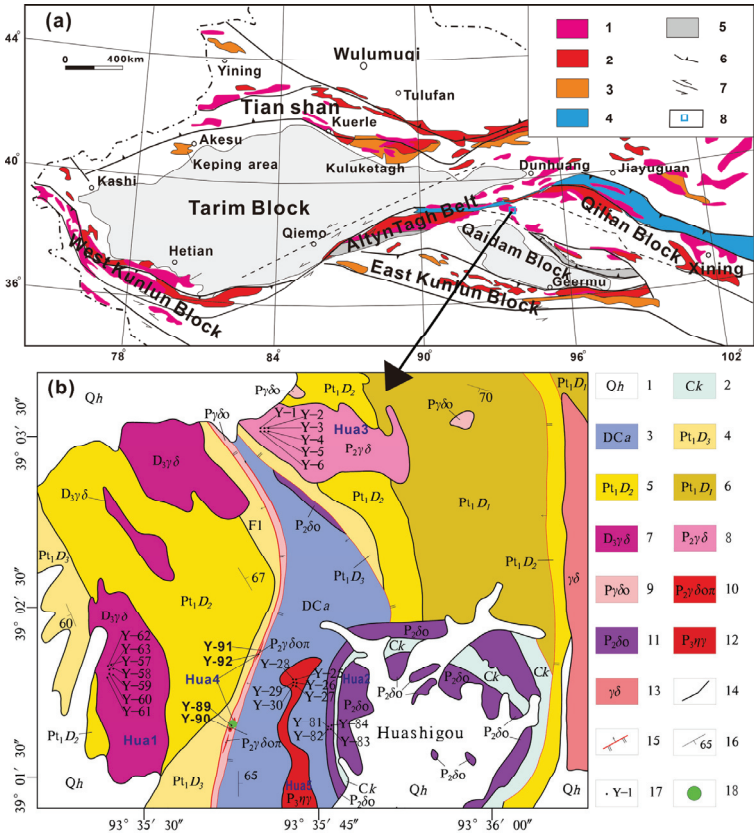
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1. Introduction

The Qilian orogenic belt, located at the northeastern margin of the Tibetan Plateau, is located in the western part of the central orogenic belt that runs across China from east to west [1–5]. The Qaidam Block is located to the south of the belt. The Tarim Craton is located northwest of the belt, delineated by the Altyn Tagh Fault (Figure 1a). A majority of studies have been conducted to investigate the evolution of the Altyn Tagh–Qilian–North Qaidam tectonic system [6–27]. These studies focus on the discovery of an ultrahigh-pressure metamorphic belt (UHPB) in the North Qaidam and Altyn Tagh regions and its comparison to the Altyn Tagh–Qilian–North Qaidam tectonic system [3,28–33]. As a ubiquitous intrusive mass in the orogenic belt, granitoids have recorded much information about plate tectonics and crustal evolution [12,34–40]. Additionally, there are similarities between the tectonic units on both sides of Altyn Tagh.



**Figure 1.** Tectonic location (a) and geological sketch map (b) of the South Qilian Orogen. (a): 1. Archean–Paleoproterozoic basement; 2. Mesoproterozoic rock; 3. Neoproterozoic rock; 4. Early Paleozoic subduction collision complex belt; 5. Early Paleozoic subduction hyperplasia complex belt; 6. thrust fault; 7. strike-slip fault; and 8. study area. (b): 1. Quaternary; 2. Carboniferous Yanghugou Group; 3. Devonian–Carboniferous Amunike Group; 4. Paleoproterozoic Dakendaban Group (the Third Rock Group); 5. Paleoproterozoic Dakendaban Group (the Second Rock Group); 6. Paleoproterozoic Dakendaban Group (the First Rock Group); 7. Late Devonian granodiorites (Hua1); 8. Middle Permian granitoids (Hua3); 9. quartz mica diorites; 10. Middle Permian quartz mica porphyritic diorites (Hua4); 11. Middle Permian quartz diorites (Hua2); 12. Late Permian monzogranites (Hua5); 13. granodiorites; 14. geological boundary; 15. faults; 16. attitude; 17. sample locations; and 18. copper deposits.



Previous studies have mainly focused on Early Paleozoic granitic rocks in the North Qilian orogenic belt, while studies on Late Paleozoic granitoids are relatively scarce. Since the closure of the Qilian orogenic belt in the Mid–Late Paleozoic, there has been a paucity of pertinent research findings. Consequently, Late Paleozoic granitic rocks serve as a pivotal means to unveil not only their geodynamic implications but also the geological evolution of the Qilian orogenic belt.

In this study, we present results from petrographic, geochronologic, and whole-rock elemental and Sr–Nd–Hf–O isotopic composition analyses in an attempt to investigate the petrogenesis of Paleozoic Huashigou granitoids in the South Qilian along the northeastern margin of the Tibetan Plateau. These data could be used to infer and determine the age, genesis, and tectonic environment of the rocks formed during that period in the South Qilian. The data were used to evaluate the crustal evolution of the Qilian Orogen in the Late Paleozoic.

## 2. Regional Geology and Petrography

The Huashigou area is located at the southwest margin of the Qilian Orogen, which is at the junction of the Altyn Tagh–Qilian–North Qaidam tectonic belt. Paleoproterozoic (Dakendaban Group), Devonian (Amunike Formation), and Carboniferous (Keluke Formation) strata are widely distributed in the study area. The Paleoproterozoic Dakendaban Group represents a major stratigraphic formation developed in this area. The Devonian and Carboniferous strata are mainly distributed at the center of the study area. Faults extend in the north–south and north–west directions. The Huashigou area consists of five types of granitic rocks, including granodiorite, biotite granodiorite, porphyritic tonalite, quartz diorite, and monzonitic granite (Figure 1b).

Three granodiorite intrusions exist, with sizes ranging from 2 to 0.1 km<sup>2</sup>, which intruded into Paleoproterozoic metamorphic rocks (Dakendaban Group). The Hua1 pluton is composed of plagioclase (47%), quartz (20%), albite (18%), biotite (10%), hornblende (5%), and accessory minerals, including apatite, zircon, sphene, and magnetite. Plagioclases are wide and tabular and are intensively altered, with sericitization, decarbonation, and clayzation alterations. Some plagioclase grains wrapped in microcline have an obvious albite reaction rim. Quartzes are in a xenomorphic–granular form, and some of them show wavy extinction in rare situations.

The Hua2 pluton is mainly located south of the study area, with extensive exposure intruding in the Paleoproterozoic Dakendaban Group and Carboniferous Keluke Group, with a long strip layout and small areas in general. The pluton exhibits a subhedral–granular texture and a blocky structure and consists of plagioclase (70%), normal hornblende (15%), quartz (10%), and biotite (5%), with minor accessory minerals, including apatite, zircon, sphene, and magnetite. Plagioclases are mainly tabular and dotted with small amounts of secondary minerals, such as clay, microcryptocrystalline zoisite, sericite, and carbonates. Hornblende is intensively altered, with actinolitization along fractures.

The Hua3 pluton is located north of the study area, covering about 2 km<sup>2</sup> in a nearly elliptical shape. With a fine-grained granite texture, the pluton mainly has a blocky structure and is composed of plagioclase (49%), orthoclase (15%), quartz (18%), biotite (15%), microcline (3%), and accessory minerals, including apatite, zircon, and magnetite. The tabular biotite is slightly wrapped in orthoclase, and the plagioclase has a visible polysynthetic twin and a mostly rapakivi structure. LA-ICP-MS zircon U–Pb dating indicated that the pluton was emplaced in the Middle Permian ( $261.1 \pm 3.8$  Ma [41]).

The irregular zonal Hua4 pluton is mainly distributed along the F1 Fault. The pluton shows typical porphyritic textures, and its phenocrysts include plagioclase and quartz. Its groundmass is composed of plagioclase, quartz, sericite, and biotite, with microgranular, cataclastic, and blocky structures. The plagioclase phenocrysts are in lenticular and elliptical shapes, and some parts have a wide tabular shape, with particle sizes ranging from 0.6 to 1.0 mm. Quartz phenocrysts have an elliptical shape, aggregating along the fractures with a sericite particle size of  $\pm 1.0$  mm.



The Hua5 pluton intruded into the Devonian Amunike Group, with an exposed surface area of about 0.4 km<sup>2</sup>. The pluton displays a fine-grained granitic and blocky structure and consists of plagioclase (45%), quartz (23%), biotite (12%), perthite (12%), microcline (7%), and minor accessory minerals, such as apatite, sphene, zircon, and magnetite. LA-ICP-MS zircon U–Pb dating indicated that the pluton was formed in the Late Permian (252.0 ± 2.1 Ma [42]).

### 3. Analytical Methods

Sixteen samples were collected from the granitic plutons in the Huashigou area, including seven from the Hua1 pluton (YQ57–YQ63), four from the Hua2 pluton (YQ81–84), and four from the Hua4 pluton (YQ89–92). The locations of the analyzed samples are shown in Figure 1b.

#### 3.1. Zircon U–Pb Age Analytical Method

Firstly, zircon grains were separated using conventional magnetic techniques and handpicked using a binocular microscope (BX51, Olympus, Tokyo, Japan). The zircon grains were mounted in an epoxy mount and polished down to a half-section. Prior to the isotope analysis, all grains were photographed under transmitted and reflected light and subsequently examined using cathode luminescence (CL) images (JSM-6510, JEOL, Tokyo, Japan). The zircon LA-ICP-MS U–Pb analyses were performed on a 7500 ICP-MS (Agilent, Santa Clara, CA, USA) with a UP193SS LA (New Wave, Seattle, WA, USA) at the Key Laboratory of Lithospheric Tectonics and Exploration of the Ministry of Education, China University of Geosciences (Beijing), China. The samples were analyzed in runs, with four GJ-1 zircon standards measured every ten to twelve samples. The analytical data were then reduced, calculated, and plotted using the Squid 1.0 and Isoplot programs (version 4.00.08.09.16, by KR Ludwig, Berkeley Geochr. Ctr., Berkeley, CA, USA) [43]. The compositions of common Pbs were corrected following the Andersen method [44]. Errors during the individual analyses are cited at 1σ, and the weighted age uncertainties are quoted at a confidence level of 95%.

#### 3.2. Whole-Rock, Sr–Nd–O, and Hf Isotopic Analytical Method

The whole-rock major elements, trace elements, and Sr–Nd–Hf isotopes were determined at the State Key Laboratory of Continental Dynamics, Northwest University, China. The samples for the whole-rock chemical analysis were crushed to 200 mesh. The major-element contents of the samples were analyzed using the RIX-2100 (RIGAKU, Tokyo, Japan) X-ray fluorescence spectrometer (XRF). The analytic uncertainties were generally less than 2% for most of the major elements and 2% to 5% for the major elements with <1 wt.% contents. Trace elements and rare-earth elements (REEs) were analyzed using the Elan-6100DRC model ICP-MS (Perkin Elmer, Waltham, MA, USA). About 50 mg of the powder samples was dissolved in high-pressure Teflon bombs using a HF + HNO<sub>3</sub> mixture. The analytical precision was better than 5%. The Nd, Sr, and Hf isotopic analyses were performed using MC-ICP-MS (Nu Instruments, North Wales, UK), and the isotopic ratios were, respectively, normalized to <sup>143</sup>Nd/<sup>144</sup>Nd = 0.7219, <sup>87</sup>Sr/<sup>86</sup>Sr = 8.3721, and <sup>176</sup>Hf/<sup>177</sup>Hf = 0.7325. The oxygen-stable isotopes of the whole-rock samples were determined at the Institute of Mineral Resources, Chinese Academy of Geological Science (Beijing, China). The oxygen isotopic compositions (δ<sup>18</sup>O) were analyzed using the BrF<sub>5</sub> method and measured using the MAT-253 mass spectrometer (MAT-253, Thermo Fisher Scientific, Waltham, MA, USA), according to international standards (SMOW), with a precision of ±0.2 ‰.

### 4. Results

Fifteen samples were collected for the major- and trace-element analyses, of which three samples were used for zircon U–Pb dating, six samples were used for Sr–Nd isotopic analyses, one sample was used for Hf isotopic analyses, and two samples were used for O isotopic analyses. The detailed data are presented in Tables 1–3.

Table 1. Major- and trace-element compositions of Huashigou granitoids.

| Lithology                           |        | Hua1   |        |        |        |        |        | Hua2   |        |        |        | Hua4    |        |         |         |
|-------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|---------|--------|---------|---------|
| Sample                              | YQ-57  | YQ-58  | YQ-59  | YQ-60  | YQ-61  | YQ-62  | YQ-63  | YQ-81  | YQ-82  | YQ-83  | YQ-84  | YQ-89   | YQ-90  | YQ-91   | YQ-92   |
| Major elements (%)                  |        |        |        |        |        |        |        |        |        |        |        |         |        |         |         |
| SiO <sub>2</sub>                    | 67.78  | 68.48  | 67.81  | 68.87  | 68.16  | 68.35  | 68.44  | 52.41  | 53.32  | 52.43  | 52.54  | 67.28   | 66.43  | 63.64   | 67.01   |
| TiO <sub>2</sub>                    | 0.41   | 0.40   | 0.48   | 0.42   | 0.44   | 0.42   | 0.41   | 1.58   | 1.40   | 1.57   | 1.57   | 0.50    | 0.49   | 0.55    | 0.48    |
| Al <sub>2</sub> O <sub>3</sub>      | 15.77  | 15.29  | 15.43  | 15.26  | 15.41  | 15.52  | 15.45  | 19.69  | 19.66  | 19.67  | 19.68  | 16.07   | 16.34  | 16.62   | 16.18   |
| TFe <sub>2</sub> O <sub>3</sub>     | 3.69   | 3.62   | 4.01   | 3.67   | 3.83   | 3.68   | 3.60   | 9.23   | 8.71   | 9.01   | 8.91   | 3.95    | 3.83   | 4.34    | 3.72    |
| MnO                                 | 0.06   | 0.06   | 0.06   | 0.06   | 0.06   | 0.06   | 0.06   | 0.09   | 0.11   | 0.09   | 0.09   | 0.03    | 0.04   | 0.06    | 0.04    |
| MgO                                 | 1.22   | 1.19   | 1.38   | 1.20   | 1.31   | 1.25   | 1.21   | 3.18   | 2.99   | 3.25   | 3.14   | 1.81    | 1.73   | 2.50    | 2.09    |
| CaO                                 | 3.80   | 3.48   | 3.72   | 3.39   | 3.65   | 3.66   | 3.56   | 8.07   | 7.97   | 8.11   | 7.91   | 1.65    | 2.08   | 2.93    | 1.82    |
| Na <sub>2</sub> O                   | 3.79   | 3.60   | 3.53   | 3.57   | 3.65   | 3.68   | 3.65   | 4.81   | 4.75   | 4.91   | 4.77   | 4.13    | 4.39   | 3.50    | 4.41    |
| K <sub>2</sub> O                    | 2.71   | 3.06   | 2.83   | 3.06   | 3.02   | 2.99   | 3.01   | 0.64   | 0.63   | 0.65   | 0.68   | 3.77    | 3.63   | 3.80    | 3.61    |
| P <sub>2</sub> O <sub>5</sub>       | 0.11   | 0.13   | 0.15   | 0.13   | 0.14   | 0.13   | 0.13   | 0.23   | 0.24   | 0.24   | 0.22   | 0.14    | 0.14   | 0.12    | 0.14    |
| LOI                                 | 0.95   | 0.90   | 0.94   | 0.82   | 0.61   | 0.67   | 0.77   | 0.31   | 0.54   | 0.34   | 0.29   | 0.95    | 1.06   | 1.47    | 0.86    |
| TOTAL                               | 100.29 | 100.21 | 100.34 | 100.45 | 100.28 | 100.41 | 100.29 | 100.24 | 100.32 | 100.27 | 99.8   | 100.28  | 100.16 | 99.53   | 100.36  |
| Mg <sup>#</sup>                     | 37.24  | 37.10  | 38.18  | 36.98  | 38.03  | 37.87  | 37.62  | 38.20  | 38.12  | 39.29  | 38.74  | 45.12   | 44.77  | 50.83   | 50.20   |
| A/CNK                               | 1.07   | 1.05   | 1.07   | 1.06   | 1.04   | 1.05   | 1.05   | 1.06   | 1.07   | 1.04   | 1.07   | 1.15    | 1.11   | 1.12    | 1.13    |
| Trace elements (×10 <sup>−6</sup> ) |        |        |        |        |        |        |        |        |        |        |        |         |        |         |         |
| Rb                                  | 90.18  | 105.55 | 95.42  | 107.30 | 106.60 | 105.01 | 105.51 | 16.78  | 17.93  | 16.61  | 18.61  | 146.57  | 140.96 | 190.47  | 164.27  |
| Cs                                  | 2.44   | 2.92   | 2.50   | 3.15   | 3.44   | 3.31   | 3.36   | 0.88   | 0.89   | 0.87   | 0.91   | 4.52    | 4.31   | 6.09    | 5.11    |
| Sr                                  | 226.50 | 211.00 | 218.50 | 205.30 | 210.30 | 213.10 | 210.50 | 585.70 | 573.90 | 584.60 | 593.10 | 172.40  | 197.90 | 217.30  | 194.90  |
| Ba                                  | 690.00 | 702.30 | 777.70 | 685.20 | 700.70 | 679.20 | 666.00 | 191.40 | 177.60 | 194.00 | 203.50 | 1066.10 | 993.00 | 1015.30 | 1103.40 |
| Sc                                  | 7.81   | 8.08   | 9.25   | 8.28   | 8.77   | 8.01   | 8.23   | 27.04  | 24.30  | 27.61  | 25.72  | 10.40   | 10.62  | 9.33    | 10.30   |
| Nb                                  | 14.02  | 14.82  | 16.40  | 15.90  | 15.31  | 14.68  | 14.69  | 11.41  | 11.29  | 11.34  | 11.80  | 13.81   | 13.30  | 13.59   | 13.18   |
| Ta                                  | 0.98   | 1.11   | 1.14   | 1.28   | 1.10   | 1.14   | 1.08   | 0.53   | 0.60   | 0.55   | 0.57   | 1.00    | 1.00   | 0.93    | 0.95    |
| Zr                                  | 196.99 | 200.86 | 195.42 | 194.65 | 223.69 | 192.78 | 230.61 | 213.65 | 227.58 | 215.93 | 194.50 | 171.99  | 184.44 | 143.45  | 155.80  |
| Hf                                  | 4.82   | 5.08   | 4.91   | 5.04   | 5.66   | 4.89   | 5.72   | 4.86   | 5.23   | 4.91   | 4.42   | 4.42    | 4.70   | 3.64    | 4.07    |
| U                                   | 1.59   | 1.62   | 1.75   | 1.61   | 1.50   | 1.46   | 1.89   | 0.54   | 0.77   | 0.58   | 0.44   | 3.48    | 3.02   | 2.50    | 1.85    |
| Th                                  | 13.76  | 19.08  | 18.32  | 20.48  | 18.26  | 17.15  | 19.12  | 2.59   | 2.59   | 2.41   | 2.99   | 14.53   | 16.05  | 9.89    | 13.48   |
| Cr                                  | 7.12   | 7.69   | 8.68   | 6.81   | 7.53   | 7.16   | 6.70   | 5.25   | 3.67   | 4.14   | 5.07   | 13.32   | 10.51  | 9.50    | 10.30   |
| Ni                                  | 6.15   | 6.34   | 7.21   | 5.88   | 6.47   | 6.20   | 6.15   | 8.80   | 6.65   | 7.46   | 9.45   | 11.71   | 10.71  | 11.99   | 9.59    |
| La                                  | 39.88  | 47.78  | 49.15  | 55.70  | 51.45  | 41.47  | 48.44  | 22.45  | 21.54  | 22.81  | 24.04  | 35.27   | 43.04  | 39.44   | 28.11   |
| Ce                                  | 71.71  | 83.73  | 90.00  | 99.07  | 89.04  | 73.19  | 84.75  | 56.02  | 55.19  | 56.33  | 56.94  | 61.80   | 72.08  | 64.31   | 49.20   |
| Pr                                  | 7.01   | 8.53   | 8.96   | 9.72   | 8.97   | 7.48   | 8.42   | 7.93   | 8.01   | 8.00   | 7.88   | 6.44    | 7.44   | 6.40    | 5.17    |
| Nd                                  | 23.53  | 28.52  | 30.33  | 32.69  | 30.10  | 25.57  | 28.36  | 36.66  | 38.06  | 36.75  | 35.55  | 22.45   | 25.07  | 22.19   | 18.42   |
| Sm                                  | 3.92   | 4.70   | 5.06   | 5.20   | 4.90   | 4.39   | 4.60   | 8.63   | 9.04   | 8.74   | 8.27   | 3.89    | 4.19   | 3.65    | 3.37    |
| Eu                                  | 1.09   | 1.04   | 1.11   | 1.03   | 1.07   | 1.05   | 1.04   | 2.40   | 2.36   | 2.42   | 2.37   | 0.82    | 0.95   | 1.58    | 0.82    |
| Gd                                  | 3.58   | 4.23   | 4.55   | 4.59   | 4.36   | 4.04   | 4.12   | 8.43   | 8.67   | 8.60   | 8.10   | 3.45    | 3.83   | 3.27    | 3.20    |
| Tb                                  | 0.53   | 0.62   | 0.67   | 0.67   | 0.64   | 0.60   | 0.60   | 1.30   | 1.35   | 1.33   | 1.25   | 0.52    | 0.57   | 0.46    | 0.50    |
| Dy                                  | 3.25   | 3.74   | 4.04   | 3.99   | 3.78   | 3.65   | 3.57   | 7.79   | 7.96   | 7.94   | 7.44   | 3.13    | 3.46   | 2.66    | 3.11    |
| Ho                                  | 0.65   | 0.75   | 0.80   | 0.80   | 0.76   | 0.74   | 0.73   | 1.54   | 1.59   | 1.57   | 1.48   | 0.64    | 0.70   | 0.55    | 0.65    |
| Er                                  | 1.91   | 2.24   | 2.36   | 2.41   | 2.27   | 2.18   | 2.13   | 4.32   | 4.45   | 4.37   | 4.13   | 1.92    | 2.10   | 1.72    | 1.91    |
| Tm                                  | 0.30   | 0.35   | 0.37   | 0.38   | 0.35   | 0.35   | 0.34   | 0.62   | 0.64   | 0.62   | 0.59   | 0.30    | 0.33   | 0.28    | 0.30    |
| Yb                                  | 1.99   | 2.32   | 2.42   | 2.49   | 2.33   | 2.29   | 2.23   | 3.75   | 3.97   | 3.77   | 3.62   | 2.03    | 2.15   | 2.01    | 1.95    |
| Lu                                  | 0.31   | 0.36   | 0.37   | 0.38   | 0.36   | 0.35   | 0.35   | 0.55   | 0.58   | 0.55   | 0.52   | 0.32    | 0.34   | 0.33    | 0.30    |
| Y                                   | 19.41  | 22.74  | 23.82  | 24.23  | 22.90  | 22.25  | 21.88  | 42.36  | 43.32  | 42.57  | 40.10  | 18.71   | 20.98  | 17.05   | 19.87   |
| ΣREE                                | 569.67 | 672.88 | 708.91 | 765.86 | 708.83 | 606.44 | 670.30 | 701.28 | 710.84 | 708.67 | 692.53 | 519.60  | 600.28 | 543.21  | 441.35  |
| (La/Yb) <sub>N</sub>                | 14.39  | 14.77  | 14.59  | 16.05  | 15.82  | 12.97  | 15.56  | 4.29   | 3.89   | 4.33   | 4.77   | 12.46   | 14.39  | 14.09   | 10.33   |
| δEu                                 | 0.89   | 0.72   | 0.71   | 0.64   | 0.71   | 0.76   | 0.73   | 0.86   | 0.82   | 0.85   | 0.89   | 0.68    | 0.72   | 1.40    | 0.76    |

Note: The contents of major elements, REEs, and trace elements were analyzed at the State Key Laboratory of Continental Dynamics, Northwest University. An XRF analysis was adopted to analyze major elements, and the experimental instrument used (RIX2100) was manufactured by the Japanese company RIGAKU. Trace elements were analyzed and graded using the Elan6100DRC model ICP-MS, supplied by Perkin Elmer, an American-based company. The relative error and relative standard deviation of the majority of elements were less than 5%.

Table 2. Sr–Nd–Hf–O isotopic compositions of Huashigou granites.

| Sample | <sup>87</sup> Sr/ <sup>86</sup> Sr   | 2s                              | Sr<br>(×10 <sup>−6</sup> ) | Rb<br>(×10 <sup>−6</sup> ) | <sup>86</sup> Sr<br>(×10 <sup>−6</sup> )  | <sup>87</sup> Rb/ <sup>86</sup> Sr       | ( <sup>87</sup> Sr/ <sup>86</sup> Sr) <sub>i</sub>   | U–Pb Age/Ga                          |                                                      |                           |                      |
|--------|--------------------------------------|---------------------------------|----------------------------|----------------------------|-------------------------------------------|------------------------------------------|------------------------------------------------------|--------------------------------------|------------------------------------------------------|---------------------------|----------------------|
| YQ-57  | 0.718408                             | 0.000121                        | 227                        | 90.2                       | 0.0985                                    | 1.153                                    | 0.712356                                             | 0.3687                               |                                                      |                           |                      |
| YQ-63  | 0.719577                             | 0.000114                        | 210                        | 106                        | 0.0985                                    | 1.452                                    | 0.711936                                             | 0.3687                               |                                                      |                           |                      |
| YQ-83  | 0.706211                             | 0.000018                        | 585                        | 16.6                       | 0.0986                                    | 0.082                                    | 0.705905                                             | 0.2618                               |                                                      |                           |                      |
| YQ-84  | 0.706309                             | 0.000023                        | 593                        | 18.6                       | 0.0986                                    | 0.091                                    | 0.705971                                             | 0.2618                               |                                                      |                           |                      |
| YQ-91  | 0.729009                             | 0.000021                        | 217                        | 190                        | 0.0984                                    | 2.542                                    | 0.719528                                             | 0.2622                               |                                                      |                           |                      |
| YX-1   | 0.732882                             | 0.000124                        | 144                        | 154                        | 0.0984                                    | 3.094                                    | 0.721339                                             | 0.2622                               |                                                      |                           |                      |
| Sample | <sup>143</sup> Nd/ <sup>144</sup> Nd | 2s                              | Nd<br>(×10 <sup>−6</sup> ) | Sm<br>(×10 <sup>−6</sup> ) | <sup>144</sup> Nd<br>(×10 <sup>−6</sup> ) | <sup>147</sup> Sm/ <sup>144</sup> Nd     | ( <sup>143</sup> Nd/ <sup>144</sup> Nd) <sub>i</sub> | ε <sub>Nd</sub> (t)                  | T <sub>2DM</sub> (Ga)                                | t <sub>CHUR</sub><br>(Ga) |                      |
| YQ-57  | 0.512070                             | 0.000013                        | 23.5                       | 3.92                       | 0.2380                                    | 0.1006                                   | 0.511827                                             | −6.555202                            | 1.6                                                  | 0.900661                  |                      |
| YQ-63  | 0.512068                             | 0.000007                        | 28.4                       | 4.60                       | 0.2380                                    | 0.9080                                   | 0.511815                                             | −6.790724                            | 1.6                                                  | 0.905239                  |                      |
| YQ-83  | 0.512587                             | 0.000008                        | 36.7                       | 8.74                       | 0.2380                                    | 0.1437                                   | 0.512341                                             | 0.778167                             | 1.0                                                  | 0.146910                  |                      |
| YQ-84  | 0.512584                             | 0.000007                        | 35.6                       | 8.27                       | 0.2380                                    | 0.1406                                   | 0.512343                                             | 0.824325                             | 1.0                                                  | 0.146764                  |                      |
| YQ-91  | 0.512032                             | 0.000006                        | 22.2                       | 3.65                       | 0.2380                                    | 0.0993                                   | 0.511861                                             | −8.569046                            | 1.7                                                  | 0.948493                  |                      |
| YX-1   | 0.512072                             | 0.000006                        | 29.2                       | 4.83                       | 0.2380                                    | 0.1001                                   | 0.511899                                             | −7.817007                            | 1.7                                                  | 0.893627                  |                      |
| Sample | <sup>176</sup> Hf/ <sup>177</sup> Hf | 2s                              | Lu<br>(×10 <sup>−6</sup> ) | Hf<br>(×10 <sup>−6</sup> ) | <sup>177</sup> Hf<br>(×10 <sup>−6</sup> ) | <sup>176</sup> Hf<br>(10 <sup>−6</sup> ) | <sup>176</sup> Lu                                    | <sup>176</sup> Lu/ <sup>177</sup> Hf | ( <sup>176</sup> Hf/ <sup>177</sup> Hf) <sub>i</sub> | ε <sub>Hf</sub> (t)       | T <sub>DM</sub> (Ga) |
| YQ-83  | 0.282543                             | 0.000009                        | 0.35                       | 5.72                       | 0.185953                                  | 0.052604                                 | 0.02584                                              | 0.0084777                            | 0.28248                                              | −2.07584                  | 1.4                  |
| Sample |                                      | Lithology                       |                            |                            |                                           |                                          |                                                      |                                      |                                                      |                           |                      |
| YQ-83  |                                      | Quartz diorite                  |                            |                            |                                           |                                          |                                                      |                                      |                                                      |                           |                      |
| YQ-91  |                                      | Quartz mica porphyritic diorite |                            |                            |                                           |                                          |                                                      |                                      |                                                      |                           |                      |

Note: The Sr–Nd–Hf isotopic compositions were analyzed at the State Key Laboratory of Continental Dynamics, Northwest University, while the composition of oxygen isotopes (δ<sup>18</sup>O) was determined at the Institute of Mineral Resources, Chinese Academy of Geological Science.

Table 3. LA-ICP-MS U–Pb zircon data of Huashigou granites.

| Spots   | <sup>238</sup> U<br>(×10 <sup>−6</sup> ) | <sup>232</sup> Th<br>(×10 <sup>−6</sup> ) | Th/U | Isotope Ratio                       |         |                                     |         |                                      |         | Isotope Age                         |    |                                     |    |  |  |
|---------|------------------------------------------|-------------------------------------------|------|-------------------------------------|---------|-------------------------------------|---------|--------------------------------------|---------|-------------------------------------|----|-------------------------------------|----|--|--|
|         |                                          |                                           |      | <sup>206</sup> Pb/ <sup>238</sup> U | 1σ      | <sup>207</sup> Pb/ <sup>235</sup> U | 1σ      | <sup>207</sup> Pb/ <sup>206</sup> Pb | 1σ      | <sup>206</sup> Pb/ <sup>238</sup> U | 1σ | <sup>207</sup> Pb/ <sup>235</sup> U | 1σ |  |  |
| YQ57-01 | 315                                      | 190                                       | 0.60 | 0.05889                             | 0.00087 | 0.48024                             | 0.01794 | 0.05914                              | 0.00222 | 369                                 | 5  | 398                                 | 12 |  |  |
| YQ57-02 | 350                                      | 116                                       | 0.33 | 0.06042                             | 0.00088 | 0.43998                             | 0.01578 | 0.05280                              | 0.0019  | 378                                 | 5  | 370                                 | 11 |  |  |
| YQ57-03 | 150                                      | 97                                        | 0.65 | 0.06003                             | 0.00108 | 0.46993                             | 0.03886 | 0.05678                              | 0.00481 | 376                                 | 7  | 391                                 | 27 |  |  |
| YQ57-05 | 316                                      | 274                                       | 0.87 | 0.05920                             | 0.00087 | 0.46580                             | 0.01765 | 0.05706                              | 0.00217 | 371                                 | 5  | 388                                 | 12 |  |  |
| YQ57-06 | 339                                      | 224                                       | 0.66 | 0.05871                             | 0.00087 | 0.42920                             | 0.01595 | 0.05301                              | 0.00198 | 368                                 | 5  | 363                                 | 11 |  |  |
| YQ57-07 | 252                                      | 232                                       | 0.92 | 0.06073                             | 0.00090 | 0.47908                             | 0.01839 | 0.05721                              | 0.00221 | 380                                 | 5  | 397                                 | 13 |  |  |
| YQ57-08 | 355                                      | 326                                       | 0.92 | 0.05921                             | 0.00087 | 0.43751                             | 0.01630 | 0.05359                              | 0.00201 | 371                                 | 5  | 368                                 | 12 |  |  |
| YQ57-09 | 293                                      | 223                                       | 0.76 | 0.05810                             | 0.00086 | 0.45036                             | 0.01849 | 0.05621                              | 0.00232 | 364                                 | 5  | 378                                 | 13 |  |  |
| YQ57-12 | 361                                      | 204                                       | 0.56 | 0.06005                             | 0.00089 | 0.48010                             | 0.01811 | 0.05798                              | 0.00220 | 376                                 | 5  | 398                                 | 12 |  |  |
| YQ57-13 | 439                                      | 288                                       | 0.66 | 0.05781                             | 0.00085 | 0.42800                             | 0.01604 | 0.05369                              | 0.00202 | 362                                 | 5  | 362                                 | 11 |  |  |
| YQ57-15 | 284                                      | 195                                       | 0.69 | 0.06071                             | 0.00091 | 0.45580                             | 0.01880 | 0.05445                              | 0.00226 | 380                                 | 6  | 381                                 | 13 |  |  |
| YQ57-16 | 348                                      | 297                                       | 0.85 | 0.05931                             | 0.00089 | 0.47418                             | 0.01820 | 0.05798                              | 0.00224 | 371                                 | 5  | 394                                 | 13 |  |  |
| YQ57-17 | 290                                      | 173                                       | 0.60 | 0.05908                             | 0.00091 | 0.43250                             | 0.01788 | 0.05308                              | 0.00222 | 370                                 | 6  | 365                                 | 13 |  |  |
| YQ57-18 | 427                                      | 293                                       | 0.69 | 0.05886                             | 0.00088 | 0.44790                             | 0.01736 | 0.05518                              | 0.00215 | 369                                 | 5  | 376                                 | 12 |  |  |
| YQ57-19 | 273                                      | 157                                       | 0.57 | 0.05829                             | 0.00088 | 0.46156                             | 0.01955 | 0.05742                              | 0.00245 | 365                                 | 5  | 385                                 | 14 |  |  |
| YQ57-20 | 440                                      | 415                                       | 0.94 | 0.05592                             | 0.00084 | 0.45384                             | 0.01804 | 0.05886                              | 0.00236 | 351                                 | 5  | 380                                 | 13 |  |  |
| YQ57-21 | 404                                      | 259                                       | 0.64 | 0.05727                             | 0.00086 | 0.43694                             | 0.01781 | 0.05533                              | 0.00227 | 359                                 | 5  | 368                                 | 13 |  |  |
| YQ57-22 | 413                                      | 271                                       | 0.66 | 0.05881                             | 0.00088 | 0.43850                             | 0.01720 | 0.05407                              | 0.00214 | 368                                 | 5  | 369                                 | 12 |  |  |
| YQ57-23 | 162                                      | 108                                       | 0.67 | 0.05978                             | 0.00094 | 0.47134                             | 0.02617 | 0.05717                              | 0.00320 | 374                                 | 6  | 392                                 | 18 |  |  |
| YQ57-25 | 330                                      | 230                                       | 0.70 | 0.05761                             | 0.00090 | 0.42060                             | 0.01812 | 0.05295                              | 0.00231 | 361                                 | 5  | 356                                 | 13 |  |  |
| YQ81-01 | 177                                      | 153                                       | 0.86 | 0.04155                             | 0.00062 | 0.29453                             | 0.01115 | 0.05141                              | 0.00196 | 262                                 | 4  | 262                                 | 9  |  |  |
| YQ81-02 | 239                                      | 228                                       | 0.95 | 0.04167                             | 0.00060 | 0.29783                             | 0.01107 | 0.05183                              | 0.00193 | 263                                 | 4  | 265                                 | 9  |  |  |
| YQ81-03 | 236                                      | 281                                       | 1.19 | 0.04182                             | 0.00061 | 0.29759                             | 0.01127 | 0.05161                              | 0.00196 | 264                                 | 4  | 265                                 | 9  |  |  |
| YQ81-04 | 99                                       | 72                                        | 0.73 | 0.04197                             | 0.00066 | 0.29891                             | 0.01434 | 0.05165                              | 0.00250 | 265                                 | 4  | 266                                 | 11 |  |  |
| YQ81-05 | 151                                      | 123                                       | 0.81 | 0.04105                             | 0.00061 | 0.29311                             | 0.01254 | 0.05178                              | 0.00223 | 259                                 | 4  | 261                                 | 10 |  |  |
| YQ81-06 | 217                                      | 204                                       | 0.94 | 0.04174                             | 0.00061 | 0.30703                             | 0.01496 | 0.05335                              | 0.00260 | 264                                 | 4  | 272                                 | 12 |  |  |
| YQ81-07 | 86                                       | 62                                        | 0.72 | 0.04313                             | 0.00069 | 0.30454                             | 0.02352 | 0.05120                              | 0.00397 | 272                                 | 4  | 270                                 | 18 |  |  |
| YQ81-08 | 149                                      | 121                                       | 0.81 | 0.04087                             | 0.00062 | 0.28327                             | 0.01129 | 0.05026                              | 0.00202 | 258                                 | 4  | 253                                 | 9  |  |  |
| YQ81-09 | 49                                       | 17                                        | 0.35 | 0.04204                             | 0.00075 | 0.29870                             | 0.02003 | 0.05152                              | 0.00349 | 265                                 | 5  | 265                                 | 16 |  |  |
| YQ81-10 | 150                                      | 129                                       | 0.86 | 0.04095                             | 0.00062 | 0.29902                             | 0.01291 | 0.05295                              | 0.00230 | 259                                 | 4  | 266                                 | 10 |  |  |
| YQ81-11 | 136                                      | 82                                        | 0.60 | 0.04043                             | 0.00062 | 0.28644                             | 0.01301 | 0.05138                              | 0.00235 | 255                                 | 4  | 256                                 | 10 |  |  |
| YQ81-12 | 120                                      | 103                                       | 0.85 | 0.04057                             | 0.00065 | 0.28818                             | 0.01395 | 0.05151                              | 0.00252 | 256                                 | 4  | 257                                 | 11 |  |  |
| YQ81-13 | 135                                      | 113                                       | 0.84 | 0.04076                             | 0.00063 | 0.29006                             | 0.01336 | 0.05161                              | 0.00240 | 258                                 | 4  | 259                                 | 11 |  |  |
| YQ81-14 | 125                                      | 108                                       | 0.87 | 0.04255                             | 0.00066 | 0.30327                             | 0.01373 | 0.05169                              | 0.00236 | 269                                 | 4  | 269                                 | 11 |  |  |
| YQ81-15 | 105                                      | 87                                        | 0.82 | 0.04228                             | 0.00068 | 0.31220                             | 0.01887 | 0.05355                              | 0.00326 | 267                                 | 4  | 276                                 | 15 |  |  |
| YQ81-16 | 159                                      | 136                                       | 0.85 | 0.04097                             | 0.00064 | 0.29132                             | 0.01328 | 0.05156                              | 0.00237 | 259                                 | 4  | 260                                 | 10 |  |  |
| YQ81-17 | 130                                      | 126                                       | 0.97 | 0.04318                             | 0.00067 | 0.29919                             | 0.01248 | 0.05024                              | 0.00212 | 273                                 | 4  | 266                                 | 10 |  |  |
| YQ81-18 | 175                                      | 148                                       | 0.85 | 0.04153                             | 0.00062 | 0.29472                             | 0.01278 | 0.05146                              | 0.00224 | 262                                 | 4  | 262                                 | 10 |  |  |
| YQ81-19 | 154                                      | 131                                       | 0.85 | 0.03991                             | 0.00061 | 0.28186                             | 0.01182 | 0.05122                              | 0.00216 | 252                                 | 4  | 252                                 | 9  |  |  |
| YQ81-20 | 161                                      | 140                                       | 0.87 | 0.04046                             | 0.00062 | 0.29061                             | 0.01533 | 0.05209                              | 0.00276 | 256                                 | 4  | 259                                 | 12 |  |  |
| YQ81-21 | 125                                      | 97                                        | 0.77 | 0.04172                             | 0.00066 | 0.29840                             | 0.01384 | 0.05187                              | 0.00243 | 263                                 | 4  | 265                                 | 11 |  |  |
| YQ81-22 | 117                                      | 102                                       | 0.87 | 0.04233                             | 0.00066 | 0.30153                             | 0.01521 | 0.05166                              | 0.00263 | 267                                 | 4  | 268                                 | 12 |  |  |
| YQ81-23 | 55                                       | 18                                        | 0.32 | 0.03984                             | 0.00075 | 0.28010                             | 0.03220 | 0.05099                              | 0.00589 | 252                                 | 5  | 251                                 | 26 |  |  |
| YQ81-24 | 114                                      | 89                                        | 0.78 | 0.04082                             | 0.00066 | 0.28811                             | 0.01330 | 0.05119                              | 0.00239 | 258                                 | 4  | 257                                 | 10 |  |  |

Table 3. Cont.

| Spots   | <sup>238</sup> U<br>(×10 <sup>−6</sup> ) | <sup>232</sup> Th<br>(×10 <sup>−6</sup> ) | Th/U | Isotope Ratio                       |         |                                     |         |                                      |         | Isotope Age                         |    |                                     |    |  |  |
|---------|------------------------------------------|-------------------------------------------|------|-------------------------------------|---------|-------------------------------------|---------|--------------------------------------|---------|-------------------------------------|----|-------------------------------------|----|--|--|
|         |                                          |                                           |      | <sup>206</sup> Pb/ <sup>238</sup> U | 1σ      | <sup>207</sup> Pb/ <sup>235</sup> U | 1σ      | <sup>207</sup> Pb/ <sup>206</sup> Pb | 1σ      | <sup>206</sup> Pb/ <sup>238</sup> U | 1σ | <sup>207</sup> Pb/ <sup>235</sup> U | 1σ |  |  |
| YQ81-25 | 40                                       | 16                                        | 0.40 | 0.03988                             | 0.00083 | 0.28361                             | 0.03353 | 0.05157                              | 0.00614 | 252                                 | 5  | 254                                 | 27 |  |  |
| YQ81-26 | 83                                       | 32                                        | 0.38 | 0.04179                             | 0.0007  | 0.29816                             | 0.01652 | 0.05175                              | 0.00290 | 264                                 | 4  | 265                                 | 13 |  |  |
| YQ81-27 | 100                                      | 83                                        | 0.83 | 0.04162                             | 0.00067 | 0.29657                             | 0.01594 | 0.05168                              | 0.00280 | 263                                 | 4  | 264                                 | 12 |  |  |
| YQ81-28 | 135                                      | 115                                       | 0.86 | 0.04160                             | 0.00065 | 0.29434                             | 0.01348 | 0.05131                              | 0.00237 | 263                                 | 4  | 262                                 | 11 |  |  |
| YQ81-29 | 76                                       | 53                                        | 0.70 | 0.04171                             | 0.00073 | 0.29603                             | 0.01754 | 0.05147                              | 0.00309 | 263                                 | 5  | 263                                 | 14 |  |  |
| YQ81-30 | 141                                      | 129                                       | 0.91 | 0.04253                             | 0.00067 | 0.30127                             | 0.01447 | 0.05138                              | 0.00249 | 268                                 | 4  | 267                                 | 11 |  |  |
| YQ81-31 | 195                                      | 179                                       | 0.92 | 0.04061                             | 0.00062 | 0.28495                             | 0.01207 | 0.05088                              | 0.00217 | 257                                 | 4  | 255                                 | 10 |  |  |
| YQ81-32 | 234                                      | 210                                       | 0.90 | 0.04081                             | 0.00061 | 0.28668                             | 0.01135 | 0.05095                              | 0.00203 | 258                                 | 4  | 256                                 | 9  |  |  |
| YQ81-33 | 49                                       | 20                                        | 0.40 | 0.04214                             | 0.00079 | 0.29406                             | 0.02197 | 0.05061                              | 0.00383 | 266                                 | 5  | 262                                 | 17 |  |  |
| YQ81-34 | 124                                      | 103                                       | 0.83 | 0.04197                             | 0.00067 | 0.29729                             | 0.01325 | 0.05137                              | 0.00232 | 265                                 | 4  | 264                                 | 10 |  |  |
| YQ81-35 | 223                                      | 206                                       | 0.92 | 0.04100                             | 0.00062 | 0.29325                             | 0.01179 | 0.05187                              | 0.00210 | 259                                 | 4  | 261                                 | 9  |  |  |
| YQ81-36 | 55                                       | 17                                        | 0.31 | 0.04195                             | 0.00077 | 0.31005                             | 0.02283 | 0.05360                              | 0.00399 | 265                                 | 5  | 274                                 | 18 |  |  |
| YQ81-37 | 77                                       | 58                                        | 0.76 | 0.04211                             | 0.00073 | 0.30065                             | 0.02180 | 0.05178                              | 0.00379 | 266                                 | 5  | 267                                 | 17 |  |  |
| YQ81-39 | 129                                      | 105                                       | 0.82 | 0.04163                             | 0.00066 | 0.29548                             | 0.01465 | 0.05147                              | 0.00258 | 263                                 | 4  | 263                                 | 11 |  |  |
| YQ81-40 | 133                                      | 106                                       | 0.80 | 0.04243                             | 0.00067 | 0.31463                             | 0.01978 | 0.05378                              | 0.00340 | 268                                 | 4  | 278                                 | 15 |  |  |
| YQ81-41 | 167                                      | 158                                       | 0.95 | 0.04050                             | 0.00063 | 0.29041                             | 0.01346 | 0.05200                              | 0.00243 | 256                                 | 4  | 259                                 | 11 |  |  |
| YQ81-42 | 45                                       | 20                                        | 0.45 | 0.04111                             | 0.00081 | 0.28552                             | 0.05593 | 0.05037                              | 0.00989 | 260                                 | 5  | 255                                 | 44 |  |  |
| YQ81-43 | 128                                      | 108                                       | 0.85 | 0.04167                             | 0.00066 | 0.29561                             | 0.01395 | 0.05144                              | 0.00245 | 263                                 | 4  | 263                                 | 11 |  |  |
| YQ81-44 | 290                                      | 334                                       | 1.15 | 0.04080                             | 0.00061 | 0.29106                             | 0.01125 | 0.05173                              | 0.00201 | 258                                 | 4  | 259                                 | 9  |  |  |
| YQ89-01 | 96                                       | 68                                        | 0.71 | 0.04075                             | 0.00065 | 0.28996                             | 0.01582 | 0.05161                              | 0.00284 | 33                                  | 4  | 259                                 | 12 |  |  |
| YQ89-02 | 153                                      | 135                                       | 0.88 | 0.04133                             | 0.00060 | 0.29282                             | 0.01196 | 0.05138                              | 0.00211 | 261                                 | 4  | 261                                 | 9  |  |  |
| YQ89-03 | 158                                      | 198                                       | 1.25 | 0.04029                             | 0.00060 | 0.28692                             | 0.01443 | 0.05164                              | 0.00261 | 255                                 | 4  | 256                                 | 11 |  |  |
| YQ89-04 | 70                                       | 43                                        | 0.62 | 0.04014                             | 0.00067 | 0.28873                             | 0.02078 | 0.05217                              | 0.00378 | 254                                 | 4  | 258                                 | 16 |  |  |
| YQ89-05 | 75                                       | 56                                        | 0.75 | 0.04080                             | 0.00077 | 0.28745                             | 0.02053 | 0.05110                              | 0.00370 | 258                                 | 5  | 257                                 | 16 |  |  |
| YQ89-06 | 92                                       | 75                                        | 0.81 | 0.04123                             | 0.00066 | 0.29329                             | 0.01421 | 0.05159                              | 0.00253 | 260                                 | 4  | 261                                 | 11 |  |  |
| YQ89-07 | 154                                      | 134                                       | 0.87 | 0.04044                             | 0.00062 | 0.29230                             | 0.01215 | 0.05242                              | 0.00220 | 256                                 | 4  | 260                                 | 10 |  |  |
| YQ89-08 | 79                                       | 74                                        | 0.94 | 0.04265                             | 0.00071 | 0.30072                             | 0.01687 | 0.05113                              | 0.00290 | 269                                 | 4  | 267                                 | 13 |  |  |
| YQ89-09 | 101                                      | 124                                       | 1.24 | 0.04169                             | 0.00065 | 0.28222                             | 0.01242 | 0.04909                              | 0.00218 | 263                                 | 4  | 252                                 | 10 |  |  |
| YQ89-10 | 86                                       | 72                                        | 0.83 | 0.04121                             | 0.00070 | 0.29268                             | 0.01854 | 0.05151                              | 0.00329 | 260                                 | 4  | 261                                 | 15 |  |  |
| YQ89-11 | 112                                      | 109                                       | 0.97 | 0.03968                             | 0.00061 | 0.28116                             | 0.01389 | 0.05139                              | 0.00256 | 251                                 | 4  | 252                                 | 11 |  |  |
| YQ89-12 | 133                                      | 157                                       | 1.19 | 0.04169                             | 0.00063 | 0.30397                             | 0.01298 | 0.05288                              | 0.00227 | 263                                 | 4  | 269                                 | 10 |  |  |
| YQ89-13 | 107                                      | 88                                        | 0.82 | 0.04228                             | 0.00066 | 0.29920                             | 0.01478 | 0.05133                              | 0.00256 | 267                                 | 4  | 266                                 | 12 |  |  |
| YQ89-14 | 120                                      | 112                                       | 0.94 | 0.04158                             | 0.00064 | 0.29572                             | 0.01355 | 0.05157                              | 0.00238 | 263                                 | 4  | 263                                 | 11 |  |  |
| YQ89-15 | 71                                       | 69                                        | 0.97 | 0.04040                             | 0.00075 | 0.28671                             | 0.01988 | 0.05147                              | 0.00362 | 255                                 | 5  | 256                                 | 16 |  |  |
| YQ89-16 | 50                                       | 25                                        | 0.49 | 0.04174                             | 0.00077 | 0.29940                             | 0.02315 | 0.05202                              | 0.00406 | 264                                 | 5  | 266                                 | 18 |  |  |
| YQ89-18 | 277                                      | 332                                       | 1.20 | 0.04179                             | 0.00060 | 0.29723                             | 0.01035 | 0.05158                              | 0.00180 | 264                                 | 4  | 264                                 | 8  |  |  |
| YQ89-19 | 110                                      | 98                                        | 0.89 | 0.04258                             | 0.00068 | 0.29946                             | 0.01645 | 0.05100                              | 0.00282 | 269                                 | 4  | 266                                 | 13 |  |  |
| YQ89-20 | 130                                      | 102                                       | 0.78 | 0.04169                             | 0.00064 | 0.29648                             | 0.01480 | 0.05158                              | 0.00259 | 263                                 | 4  | 264                                 | 12 |  |  |
| YQ89-21 | 156                                      | 94                                        | 0.60 | 0.04102                             | 0.00061 | 0.29012                             | 0.01148 | 0.05129                              | 0.00204 | 259                                 | 4  | 259                                 | 9  |  |  |
| YQ89-22 | 150                                      | 132                                       | 0.88 | 0.04170                             | 0.00064 | 0.29589                             | 0.01280 | 0.05145                              | 0.00224 | 263                                 | 4  | 263                                 | 10 |  |  |
| YQ89-23 | 137                                      | 120                                       | 0.88 | 0.04067                             | 0.00063 | 0.28716                             | 0.01239 | 0.05120                              | 0.00223 | 257                                 | 4  | 256                                 | 10 |  |  |
| YQ89-24 | 159                                      | 151                                       | 0.95 | 0.04117                             | 0.00063 | 0.29021                             | 0.01297 | 0.05112                              | 0.00230 | 260                                 | 4  | 259                                 | 10 |  |  |
| YQ89-25 | 220                                      | 238                                       | 1.08 | 0.04086                             | 0.00060 | 0.29023                             | 0.01096 | 0.05151                              | 0.00195 | 258                                 | 4  | 259                                 | 9  |  |  |
| YQ89-27 | 148                                      | 134                                       | 0.90 | 0.04272                             | 0.00063 | 0.30245                             | 0.01298 | 0.05134                              | 0.00221 | 270                                 | 4  | 268                                 | 10 |  |  |
| YQ89-28 | 122                                      | 111                                       | 0.91 | 0.04204                             | 0.00064 | 0.29958                             | 0.01387 | 0.05168                              | 0.00241 | 265                                 | 4  | 266                                 | 11 |  |  |
| YQ89-30 | 94                                       | 90                                        | 0.96 | 0.04198                             | 0.00067 | 0.29843                             | 0.01473 | 0.05155                              | 0.00257 | 265                                 | 4  | 265                                 | 12 |  |  |
| YQ89-31 | 97                                       | 77                                        | 0.80 | 0.04149                             | 0.00065 | 0.29636                             | 0.01567 | 0.05180                              | 0.00276 | 262                                 | 4  | 264                                 | 12 |  |  |
| YQ89-32 | 88                                       | 66                                        | 0.75 | 0.04180                             | 0.00068 | 0.29623                             | 0.01546 | 0.05139                              | 0.00271 | 264                                 | 4  | 263                                 | 12 |  |  |
| YQ89-34 | 58                                       | 18                                        | 0.31 | 0.04209                             | 0.00074 | 0.29816                             | 0.01956 | 0.05137                              | 0.00341 | 266                                 | 5  | 265                                 | 15 |  |  |
| YQ89-35 | 83                                       | 81                                        | 0.98 | 0.04170                             | 0.00068 | 0.29736                             | 0.01812 | 0.05172                              | 0.00318 | 263                                 | 4  | 264                                 | 14 |  |  |
| YQ89-36 | 58                                       | 29                                        | 0.50 | 0.04095                             | 0.00078 | 0.28665                             | 0.02375 | 0.05076                              | 0.00425 | 259                                 | 5  | 256                                 | 19 |  |  |
| YQ89-37 | 47                                       | 30                                        | 0.64 | 0.04207                             | 0.00086 | 0.31336                             | 0.04643 | 0.05402                              | 0.00808 | 266                                 | 5  | 277                                 | 36 |  |  |
| YQ89-38 | 253                                      | 264                                       | 1.04 | 0.04198                             | 0.00060 | 0.30187                             | 0.01175 | 0.05215                              | 0.00203 | 265                                 | 4  | 268                                 | 9  |  |  |
| YQ89-39 | 107                                      | 88                                        | 0.82 | 0.04285                             | 0.00067 | 0.30212                             | 0.01287 | 0.05113                              | 0.00220 | 270                                 | 4  | 268                                 | 10 |  |  |
| YQ89-40 | 183                                      | 139                                       | 0.76 | 0.04186                             | 0.00062 | 0.29311                             | 0.01096 | 0.05078                              | 0.00191 | 264                                 | 4  | 261                                 | 9  |  |  |
| YQ89-41 | 167                                      | 210                                       | 1.26 | 0.04140                             | 0.00061 | 0.29503                             | 0.01168 | 0.05168                              | 0.00206 | 262                                 | 4  | 263                                 | 9  |  |  |
| YQ89-42 | 210                                      | 211                                       | 1.01 | 0.04211                             | 0.00061 | 0.28727                             | 0.01011 | 0.04947                              | 0.00175 | 266                                 | 4  | 256                                 | 8  |  |  |
| YQ89-43 | 218                                      | 219                                       | 1.00 | 0.04169                             | 0.00061 | 0.29750                             | 0.01151 | 0.05175                              | 0.00201 | 263                                 | 4  | 264                                 | 9  |  |  |
| YQ89-44 | 106                                      | 114                                       | 1.08 | 0.04212                             | 0.00068 | 0.31096                             | 0.03124 | 0.05354                              | 0.00539 | 266                                 | 4  | 275                                 | 24 |  |  |

Notes: The analytical results are reported with a 1σ error. Zircon U–Pb dating with a beam size of 30–40 μm was conducted using LA-ICP-MS at the Key Laboratory of Lithospheric Tectonics and Exploration of the Ministry of Education from the China University of Geosciences (Beijing).

4.1. Geochronology

In this study, three granitic plutons from the Huashigou area were chosen for zircon U–Pb dating. The zircons used were primarily colorless to transparent and euhedral to subeuhedral, with elongated to stubby grains (50–250 μm long with length-to-width ratios of 2:1–4:1). Typical magmatic oscillatory zonation was common, and several inherited cores were observed (see insets in Figure 2). The contents of Th (16–415 × 10<sup>−6</sup>) and U (40–440 × 10<sup>−6</sup>) were different among these zircons, and the Th/U ratios were consistent with a magmatic origin [45–48]. The detailed analytical results are listed in Table 3. The U–Pb concordia diagrams for Huashigou granitic rocks are shown in Figure 3.

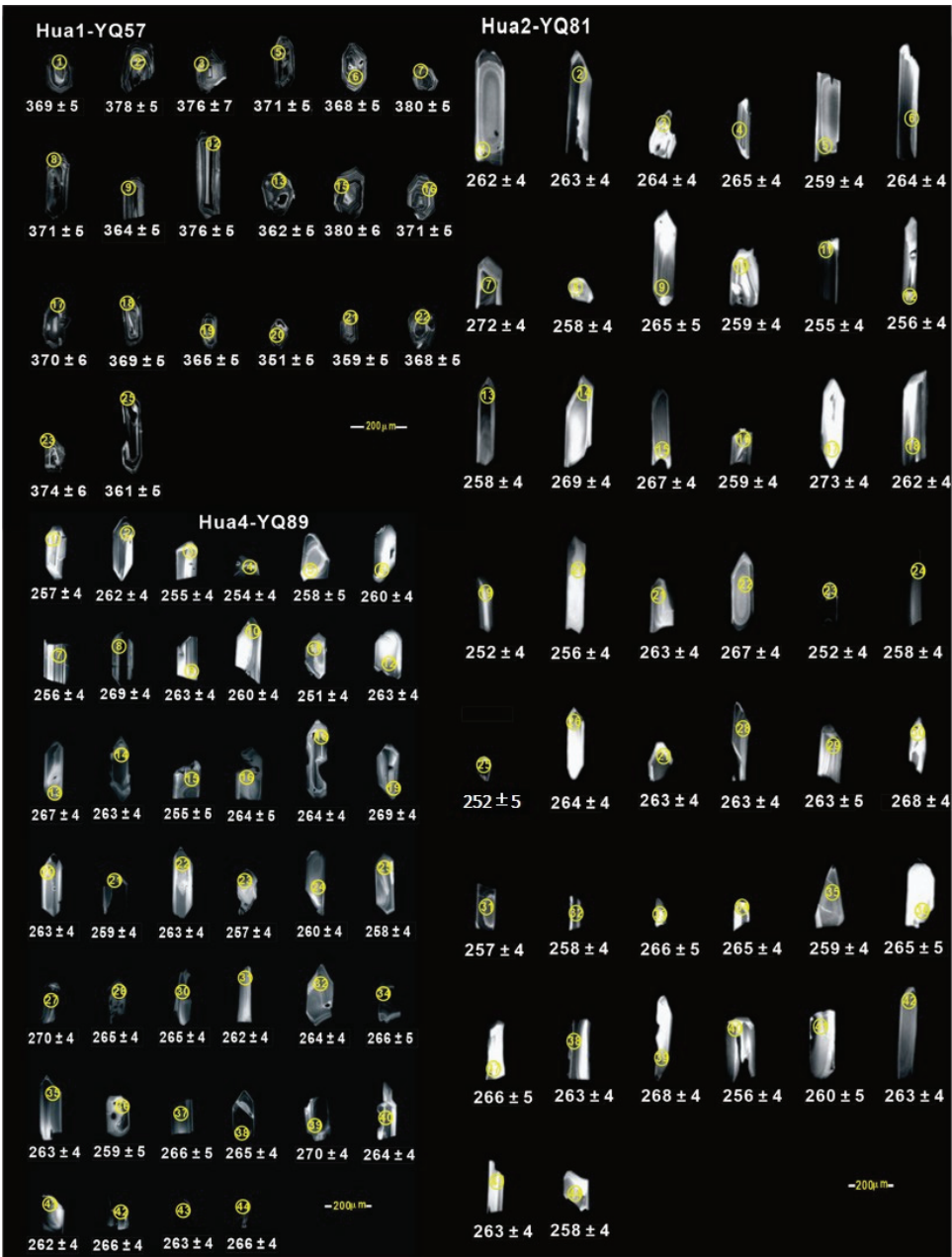
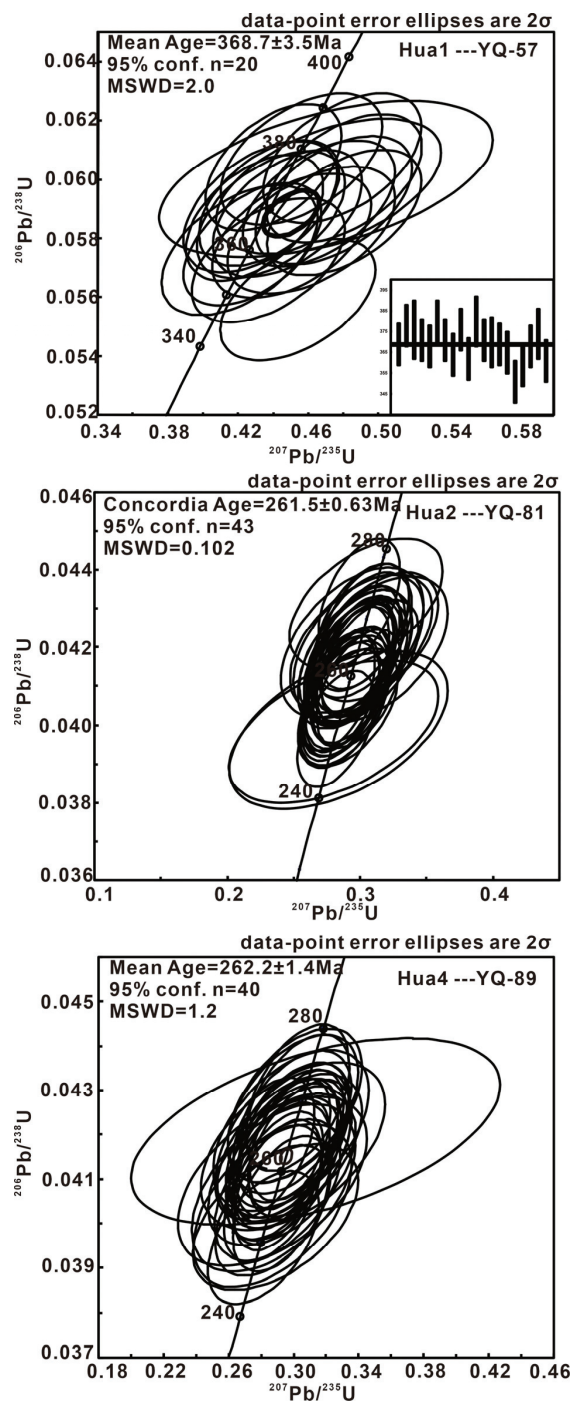


Figure 2. Cathodoluminescence images of zircon grains of granitic rocks from the Huashigou area (ages in Ma).



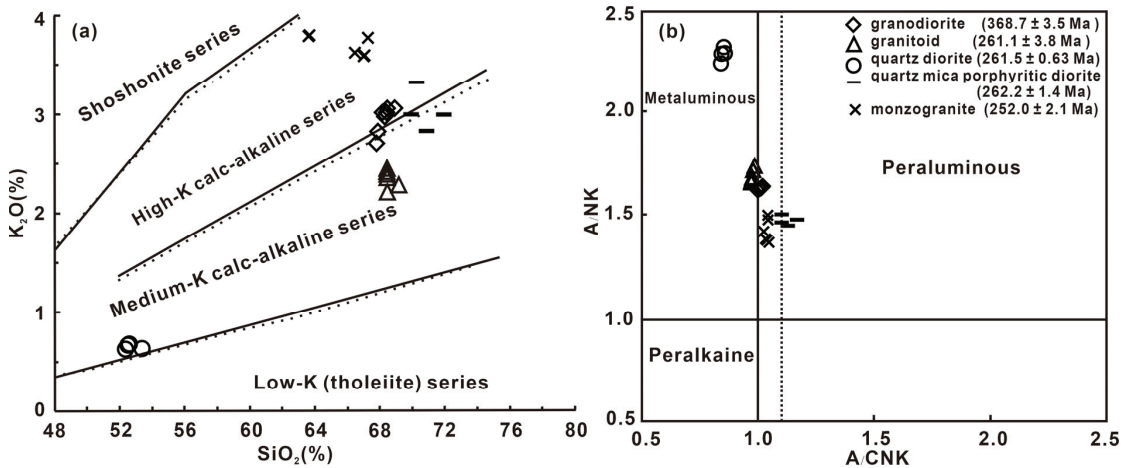
**Figure 3.** Zircon concordia diagram of granitic rocks. The weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  ages for samples YQ-57, YQ-81, and YQ-89 are  $368.7 \pm 3.5 \text{ Ma}$  (MSWD = 2.0;  $2\sigma$ ),  $261.5 \pm 0.63 \text{ Ma}$  (MSWD = 0.102;  $2\sigma$ ), and  $262.2 \pm 1.4 \text{ Ma}$  (MSWD = 1.2;  $2\sigma$ ), respectively.



## 4.2. Whole-Rock Geochemistry

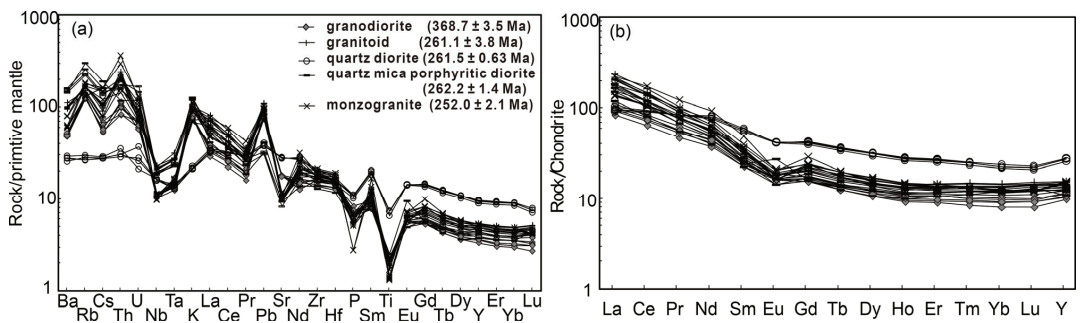
### 4.2.1. Hua1 Pluton

Seven samples of granitic rocks (YQ57–YQ63) from the Hua1 pluton were analyzed for major- and trace-element compositions. Loss on ignition (LOI) for all samples was less than 1 wt.%. The granitic samples showed high contents of  $\text{SiO}_2$  (67.78–68.48 wt.%) and  $\text{Al}_2\text{O}_3$  (15.26–15.77 wt.%) but low contents of  $\text{MgO}$  (1.19–1.38 wt.%) with low  $\text{Mg}^\#$  (about 38). Their contents of  $\text{CaO}$  and  $\text{TiO}_2$  were 3.39–3.80 wt.% and 0.40–0.48 wt.%, respectively. The Hua1 pluton samples showed total alkali contents ranging from 6.36 to 6.67 wt.% and a slight sodium enrichment ( $\text{Na}_2\text{O}/\text{K}_2\text{O} = 1.16\text{--}1.39$ ). They belong to the calc-alkaline series in the  $\text{SiO}_2\text{--K}_2\text{O}$  diagram (Figure 4a). Their A/CNK ratios ranged from 0.97 to 0.99, indicating that the Hua1 granites are metaluminous (Figure 4b).



**Figure 4.** (a) Diagram of  $\text{SiO}_2\text{--K}_2\text{O}$  contents; (b) ANK-ACNK diagram of granitic rocks from the Huashigou area.  $\text{A}/\text{NK} = \text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O})$ ;  $\text{A}/\text{CNK} = \text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ .

The Late Devonian granodiorites showed low Sr contents ( $205.34\text{--}226.54 \times 10^{-6}$ ) and high Y contents ( $19.41\text{--}23.82 \times 10^{-6}$ ), with Sr/Y ratios of 9.17–11.67. The Nb/U and Nb/Ta ratios of the Late Devonian granodiorites were 7.77–10.21 and 12.42–14.39, respectively, which are comparable to those of the Earth's crust, i.e., 9–12 [49–52] and 12–13 [53]. The Late Devonian granodiorite samples contained relatively high REE contents ( $\Sigma\text{REE} = 570\text{--}766 \times 10^{-6}$ ) and were relatively enriched in light rare-earth elements (LREEs) with moderate LREE/HREE fractionation ( $(\text{La}/\text{Yb})_{\text{N}} = 12.99\text{--}16.05$  and  $(\text{La}/\text{Sm})_{\text{N}} = 6.1\text{--}6.91$ ). Additionally, they showed a flat distribution pattern of heavy rare-earth elements (HREEs) and negative Eu anomalies ( $\delta\text{Eu} = 0.64\text{--}0.89$ ). In a primitive-mantle-normalized trace element spider diagram (Figure 5a), the samples showed a notable enrichment in Rb, K, La, Th, and Ce and a relative depletion in Ba, Sr, and Cs. In terms of high-field-strength elements (HFSEs), a notable depletion in Nb, Ta, and Ti and a relative enrichment in Zr and Hf can be observed for these samples.



**Figure 5.** Primitive-mantle-normalized trace element spider diagrams for granitoids (a); chondrite-normalized REE patterns of granitic rocks from the Huashigou area (b) (PM values and chondrite values are derived from [54]).

#### 4.2.2. Hua2 Pluton

The quartz diorites (YQ81–YQ84) from the Hua2 pluton showed relatively low contents of  $\text{SiO}_2$  (52.41–53.32 wt.%) and high contents of  $\text{Al}_2\text{O}_3$  (19.67–19.69 wt.%),  $\text{TiO}_2$  (1.4–1.58 wt.%),  $\text{TFe}_2\text{O}_3$  (8.71–9.23 wt.%),  $\text{MgO}$  (2.99–3.25 wt.%), and  $\text{CaO}$  (7.91–8.11 wt.%). Their total alkali contents ranged from 5.38 wt.% to 5.56 wt.%, and the quartz diorites were evidently sodium-enriched and potassium-depleted ( $\text{Na}_2\text{O}/\text{K}_2\text{O} = 7.01\text{--}7.55$ ); thus, they were plotted in the calc-alkaline field in a  $\text{SiO}_2\text{--K}_2\text{O}$  diagram (Figure 4a). Based on the plot of the A/NK vs. A/CNK diagram, all of the samples are peraluminous (Figure 4b).

As can be seen from the primitive-mantle-normalized diagram (Figure 5a), the quartz diorites were enriched in LILEs, Ba, Rb, Th, and U and depleted in HFSEs, Nb, Ta, and Ti, with high Sr ( $573.85\text{--}593.13 \times 10^{-6}$ ) and Y ( $40.1\text{--}43.32 \times 10^{-6}$ ) contents and a low Sr/Y ratio (13.25–14.79). As shown in the chondrite-normalized distribution pattern (Figure 5b), the quartz diorites were slightly enriched in LREEs ( $(\text{La}/\text{Yb})_N = 3.89\text{--}4.76$ ,  $(\text{La}/\text{Sm})_N = 1.54\text{--}1.88$ , and  $(\text{Gd}/\text{Yb})_N = 1.81\text{--}1.89$ ), with slightly negative Eu anomalies ( $\delta\text{Eu} = 0.81\text{--}0.89$ ).

#### 4.2.3. Hua4 Pluton

The Middle Permian porphyritic tonalites (YQ89–YQ92) from the Hua4 pluton showed high contents of  $\text{SiO}_2$  (63.64–68.51 wt.%),  $\text{Al}_2\text{O}_3$  (14.89–16.62 wt.%), Mg ( $\text{MgO} = 0.71\%\text{--}2.5$  wt.%,  $\text{Mg}^\# = 45\text{--}51$ ), and total alkali ( $\text{Na}_2\text{O} + \text{K}_2\text{O} = 7.3\text{--}8.02$  wt.%) and low contents of  $\text{CaO}$  (1.47–2.93 wt.%). In the  $\text{K}_2\text{O}$  vs.  $\text{SiO}_2$  diagram (Figure 4a), all of the samples are plotted as part of the calc-alkaline series. Based on the plot of A/NK vs. A/CNK, all of the samples are peraluminous (Figure 4b).

As can be seen in the primitive-mantle-normalized diagram (Figure 5a), the porphyritic tonalites were enriched in Rb, Ba, and Th and relatively depleted in Nb, Ta, and Ti, with low contents of Sr ( $172.43\text{--}217.28 \times 10^{-6}$ ) and Y ( $17.05\text{--}20.98 \times 10^{-6}$ ) and a low Sr/Y ratio (9.22–12.74). As shown in the chondrite-normalized distribution pattern (Figure 5b), the porphyritic tonalites were enriched in LREEs ( $(\text{La}/\text{Yb})_N = 10.34\text{--}14.36$ ,  $(\text{La}/\text{Sm})_N = 5.38\text{--}6.98$ , and  $(\text{Gd}/\text{Yb})_N = 1.35\text{--}1.47$ ), with negative Eu anomalies ( $\delta\text{Eu} = 0.68\text{--}0.76$ ).

#### 4.3. Whole-Rock Sr–Nd–O and Hf Isotopes

Whole-rock Sr–Nd–O isotope data are presented in Table 2. The Late Devonian granodiorites (YQ57 and YQ63) from the Hua1 pluton showed high values for the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (0.712356 and 0.71195) and low values for the initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio (0.511827 and 0.511815), with negative  $\varepsilon_{\text{Nd}}(t)$  values of  $-6.56$  and  $-6.14$  and a model age ( $T_{\text{DM}}$ ) of 1.6 Ga. In addition, the sample YQ63 showed an initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio value of 0.282484, with an  $\varepsilon_{\text{Hf}}(t)$  value of  $-2.06$  and a crustal model age of 1.4 Ga.

The Middle Permian granites from the Hua2 pluton showed high  $I_{Sr}$  values of 0.705906 and 0.705970 for quartz diorites (YQ83 and YQ84). Porphyritic tonalite (YQ91) showed the highest  $(^{87}Sr/^{86}Sr)_{ir}$  value of 0.719527. The quartz diorites (YQ83 and YQ84) showed  $\epsilon_{Nd}(t)$  values of +0.78 and +0.82. The porphyritic tonalite (YQ91) from the Hua4 pluton showed the lowest  $\epsilon_{Nd}(t)$  value of −8.57. In addition, the values of  $\delta^{18}O_{V-SMOW}$  for quartz diorite (YQ83) from the Hua2 pluton and porphyritic tonalite (YQ91) from the Hua4 pluton were all relatively higher (12.4‰ and 11.8‰, respectively).

## 5. Discussion

### 5.1. Petrogenesis

#### 5.1.1. Petrogenesis of the Hua1 Pluton

The Late Devonian granodiorites (YQ57–YQ63) from the Hua1 pluton were rich in Al but poor in Mg, and they were slightly sodium-enriched and potassium-depleted. Additionally, they belong to the metaluminous calc-alkaline series (Figure 6). They showed high contents of Cs, Ba, Rb, Th, and Pb, low contents of Nb, Ta, Sr, and Ti (Figure 5a), high total REEs and LREEs, and a flat HREE pattern (Figure 5b) [34,55,56]. The flat pattern of HREEs implies that there is no garnet residual in the source region. The low Sr and negative Eu anomalies suggest fractional crystallization of plagioclase during magma evolution, indicating that the depth of partial melting is shallow [57]. The negative anomalies of P and Ti, high  $I_{Sr}$  values, and negative  $\epsilon_{Nd}(t)$  and  $\epsilon_{Hf}(t)$  values are potentially the result of the fractional crystallization of apatite and Fe-Ti oxide in the plagioclase-stable region. The  $\epsilon_{Nd}(t)$  vs.  $\epsilon_{Hf}(t)$  diagram is similar to that of the lower crust (Figure 7). The Sr–Nd–Hf isotopic compositions of granites suggest that they may have been derived from the partial melting of the underplated lower crust.

#### 5.1.2. Petrogenesis of the Hua4 Pluton and Hua2 Pluton

Middle Permian granodiorites resemble the features of the continental crust because of their higher contents of  $SiO_2$ ,  $Al_2O_3$ , and  $K_2O$ , as well as because they are rich in Ba, Rb, and Th but poor in Nb, Ta, Ti, Sr, etc., and have a higher positive Pb anomaly relative to REEs (Figure 5a), with high  $I_{Sr}$ , negative  $\epsilon_{Nd}(t)$ , and high  $\delta^{18}O_{V-SMOW}$  values. The fractional crystallization of plagioclase occurred during the process of rock formation, as evidenced by a slightly negative Eu anomaly (Figure 5b). The negative P and Ti anomalies imply the fractional distillation of apatite and Fe-Ti oxide. In addition, the low Nb/U ratio and Nb content are related to the contamination of materials from the upper crust [53,58]. The high content of Sr and the low contents of Yb and Y in the granodiorites were similar to the contents of those elements [59,60]. However, the isotopic characteristics of low  $Mg^\#$  content ( $\approx 40$ ), high  $I_{Sr}$ , low  $I_{Nd}$ , and positive  $\epsilon_{Nd}(t)$  (+5.51, Sample YQ3) values are clearly different from the isotopic characteristics of typical adakites formed by the partial melting of juvenile subduction slabs [59–64]; however, they are close to the isotopic characteristics of adakites generated by the partial melting of the underplated basaltic lower crust (Figure 5a) [65–67]. Thus, these adakites were formed in crustal environments with thickened slabs at high temperatures after magmas were contaminated by upper crustal materials during magma ascent and certain fractional crystallization of plagioclases [41].

As for Middle Permian granodiorites, the Nb/U and Nb/Ta ratios were slightly higher than those of the continental crust, and the positive  $\epsilon_{Nd}(t)$  values indicate that granodiorites originated from the partial melting of the underplated basaltic lower crust with the involvement of mantle materials. The low Nb/U ratio of quartz mica porphyritic diorite also implies magma contamination with upper crust materials during its ascent. The  $\delta^{18}O_{V-SMOW}$  values of quartz diorite and quartz mica porphyritic diorite were significantly higher than the typical mantle values ( $5.4 \pm 0.3$ ‰ [68]), indicating that these granitic rocks are derived from the partial melting of the lower crust. With regard to this, we speculate that Middle Permian granitic rocks are the products of post-collisional slab break-off [69].

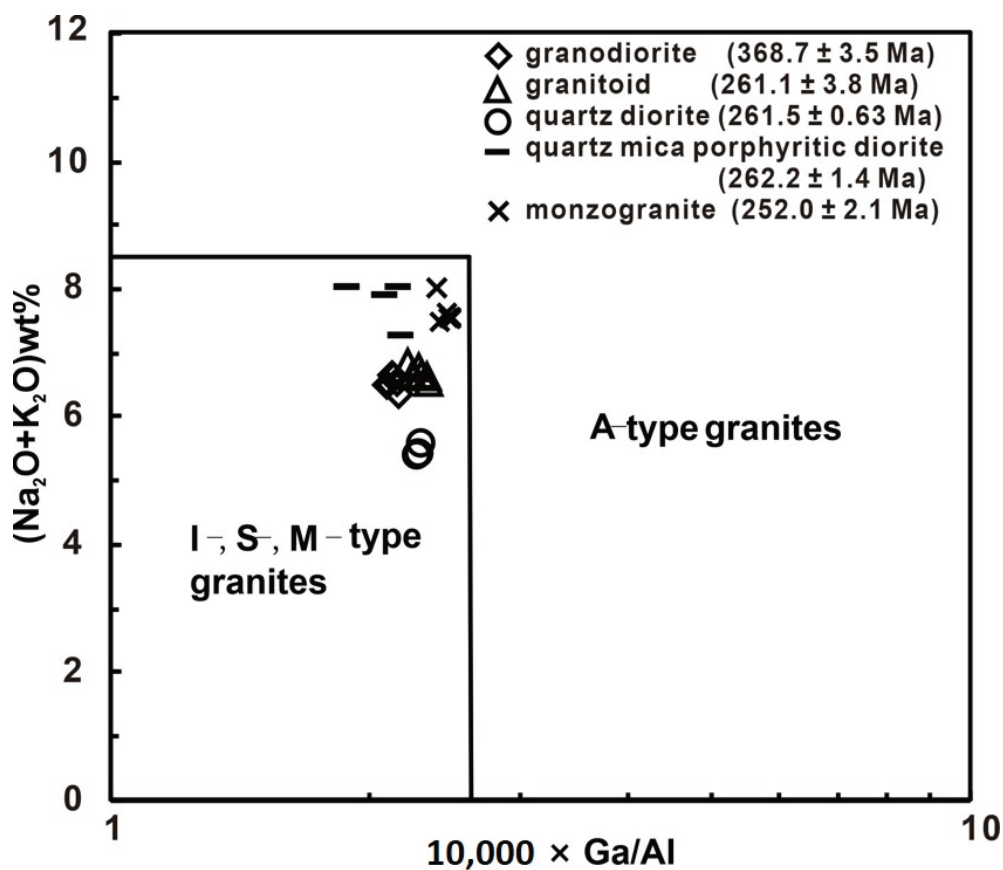


Figure 6. Plot of  $10,000 \times \text{Ga/Al}$  vs.  $(\text{Na}_2\text{O} + \text{K}_2\text{O})$  in Huashigou granites.

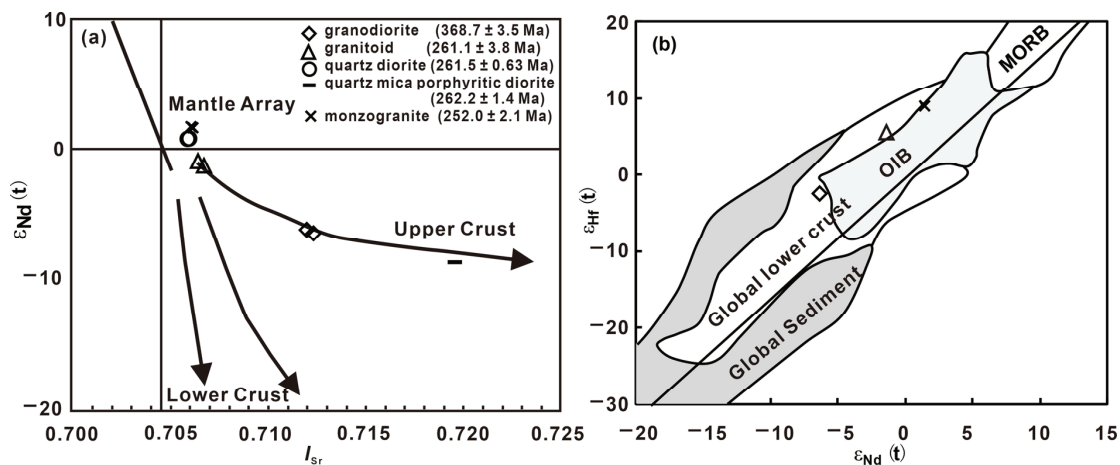


Figure 7. Plots of (a)  $I_{\text{Sr}}$  vs.  $\epsilon_{\text{Hf}}(t)$  and (b)  $\epsilon_{\text{Nd}}(t)$  vs.  $\epsilon_{\text{Hf}}(t)$  of granites.

The geochemistry characteristics of Middle Permian granitoids are similar to those of Late Permian monzogranites from the Hua5 pluton [42] because of their high contents of Si and Al and low contents of Ti and Mg, as well as Cs, Ba, Rb, Th, and Pb enrichment and Nb, Ta, Sr, and Ti depletion. The Sr–Nd–Hf isotopic compositions showed that monzogranites derived from the partial melting of the underplated Mid-Neoproterozoic basaltic lower crust from the underplating heating of Late Paleozoic basaltic magma [42].

The  $\epsilon_{\text{Nd}}(t)$  values of Middle Permian quartz diorite and Late Permian monzogranite were greater than 0 [42], which is similar to some granites formed in environments with extensional tectonics. Granitic rocks with these characteristics have been found only in several areas in the world, such as the New England Batholith [70], northeastern US, southern Quebec of Canada [71,72], the Central Asia–Mongolia fold belt [73–75], etc. These two types of granitic rocks in this area have even lower  $\epsilon_{\text{Nd}}(t)$  values. Generally, the characteristic of  $\epsilon_{\text{Nd}}(t) < 0$  indicates that a depleted mantle component played an important role in magma formation. In addition, the geochemical characteristics of Middle Permian quartz diorite and Late Permian monzogranite did not show any evidence of crust–mantle mixing in the source region [42]. Comparing this to other granites with  $\epsilon_{\text{Nd}}(t) > 0$ , granites in this area had lower  $\epsilon_{\text{Nd}}(t)$  (closer to 0) values. Therefore, the characteristic of the  $\epsilon_{\text{Nd}}(t)$  value, which is slightly greater than 0, may indicate that Middle Permian quartz diorite and Late Permian monzogranite were derived from the partial melting of basic materials in the lower crust formed by underplating.

## 5.2. Tectonic Setting of Huashigou Granitoids

Wu et al. [76] considered that granite in Phase 4 is related to isostatic adjustments between and among different rock bodies after orogenesis. Leake et al. [77] identified that, during the continental crash with the orogenic belt, the granitic emplacements caused by local temperatures and stresses while intrusions and tensility slumps happened in many ancient orogenic belts in the world were synchronous, e.g., the Sevier orogenic belt in southeast California, USA [78]; Guitiriz granite in the Variscan belt in Northern Spain [79]; and the Proterozoic orogenic belt in South Greenland. Foster et al. [80] showed that rapid exhumation could cause the decompression and partial melting of the lower or upper mantle, leading to the formation of Eocene intrusive rocks. For Late Devonian Huashigou granitoids, the geochemical characteristics indicate that they were formed from the partial melting of the lower crust, and their formation age is the same as that of Phase 4 granitic magma in the North Qaidam, as classified by [76]. In addition, the granites from Tula in the South Altyn Tagh Fault and Yusupuleke Tagh belong to the same period [39,76]. All of them were formed in the background of extensional tectonics after orogenesis. In Haker's diagram (Figure 8), granitic rocks from different eras show favorable correlations, and their contents of  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ , and  $\text{TFeO}$  decrease gradually as the  $\text{SiO}_2$  content increases, indicating a distinct negative correlation.  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  show a positive correlation, and Rb, Sr, and Zr increase gradually as  $\text{SiO}_2$  contents increase. Additionally, Ba shows a negative correlation (Figure 9). These characteristics showed that the sources of different types of granitic rocks in the Huashigou area are similar. As shown in Figure 10, all samples are plotted in a post-collisional tectonic setting. Combined with the regional tectonic setting, we believe that the rocks were formed during a post-collisional tectonic setting where the previously subducted slab underwent detachment, leading to slab break-off magmatism and the formation of a significant number of granitic rocks.

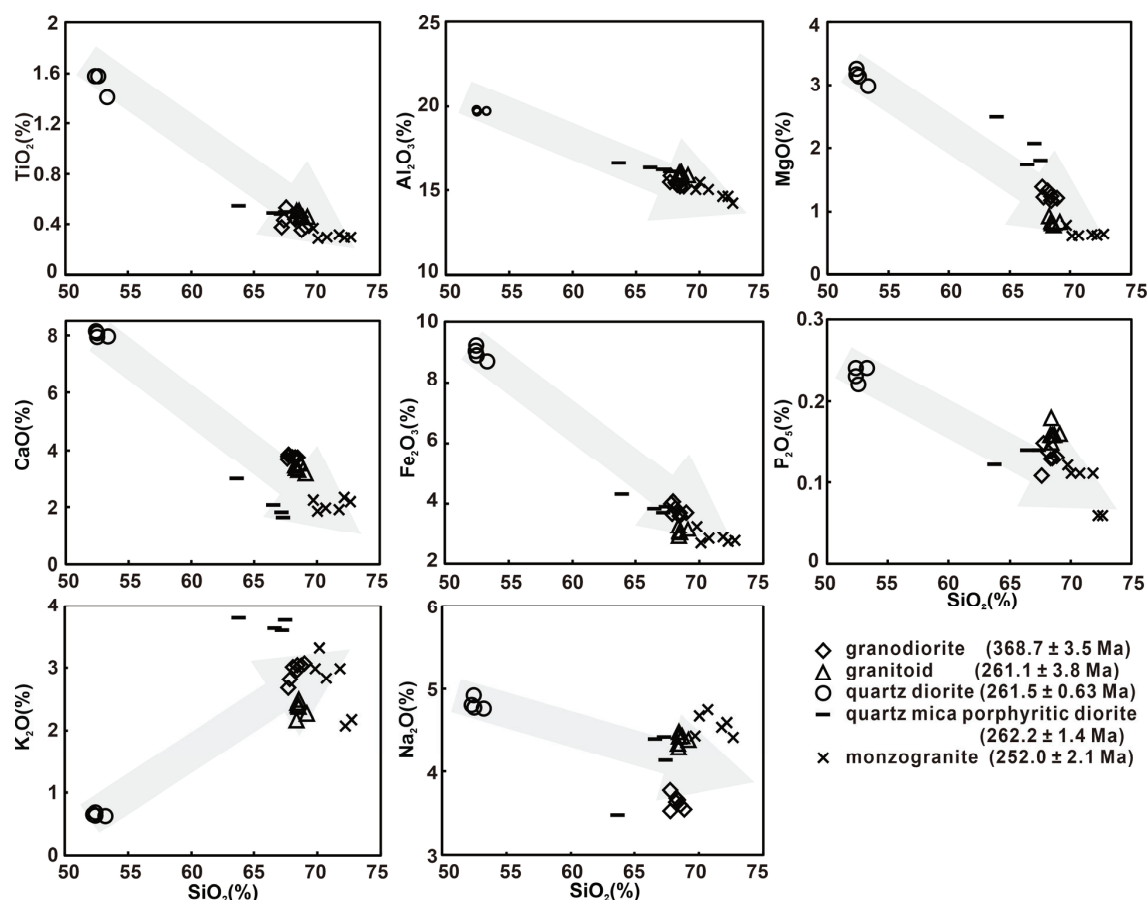


Figure 8. Harker diagrams of Huashiou granitic rocks.

Mid–Late Permian granitoids are comparable to Phase 5 Paleozoic granites in the North Qaidam, as determined by Wu et al. [76], due to the closing of the Paleo-Tethys Ocean, causing the regional tectonic setting to change from tensility to shrinkage. The continental subduction happened before the crust thickened rapidly. In addition, the delamination of the lower crust induced the underplating of basaltic magma, which further elicited the partial melting of the lower crust. Eventually, Mid–Late Permian granitoids were formed. Possessing characteristics of adakites, Mid–Late Permian granodiorites were formed under pressures greater than 1.5 GPa [64,72–87], indicating that the crust thickness could be over 50 km [87,88]. Quartz diorites with high Sr and Yb contents were formed under medium or relatively high pressures, while quartz mica porphyritic diorites with high Sr and Yb contents were formed under medium pressures. The formation depth is estimated to be around 30 km. The depth of the source regions of partial melting decreases gradually from Middle Permian granodiorite to quartz diorite to quartz mica porphyritic diorite. Furthermore, Late Permian monzogranite is similar to granite, with low Sr but high Yb contents. Granite formed under low pressure and potentially at normal crustal thicknesses ( $\approx 30$  km). Therefore, the thickness of the continental crust in the study area might have changed from thick to normal during the Late Permian.



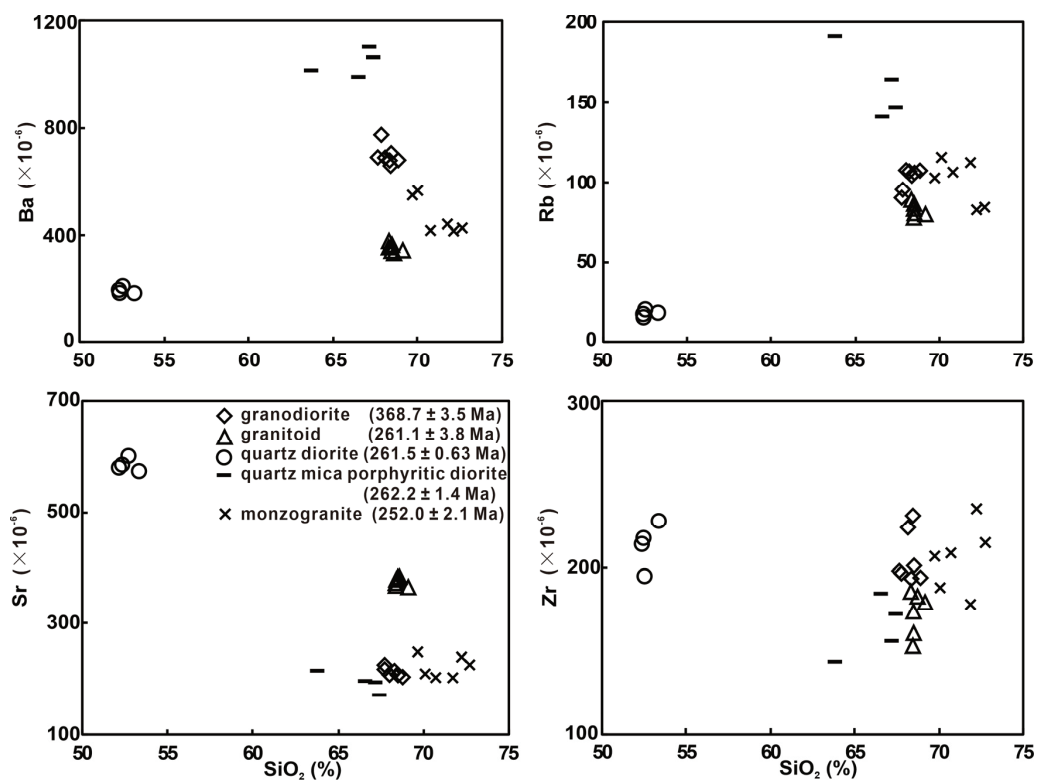


Figure 9. Trace element variation diagrams of granitic rocks from the Huashigou area.

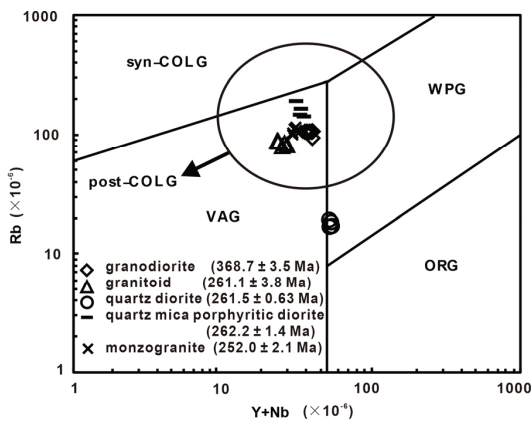


Figure 10. Rb – (Y + Nb) diagram for discriminating the tectonic setting of granitic rocks from the Huashigou area. VAG: volcanic arc granite; ORG: ocean ridge granite; WPG: within-plate granite; syn-COLG: syn-collisional granite; post-COLG: post-collisional granite (after [81]).

It can be concluded that there were at least two important compressional–extensional tectonic transformation phases (c. 369 Ma and c. 262–252 Ma, respectively), with intrusions of granitic magma, which happened in the study area during the period of the Late Paleozoic. Additionally, this demonstrated that the evolution of the Altyn Tagh–Qilian–

North Qaidam tectonic mechanism was evidently divided into phases. The magmatic activities and geochemical characteristics of granites indicate that the crust thickness before c. 369 Ma may have been less than 35 km, with low contents of Sr and high contents of Y. This corresponds to Late Devonian continental lava and volcanic pyroclastic deposits (products of tectonic evolution in the post-orogenic period) developed in the North Qaidam and East Kunlun regions, which are related to extensions of the continental crust [89]. After a short period of extension in the Devonian, the North Margin of the Qinghai–Tibet Plateau was influenced by tectonic movements in the Paleo-Tethys tectonic domain, especially subductions [89]. The ancient Tethys Ocean’s collision transpired between the Carboniferous–Permian continents of Asia and the Gondwana continent as the crust was renewed and intensified the compression. The crust underwent rapid thickening, reaching a thickness of up to 50 km in the Mid–Late Permian (262–252 Ma). Simultaneously, there was a transition phase in the tectonic system from compression to extension, and the basaltic lower crust was partially melted due to the heating of underplated basaltic magma, causing the formation of Mid–Late Permian granites. In conclusion, magmatic activities in the study area in the Early Paleozoic–Devonian were mainly affected by the Altyn Tagh–Qilian–North Qaidam tectonic mechanism, and those of the Carboniferous–Mesozoic–Cenozoic were restricted by the tectonic mechanism of the Paleo-Tethys Plate.

### 5.3. Tectonic Implications

#### 5.3.1. Tectonic System of Altyn Tagh

Altyn Tagh is an important tectonic belt in the Northern Qinghai–Tibet Plateau, which includes a calc-alkaline granitic body dated at c. 575 Ma [90]. These granodiorites were formed at the active continental margin, meaning that plate subduction happened between the end of the Neoproterozoic and the beginning of the Paleozoic. In the Early Paleozoic, the Altyn Tagh region had started the ocean–continent evolution, as evidenced by two major ophiolite belts of such age. The c. 508–449 Ma Hongliugou–Lapeiquan ophiolite [91,92] is comparable to the Mangnai ophiolite, dated at c. 481 Ma [91]. In recent years, the discovery of high-pressure and ultrahigh-pressure metamorphic rocks in southern Altyn Tagh revealed the existence of a UHP metamorphic belt [7,11,12,28,29,93], formed ca. 504–486 Ma [94], which is 40–60 Ma older than that of eclogite in the UHP metamorphic belt in the North Qaidam Margin. Post-collisional extension was the major tectonic evolution process in the Altyn Tagh region, with weak magmatic activity and small rock masses [89].

#### 5.3.2. North Qaidam–Qilian Tectonic System

North Qaidam–Qilian is a Cambrian–Ordovician orogenic belt. The Southern Qilian region is a small, active ocean basin. The oceanic crust subducted toward the Middle Qilian continental crust, and the ocean basin soon closed and formed the tectonic pattern of today. In recent years, the discovery of eclogites in the Xitie Mountain, Dachaidan, Yuka River, Dulan, and Shaliu River [9,12,95] proved that, during ca. 495–466 Ma, the subducted oceanic crust towed the Qaidam continental crust, causing it to subduct continuously. As a result, different types of rocks in Northern Qaidam experienced Early Paleozoic UHP metamorphism [12,17,18]. Furthermore, coesite and pseudomorph in eclogite and paragneiss [9,12], garnet peridotite, and diamond inclusions, as well as the phenomenon that clinopyroxene and rutile were exsolved in garnet [7], are consistent with these results. Several rocks were subducted to a mantle depth of 100–200 km. In the Early Silurian–Devonian, the continental crust began an exhumation process because of the subducted oceanic crust’s earlier delamination and violent crustal uplift during orogenesis, with magmatic activities in the crust. Molasse formations were broadly developed in the Early Devonian [19,21,96]. Furthermore, quartz diorite of the Aolao River in North Qaidam, small rock bodies southeast of the Bagaqaidam Lake, Datouyangou rock bodies in the Dachaidan region, and Late Devonian granodiorites were formed by the partial melting that occurred during extensions between different blocks in the orogenic zone after the UHP metamorphic belt was subducted and exhumed, indicating the uplifting stage of the North

Qaidam–Qilian region after its orogenesis. This orogenesis stopped in the Carboniferous when the marine-paralic continental deposition belt covered the whole Qilian Caledonides tectonic belt [21]. In the Late Carboniferous, intracontinental subduction happened in North Qaidam as the Paleo-Tethys Ocean closed. Large amounts of granodiorite–monzogranite magmas were created in the middle–lower crust [97], such as the Sanchagou rock body in the west section of North Qaidam [21] and Late Permian monzogranite. These granites were formed under local tectonic stress changes from extension to compression, leading to intracontinental subduction and the upward intrusion of deep-mantle-derived materials. The middle–lower crust was eventually remelted.

### 5.3.3. Tectonic Setting of Altyn Tagh and North Qaidam–Qilian

Ge et al. [98] considered the tectonic units on both sides of the Altyn Tagh Fault before the Cenozoic Era to be comparable to the Alashan–Beishan–Tarim Block, the North Qilian–Hexi Corridor–Manjiaer Rift Trough, the Middle Qilian Uplift–Middle Uplift of Tarim, the South Qilian–North Qaidam–South Tarim, and the East Kunlun–West Kunlun. Based on a study of eclogites in the North Qaidam and South Altyn Tagh UHP metamorphic belts, Yang et al. [9] concluded that the South Altyn Tagh UHP metamorphic belt was a westward extension of the Northern Qaidam UHP metamorphic belt, with a stagger of 400 km by the Altyn Tagh Fault. Chen et al. [99] considered the east section of Altyn Tagh and the west section of the Qilian Mountain to be similar and comparable, estimating that the total displacement of the sinistral strike-slip of the Altyn Tagh Fault is about 400 km. Research on the metamorphic ages of eclogites has been conducted in Altyn Tagh and North Qaidam. Liu et al. [93] found that the peak metamorphic age of rocks in the Altyn Tagh high-pressure–ultrahigh-pressure metamorphic belt (c. 504–480 Ma) was c. 40–60 Ma earlier than that of Northern Qaidam (c. 461–420 Ma), which is c. 30–55 Ma earlier than the retrograde metamorphic age. Thus, it is considered that eclogites in Altyn Tagh and Northern Qaidam do not belong to the same high-pressure–ultrahigh-pressure metamorphic belts.

Late Paleozoic granites in Northern Qaidam–Qilian can be distinguished in the Late Devonian (c. 385–367 Ma) and Permian (c. 275–252 Ma). However, Late Paleozoic granites are rare in Altyn Tagh. Chen et al. [99] considered that the Early Paleozoic Era (c. 490–385) was the active stage due to magmatic activities in the north margin of Altyn Tagh. Hence, the granite in Altyn Tagh was not found in the study area, which may be caused by the different active ages of the Altyn Tagh and North Qaidam UHP metamorphic belts. Accordingly, the South Altyn Tagh and North Qaidam UHP metamorphic belts may not belong to one UHP metamorphic belt.

### 5.3.4. Nd Model Age and Attribution of Precambrian Basement in the Qilian Block

The Proterozoic crystalline basements within the Qilian orogenic belt predominantly emerge in the Yemnan Mountains in the western segment, Huangyuan in the central portion, and Maxianshan in the eastern section. These formations comprise high-grade metamorphic and granitic rocks. Generally, there are two models of the tectonic affinity of the Precambrian basement in the Qilian orogenic belt. Researchers consider that the Qilian Block belongs to the North China Craton [100–102]. However, geochemical and isotopic geochronological results led some researchers to consider that the Qilian Block was genetically related to the Yangtze Block. By analyzing the age spectrum of detrital and magmatic zircons in the Qilian Block, we concluded that the Qilian Block and Yangtze Block may have been in a uniform block in the Neoproterozoic Era and both belonged to Gondwana [33,103,104]. Through the study of Precambrian basement rocks in the Qilian orogenic belt and Pb–Nd isotopic compositions of granites, Zhang et al. [88] concluded that the Qilian orogenic belt is similar to the Yangtze Block and expanded the northwest boundary of the Yangtze Block to the north of the Qilian orogenic belt.

Based on the Nd isotope model ages of granites, we concluded that the basement of the North China Plate was formed in the Archean. The most important crustal growth

period was between 2.8 and 2.6 Ga, and the less important crustal growth period was from 1.8 to 2.2 Ga [105]. Simultaneously, through comprehensive data processing and analysis, Wu et al. [106] determined that the Nd isotope model ages of the North China Craton are mainly between 2.4 Ga and 3.6 Ga, and the Nd isotope model ages of the whole South China Craton are mainly between 0.9 Ga and 2.3 Ga, while the intermediate acid igneous rocks in the Yangtze Block are between 0.7 and 2.2 Ga [72]. Furthermore, the Nd model ages of Huashigou granitoids are evidently divided into two phases: 0.9–1.1 Ga, represented by Middle Permian granodiorite, Middle Permian quartz diorite, and Late Permian monzogranite, and 1.6–1.7 Ga, represented by Late Devonian granodiorite and Middle Permian porphyritic tonalite [41,42]. This confirmed that the Mesoproterozoic Era was a crustal growth period in the Qilian region. The results indicate that the crustal growth history of the Qilian orogenic belt is similar to that of the South China Craton but different from that of the North China Craton. Furthermore, the Nd isotope model ages indicated that the Qilian Block and Yangtze Block might have been in a uniform block in the Mesoproterozoic Era.

The results highlighted two stages of granitic production in the Huashigou area, which included Late Devonian granodiorite (c. 369 Ma), Middle Permian biotite granodiorite, quartz diorite, porphyritic tonalite (c. 262–261 Ma), and Late Permian monzonitic granite (252 Ma).

## 6. Conclusions

- (1) Zircon U–Pb dating yielded crystallization ages of  $368.7 \pm 3.5$  Ma,  $261.5 \pm 0.63$  Ma, and  $262.2 \pm 1.4$  Ma for the Hua1, Hua2, and Hua4 plutons, respectively.
- (2) Trace elements and Sr–Nd–Hf–O isotopes indicated that Huashigou granitoids were derived from the partial melting of the lower crust.
- (3) Huashigou granitoids were formed in the orogenic–post-orogenic extensional tectonic setting, and they were derived from different tectonic levels or crustal depths. Late Devonian granitoids were formed from the decompression melting of enriched and shallow-depth crustal materials. Middle–Late Permian granitoids resulted from the partial melting of the basaltic lower crust through heating by underplating basaltic magma. Additionally, they may have been formed by slab break-off magmatism.

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## Article

# Geochronology, Geochemical Characterization and Tectonic Background of Volcanic Rocks of the Longjiang Formation in the Lengjimanda Plate Area, Middle Da Hinggan Mountains

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**Abstract:** The Lengjimanda plate is situated in the middle section of the Da Hinggan mountains, in the eastern section of the Tianshan Xingmeng orogenic belt. To determine the formation age of the volcanic rocks in the Longjiang formation in this area, to explore their origin and tectonic background, and to reconstruct the geodynamic evolution of the region, this study conducted petrological, zircon U–Pb geochronological, geochemical, and isotopic analyses of the volcanic rocks in the Longjiang formation. The Longjiang formation's volcanic rocks are primarily composed of trachyandesite, trachyte trachydacite, and andesite, which are intermediate basic volcanic rocks. They are enriched in large-ion lithophile elements, are depleted in high-field-strength elements, are significantly fractionated between light and heavy rare earth elements, and exhibit a moderate negative Eu anomaly in most samples. The results of the LA–ICP–MS zircon U–Pb dating indicate that the volcanic rocks in this group were formed in the Early Cretaceous period at  $129.1 \pm 0.82$  Ma. The zircon  $\varepsilon_{\text{Hf}}(t)$  ranges from +1.13 to +43.77, the  $t_{\text{DM2}}$  ranges from +655 to +1427 Ma, the initial Sr ratio ( $^{87}\text{Sr}/^{86}\text{Sr}$ )<sub>i</sub> ranges from 0.7030 to 0.7036, and the  $\varepsilon_{\text{Nd}}(t)$  ranges from +2.1 to +6.6. Based on the geochemical compositions and isotopic characteristics of the rocks, the initial magma of the volcanic rocks in the Longjiang formation originated from the partial melting of basaltic crustal materials, with a source material inferred to be depleted mantle-derived young crustal. These rocks were formed in a superimposed post-collisional and continental arc environment, possibly associated with the Mongol–Okhotsk Ocean closure and the oblique subduction of the Pacific plate. This study addresses a research gap regarding the volcanic rocks of the Longjiang formation in this area. Its findings can be applied to exploration and prospecting in the region.

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## 1. Introduction

The Central Asian orogeny is a large Phanerozoic orogenic belt located between the North China, Tarim, and Siberian plates [1,2]. The Da Hinggan mountain region is situated in the eastern part of the Central Asian orogenic belt, between the Mongolia–Okhotsk suture line and the Xilamulun Yanji suture zone. It is a significant region, where the Paleozoic Paleo-Asian Oceanic metallogenetic tectonic domain is strongly superimposed, compounded, and transformed by the Mesozoic and Neo-Mesozoic Pacific metallogenetic tectonic domains [3–5]. The Paleozoic was characterized by the collision of small land masses and the closure of the Paleo-Asian Ocean [6,7], whereas the Mesozoic was characterized by the superposition and modification of the Paleo-Pacific plate and the Mongolian–Okhotsk plate [8,9]. Multiple phases of volcanic eruptions have resulted in

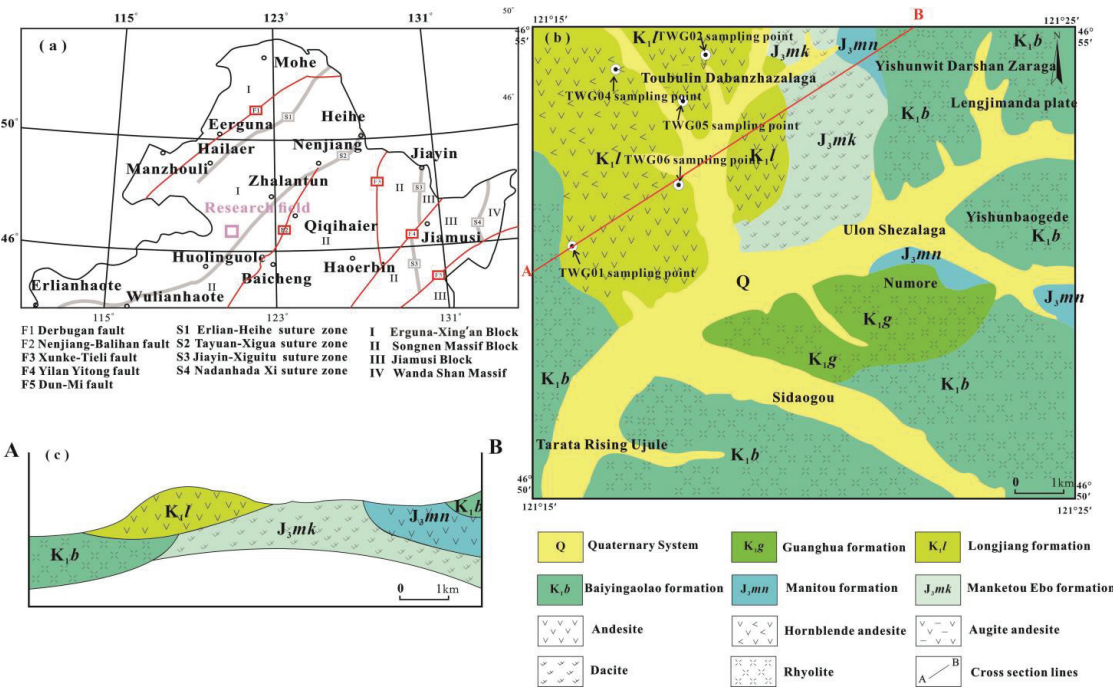


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favorable metallogenic geological conditions in the area, with a variety of rock types [10] and extensive development of Mesozoic volcanic and granitic rocks [1,11]. The volcanic rocks are mainly Early Cretaceous rhyolite and basaltic andesite, distributed in facies-like formations [12]. The rock assemblage of the Mesozoic granites is primarily composed of granodiorite, monzogranite, and syenogranite, with a presence of A-type granites [13]. Several researchers have investigated the chronology and tectonic background of Mesozoic magmatism in the Da Hinggan mountains, and a basic understanding of the chronological framework delineation of different contemporaneous volcanic rocks has been achieved [14–16]; however, there are still some controversies regarding the tectonic background of these mountains, such as the subduction orogeny of the Ancient Pacific plate [17,18], and the post-orogenic extension in the Mongol-Okhotsk ocean [19,20]. Studies on the Da Hinggan mountains' Mesozoic stratigraphy have focused on the Tamulangou formation [21], Manketou Ebo formation [22], Manitou formation [23,24], and Baiyingaolao formation [25,26]. There are fewer studies on the Longjiang formation, and these studies do not provide a unified understanding of the era in which the Longjiang formation's volcanic rocks were formed [27,28]. Furthermore, these works mainly focused on the chronology and whole-rock geochemistry and lacked comprehensive studies of the Sr–Nd–Pb and Lu–Hf isotopes [29,30]. The strong stability of zircon minimizes the influence of later geological events on its Hf isotopic composition, while its extremely low Lu content allows us to accurately determine its Hf isotopic composition at the time of its formation. These properties make zircon an important tool for studying crustal evolution and tracing rock source regions [31–33]. Sr–Nd–Pb isotopic analyses are important in determining the petrogenesis of a formation, as they indicate the magma source and reveal the evolutionary pathways of rocks [34–37]. This study aimed to address the research gap concerning the volcanic rocks of the Longjiang formation. The objectives were to determine the formation age of the Longjiang formation's volcanic rocks, investigate their genesis and tectonic background, and reconstruct the geodynamic evolution of the region. This paper presents detailed petrological, zircon U–Pb geochronological, geochemical, and isotopic chemical analyses of the volcanic rocks of the Longjiang formation conducted through extensive field geological surveys using a geological map of the Lengjimanda plate at a scale of 1:25,000. The objective of this research is to provide reliable data for understanding the dynamic history of the Da Hinggan mountains.

## 2. Geological Background

The Lengjimanda plate area in the middle of the Da Hinggan mountains is located at the junction of the Xing'an block and the Songnen block in the eastern part of the Central Asian orogenic belt, which belongs to the Zhalantun Duobaoshan island arc (Figure 1a). During the Paleozoic, it was in the accretionary stage of the ancient Asian oceanic continental margin, forming an inland sedimentary basin. During the Mesozoic, it experienced the superposition, complexation, and transformation of the Paleo-Pacific tectonic domain and the Mongolian-Okhotsk oceanic tectonic domain [38], forming an inland volcanic basin [39]. In the Da Hinggan mountain region, the area was affected by the subduction of the Mongolian-Okhotsk oceanic plate during the Triassic. The study area experienced uplift and orogenic movements, resulting in the development of fragmented alteration or thrust faults in both the near-EW and near-NE directions [40]. During the Cretaceous, the area was influenced by the eastward subduction of the Paleo-Pacific plate towards the East Asian continent, forming volcanic rift basins and uplifts that were mainly distributed in the NNE direction. Due to the influence of multiple tectonic environments and superpositions, three main stages of structures developed in the study area. The first stage is characterized by NE reverse faults, the second stage by NNE shear zones, and the third stage by near-EW normal faults.



**Figure 1.** (a) The sample structural map in the Northeast region [40]; (b) plate geological map of LingjiManda plate, Da Hinggan Mountains [41]; and (c) geological cross-section view of LingjiManda plate.

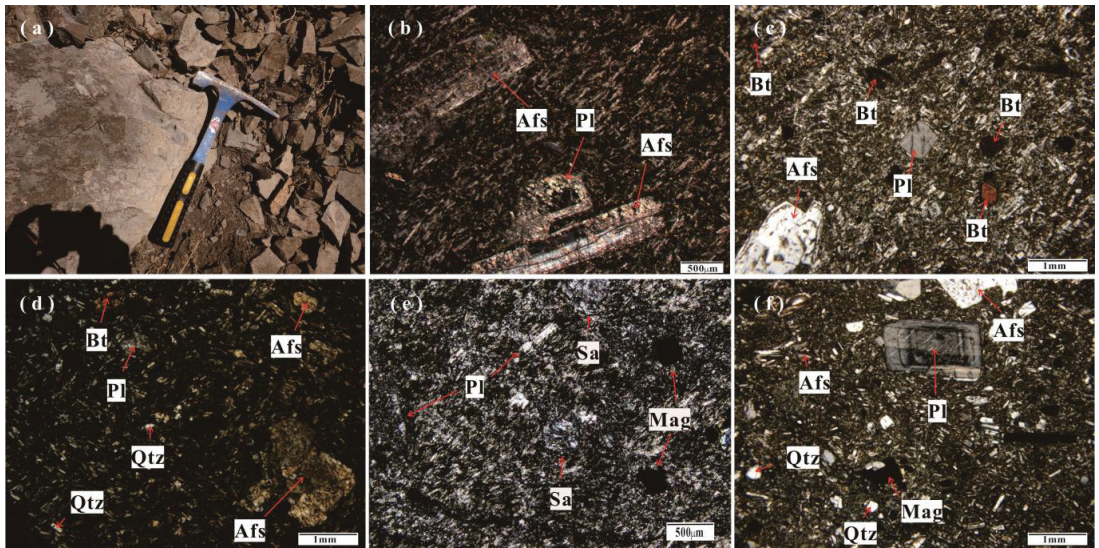
The region is primarily characterized by Early Cretaceous intrusive rocks derived from the upper crust, with intrusion depths ranging from moderate to shallow. Several lithologies can be recognized, including granite quartz-bearing diorite, quartz-bearing monzonite, and granodiorite belonging to the high-potassium calc-alkaline series. Three types of vein rocks developed in the study area. They are mainly gray-black andesite, light pinkish-red syenite, and gray-white granite aplites. These three varieties occur together in the same location and have a NE distribution pattern, suggesting that they may have been formed by intrusion along a tectonic line.

The study area mainly consists of middle Jurassic Lower Cretaceous formations, which are the Wanbao formation (J<sub>2</sub>wb), Manketou Ebo formation (J<sub>2</sub>mk), Manitou formation (J<sub>3</sub>mn), Baiyingaolao formation (K<sub>1</sub>b), Longjiang formation (K<sub>1</sub>l), and Guanghua formation (K<sub>1</sub>g). The Longjiang formation is a suite of intermediate volcanic rocks characterized by different lithological types, including effusive basalt, explosive basaltic breccia tuff (comprising crystal and lithic fragments), volcanoclastic flow breccia tuff of a basaltic composition, and subvolcanic andesite. In the western part of the study area, particularly in the Tubulin Daban Zhalaga section, the Longjiang formation mainly consists of a suite of neutral to slightly alkaline volcanic rocks, with lithological assemblages including porphyritic rock, porphyritic andesite, andesite, andesitic brecciated tuff with angular lithic fragments, and locally developed andesitic volcanoclastic breccia (Figure 1b).

Sample TWG01 of the Longjiang formation was collected from the Toubulingda Zalaga area in the western part of LingjiManda Banxi. The sampling coordinates are 46° 52' 48" N, 121° 15' 36" E (Figure 2b). The weathered surface appears yellowish-brown, while the fresh surface is light gray. It exhibits a volcanic breccia structure with 30% angular clasts and 10% rock fragments composed of andesite. Crystals include 10% plagioclase and 20%



alkali feldspar. The volcanic glassy matrix is reddish-brown, flame-like, with 50% content, showing trachyandesite under indoor microscopic identification.



**Figure 2.** Hand specimen photo (a) and microscope photos (b–f) of the Lengjimanda plate. (a) TWG05; (b) TWG01; (c) TWG02; (d) TWG04; (e) TWG05; (f) TWG06, Sa: sanidine; Pl: plagioclase; Mag: magnetite; Afs: alkali feldspar; Bt: biotite; Qtz: quartz.

Sample TWG02 of the Longjiang formation was collected from the same area, with coordinates  $46^{\circ} 54'36''$  N,  $121^{\circ}17'24''$  E (Figure 2c). The weathered surface is yellowish-brown, and the fresh surface is light yellow with patchy structures and an interwoven matrix. The phenocrysts include 20% alkali feldspar, 10% plagioclase, and 5% biotite. The matrix has a microcrystalline interwoven structure of plagioclase, identified indoors as biotite trachyte rock.

Sample TWG04 of the Longjiang formation was collected nearby, with coordinates  $46^{\circ} 53'59''$  N,  $121^{\circ}50'11''$  E (Figure 2d). The weathered surface is light gray, and the fresh surface is dark gray with patchy structures and an interwoven matrix. Phenocrysts include 20% alkali feldspar, 10% plagioclase, and 5% biotite. The matrix has a microcrystalline interwoven structure of plagioclase, identified indoors as biotite trachyandesite.

Sample TWG05 of the Longjiang formation was collected with coordinates  $46^{\circ}53'30''$  N,  $121^{\circ}52'15''$  E (Figure 2e). The fresh surface is gray-brown with patchy and vesicular structures. Under polarized light microscopy, phenocrysts constitute approximately 5% to 10% of the sample, ranging from 2 to 4 mm in size, mainly composed of translucent feldspar and plagioclase. The feldspar phenocrysts exhibit tabular self-shaped structures, while the plagioclase phenocrysts are elongated tabular with semi- to self-shaped structures, some showing zoning. Phenocrysts and matrix display weak orientation, with the matrix predominantly glassy or cryptocrystalline, about 80%, occasionally showing fine needle-columnar plagioclase in microcrystalline interwoven structures.

Sample TWG06 of the Longjiang formation was collected with coordinates  $46^{\circ} 53'21''$  N,  $121^{\circ}52'18''$  E (Figure 2f). The weathered surface is yellowish-brown, and the fresh surface is dark gray with patchy structures and an interwoven matrix. Phenocrysts include 15% alkali feldspar, 20% plagioclase, and 2% magnetite. Alkali feldspar fills gaps between plagioclase microcrystals, identified indoors as trachyandesite.



### 3. Materials and Methods

The trachyandesite (TWG01, TWG04, and TWG06) and trachyte trachydacite (TWG02, TWG05) samples were picked up from the Toubulin-Dabanzhazalaga area in the western part of the study area (Figure 1b). They were subjected to zircon LA-ICP-MS dating (except sample TWG02), whole rock major and trace element analyses, and Sr-Nb-Pb isotopic analyses (except sample TWG02). Zircon Lu-Hf isotope analyses were performed on a coarse-grained andesite sample (TWG01).

#### 3.1. Major and Trace Element Analyses

Rock geochemical analysis was conducted at the Shenyang geological survey center, China geological survey. Fresh and unweathered samples were selected and then ground to a very fine power of about 80–200  $\mu\text{m}$  for major and trace element analysis. A Rigaku Primus II X-ray fluorescence spectrometer (XRF-1500) was used for the determination of major element contents and analysis standards, according to Zhuo [42]. Chemical titration was used for the determination of FeO, and chemical mass analysis was used for the determination of loss on ignition, with analytical accuracy better than 1% to 5%. The trace and rare earth elements were determined using an Agilent 7500a inductively coupled plasma mass spectrometer (X-Series 2) with analytical accuracy better than 2% to 5%.

#### 3.2. LA-ICP-MS Zircon U-Pb Dating

The separation, mounting, and microscopic image acquisition of zircon grains were conducted at the State Key Laboratory of Geological Processes and Mineral Resources at the Geosciences China University (Wuhan). First, samples were crushed to a particle size of 80–100 mesh using conventional methods. After magnetic and organic heavy liquid separations, zircon grains with consistent colors, crystal shapes, sizes, and low degrees of abrasion were selected. The selected zircon grains were then mounted on an epoxy resin, polished to half of their thickness, and coated with a gold film. The zircons selected from various samples exhibited morphological differences, including short prismatic and long prismatic shapes. Based on the CL images (Figure 3), zircons exhibiting the greatest degree of euhedry and oscillatory zoning, as well as the fewest inclusions, alterations, and cracks, were selected for experimentation. Zircon U-Pb dating was performed at the Qingdao National Laboratory for Marine Science and Technology, Chinese Academy of Sciences, using an Agilent 7500a LA-ICP-MS system coupled to a resolution M50 laser ablation system. The experiment employs helium as the carrier gas for the ablation material, and NIST 610 glass was used as the instrument monitoring standard. The age determination was calibrated using standard zircon 91500 and monitoring standard zircon Plešovice, and the laser spot diameter was 32  $\mu\text{m}$  at a frequency of 7 Hz. The experimental procedures were like those described in Yuan [43]). Glitter software was used for signal selection, correction, and quantitative standardization of the experimental data, and ordinary Pb correction was performed using the method proposed by Andersen [44]. Age calculations and concordance plots were performed using Isoplot.

The measured age of the Plešovice zircon  $^{206}\text{Pb}/^{238}\text{U}$  in the experiment was  $342.21 \pm 5.53$  Ma, which is consistent with the standard value ( $337.13 \pm 0.37$  Ma; Sláma [45]) within the error range. The 91500 zircon  $^{206}\text{Pb}/^{238}\text{U}$  age was  $1062.44 \pm 15.44$  Ma, which is consistent with the standard value ( $1062.4 \pm 0.8$  Ma; Wiedenbeck [34]) within the error margin, indicating high accuracy and reliability.



**Figure 3.** U–Pb zircons cathodoluminescence images from the volcanic rocks of the Longjiang formation at Lengjimanda plate. Circles indicate the locations of U–Pb analysis on zircons, along with their respective zircon numbers, and age information listed below. (a) TWG01, (b) TWG04, (c) TWG05, (d) TWG06.

### 3.3. The Sr–Nd–Pb Isotope Analysis

The pre-treatment and mass spectrometric determination of Sr–Nd–Pb isotopic analysis of volcanic rocks from the Longjiang formation were conducted at the State Key Laboratory for Mineral Deposits Research, Nanjing University, focusing on the ore-forming mechanisms of endogenous metal deposits. After dissolving the whole rock sample with a mixture of HF and HNO<sub>3</sub>, AG50W×8 cation exchange resin was used for the separation and purification of Sr and Nd using different eluents. For specific details of the procedure, please refer to Wei [46].

Sr–Nd isotopic analyses were performed using thermal ionization mass spectrometry (TIMS) on a solid isotope mass spectrometer. For the Sr isotope ratio determination, instrumental mass fractionation correction was performed using a reference value of  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$  with NIST SRM 987 as the external standard. For the Nd isotope analysis, the instrument mass fractionation correction was performed using a reference value of  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$  with the Nd isotope international standard material JNdi-1 as the external standard. The measurement accuracy was within 5 ppm for  $^{143}\text{Nd}/^{144}\text{Nd}$  and within 10 ppm for  $^{87}\text{Sr}/^{86}\text{Sr}$ .

For Pb isotope analysis, the sample was dissolved in a mixture of HNO<sub>3</sub> and HF solutions in a volume ratio of 1:4. The Pb isotopes were then separated and purified using HBr and cation exchange resin. Pb isotopic testing and analysis were performed using thermal ionization mass spectrometry (TIMS), with instrumental mass fractionation correction using NIST Pb-981 and isotopic fractionation correction using NBS 981. The precision of the measurements was  $^{206}\text{Pb}/^{204}\text{Pb} < 0.2\%$ .

### 3.4. Zircon Lu–Hf Isotope Analysis

A micro-area Hf isotopic analysis was conducted on the samples based on the LA-ICP-MS zircon U–Pb isotopic analysis. Zircon Hf isotope analyses were performed at the State Key Laboratory for Mineral Deposits Research, Nanjing University. The experimental analysis used a Neptune MC–ICP-MS coupled with a COMPEX GeoLas Pro 193 nm ArF excimer laser ablation system. A laser spot diameter of 32 µm was used based on the size of the zircon grains, with a laser pulse frequency of 7 Hz. Helium was used as the ablation carrier gas. Zircon 91500 and MT were used as external reference materials. The obtained  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio was determined to be  $0.282948 \pm 0.000038$ , which is within the error margin of the recommended value ( $0.282302 \pm 8$ ; Goolaerts [47]). Further details of the analytic procedure can be found in Wu [48].

## 4. Results

### 4.1. Major and Trace Element Compositions

The results of the major and trace element analyses of the volcanic rocks from the Longjiang formation are presented in Table 1.

**Table 1.** Major and trace element compositions of Lengjiamanda plate of the Longjiang formation volcanic rocks.

[illegible]

Table 1. Cont.

| Sample | TWG01YQ1 |  |  |  |  |  |  |  |  |  | TWG01YQ2 |  |  |  |  |  |  |  |  |  | TWG01YQ3 |  |  |  |  |  |  |  |  |  | TWG01YQ4 |  |  |  |  |  |  |  |  |  | TWG01YQ5 |  |  |  |  |  |  |  |  |  | TWG02YQ1 |  |  |  |  |  |  |  |  |  | TWG02YQ2 |  |  |  |  |  |  |  |  |  | TWG02YQ3 |  |  |  |  |  |  |  |  |  | TWG02YQ4 |  |  |  |  |  |  |  |  |  | TWG02YQ5 |  |  |  |  |  |  |  |  |  | TWG02YQ6 |  |  |  |  |  |  |  |  |  | TWG02YQ7 |  |  |  |  |  |  |  |  |  | TWG02YQ8 |  |  |  |  |  |  |  |  |  | TWG02YQ9 |  |  |  |  |  |  |  |  |  | TWG02YQ10 |  |  |  |  |  |  |  |  |  | TWG02YQ11 |  |  |  |  |  |  |  |  |  | TWG02YQ12 |  |  |  |  |  |  |  |  |  | TWG02YQ13 |  |  |  |  |  |  |  |  |  | TWG02YQ14 |  |  |  |  |  |  |  |  |  | TWG02YQ15 |  |  |  |  |  |  |  |  |  | TWG02YQ16 |  |  |  |  |  |  |  |  |  | TWG02YQ17 |  |  |  |  |  |  |  |  |  | TWG02YQ18 |  |  |  |  |  |  |  |  |  | TWG02YQ19 |  |  |  |  |  |  |  |  |  | TWG02YQ20 |  |  |  |  |  |  |  |  |  | TWG02YQ21 |  |  |  |  |  |  |  |  |  | TWG02YQ22 |  |  |  |  |  |  |  |  |  | TWG02YQ23 |  |  |  |  |  |  |  |  |  | TWG02YQ24 |  |  |  |  |  |  |  |  |  | TWG02YQ25 |  |  |  |  |  |  |  |  |  | TWG02YQ26 |  |  |  |  |  |  |  |  |  | TWG02YQ27 |  |  |  |  |  |  |  |  |  | TWG02YQ28 |  |  |  |  |  |  |  |  |  | TWG02YQ29 |  |  |  |  |  |  |  |  |  | TWG02YQ30 |  |  |  |  |  |  |  |  |  | TWG02YQ31 |  |  |  |  |  |  |  |  |  | TWG02YQ32 |  |  |  |  |  |  |  |  |  | TWG02YQ33 |  |  |  |  |  |  |  |  |  | TWG02YQ34 |  |  |  |  |  |  |  |  |  | TWG02YQ35 |  |  |  |  |  |  |  |  |  | TWG02YQ36 |  |  |  |  |  |  |  |  |  | TWG02YQ37 |  |  |  |  |  |  |  |  |  | TWG02YQ38 |  |  |  |  |  |  |  |  |  | TWG02YQ39 |  |  |  |  |  |  |  |  |  | TWG02YQ40 |  |  |  |  |  |  |  |  |  | TWG02YQ41 |  |  |  |  |  |  |  |  |  | TWG02YQ42 |  |  |  |  |  |  |  |  |  | TWG02YQ43 |  |  |  |  |  |  |  |  |  | TWG02YQ44 |  |  |  |  |  |  |  |  |  | TWG02YQ45 |  |  |  |  |  |  |  |  |  | TWG02YQ46 |  |  |  |  |  |  |  |  |  | TWG02YQ47 |  |  |  |  |  |  |  |  |  | TWG02YQ48 |  |  |  |  |  |  |  |  |  | TWG02YQ49 |  |  |  |  |  |  |  |  |  | TWG02YQ50 |  |  |  |  |  |  |  |  |  | TWG02YQ51 |  |  |  |  |  |  |  |  |  | TWG02YQ52 |  |  |  |  |  |  |  |  |  | TWG02YQ53 |  |  |  |  |  |  |  |  |  | TWG02YQ54 |  |  |  |  |  |  |  |  |  | TWG02YQ55 |  |  |  |  |  |  |  |  |  | TWG02YQ56 |  |  |  |  |  |  |  |  |  | TWG02YQ57 |  |  |  |  |  |  |  |  |  | TWG02YQ58 |  |  |  |  |  |  |  |  |  | TWG02YQ59 |  |  |  |  |  |  |  |  |  | TWG02YQ60 |  |  |  |  |  |  |  |  |  | TWG02YQ61 |  |  |  |  |  |  |  |  |  | TWG02YQ62 |  |  |  |  |  |  |  |  |  | TWG02YQ63 |  |  |  |  |  |  |  |  |  | TWG02YQ64 |  |  |  |  |  |  |  |  |  | TWG02YQ65 |  |  |  |  |  |  |  |  |  | TWG02YQ66 |  |  |  |  |  |  |  |  |  | TWG02YQ67 |  |  |  |  |  |  |  |  |  | TWG02YQ68 |  |  |  |  |  |  |  |  |  | TWG02YQ69 |  |  |  |  |  |  |  |  |  | TWG02YQ70 |  |  |  |  |  |  |  |  |  | TWG02YQ71 |  |  |  |  |  |  |  |  |  | TWG02YQ72 |  |  |  |  |  |  |  |  |  | TWG02YQ73 |  |  |  |  |  |  |  |  |  | TWG02YQ74 |  |  |  |  |  |  |  |  |  | TWG02YQ75 |  |  |  |  |  |  |  |  |  | TWG02YQ76 |  |  |  |  |  |  |  |  |  | TWG02YQ77 |  |  |  |  |  |  |  |  |  | TWG02YQ78 |  |  |  |  |  |  |  |  |  | TWG02YQ79 |  |  |  |  |  |  |  |  |  | TWG02YQ80 |  |  |  |  |  |  |  |  |  | TWG02YQ81 |  |  |  |  |  |  |  |  |  | TWG02YQ82 |  |  |  |  |  |  |  |  |  | TWG02YQ83 |  |  |  |  |  |  |  |  |  | TWG02YQ84 |  |  |  |  |  |  |  |  |  | TWG02YQ85 |  |  |  |  |  |  |  |  |  | TWG02YQ86 |  |  |  |  |  |  |  |  |  | TWG02YQ87 |  |  |  |  |  |  |  |  |  | TWG02YQ88 |  |  |  |  |  |  |  |  |  | TWG02YQ89 |  |  |  |  |  |  |  |  |  | TWG02YQ90 |  |  |  |  |  |  |  |  |  | TWG02YQ91 |  |  |  |  |  |  |  |  |  | TWG02YQ92 |  |  |  |  |  |  |  |  |  | TWG02YQ93 |  |  |  |  |  |  |  |  |  | TWG02YQ94 |  |  |  |  |  |  |  |  |  | TWG02YQ95 |  |  |  |  |  |  |  |  |  | TWG02YQ96 |  |  |  |  |  |  |  |  |  | TWG02YQ97 |  |  |  |  |  |  |  |  |  | TWG02YQ98 |  |  |  |  |  |  |  |  |  | TWG02YQ99 |  |  |  |  |  |  |  |  |  | TWG02YQ100 |  |  |  |  |  |  |  |  |  | TWG02YQ101 |  |  |  |  |  |  |  |  |  | TWG02YQ102 |  |  |  |  |  |  |  |  |  | TWG02YQ103 |  |  |  |  |  |  |  |  |  | TWG02YQ104 |  |  |  |  |  |  |  |  |  | TWG02YQ105 |  |  |  |  |  |  |  |  |  | TWG02YQ106 |  |  |  |  |  |  |  |  |  | TWG02YQ107 |  |  |  |  |  |  |  |  |  | TWG02YQ108 |  |  |  |  |  |  |  |  |  | TWG02YQ109 |  |  |  |  |  |  |  |  |  | TWG02YQ110 |  |  |  |  |  |  |  |  |  | TWG02YQ111 |  |  |  |  |  |  |  |  |  | TWG02YQ112 |  |  |  |  |  |  |  |  |  | TWG02YQ113 |  |  |  |  |  |  |  |  |  | TWG02YQ114 |  |  |  |  |  |  |  |  |  | TWG02YQ115 |  |  |  |  |  |  |  |  |  | TWG02YQ116 |  |  |  |  |  |  |  |  |  | TWG02YQ117 |  |  |  |  |  |  |  |  |  | TWG02YQ118 |  |  |  |  |  |  |  |  |  | TWG02YQ119 |  |  |  |  |  |  |  |  |  | TWG02YQ120 |  |  |  |  |  |  |  |  |  | TWG02YQ121 |  |  |  |  |  |  |  |  |  | TWG02YQ122 |  |  |  |  |  |  |  |  |  | TWG02YQ123 |  |  |  |  |  |  |  |  |  | TWG02YQ124 |  |  |  |  |  |  |  |  |  | TWG02YQ125 |  |  |  |  |  |  |  |  |  | TWG02YQ126 |  |  |  |  |  |  |  |  |  | TWG02YQ127 |  |  |  |  |  |  |  |  |  | TWG02YQ128 |  |  |  |  |  |  |  |  |  | TWG02YQ129 |  |  |  |  |  |  |  |  |  | TWG02YQ130 |  |  |  |  |  |  |  |  |  | TWG02YQ131 |  |  |  |  |  |  |  |  |  | TWG02YQ132 |  |  |  |  |  |  |  |  |  | TWG02YQ133 |  |  |  |  |  |  |  |  |  | TWG02YQ134 |  |  |  |  |  |  |  |  |  | TWG02YQ135 |  |  |  |  |  |  |  |  |  | TWG02YQ136 |  |  |  |  |  |  |  |  |  | TWG02YQ137 |  |  |  |  |  |  |  |  |  | TWG02YQ138 |  |  |  |  |  |  |  |  |  | TWG02YQ139 |  |  |  |  |  |  |  |  |  | TWG02YQ140 |  |  |  |  |  |  |  |  |  | TWG02YQ141 |  |  |  |  |  |  |  |  |  | TWG02YQ142 |  |  |  |  |  |  |  |  |  | TWG02YQ143 |  |  |  |  |  |  |  |  |  | TWG02YQ144 |  |  |  |  |  |  |  |  |  | TWG02YQ145 |  |  |  |  |  |  |  |  |  | TWG02YQ146 |  |  |  |  |  |  |  |  |  | TWG02YQ147 |  |  |  |  |  |  |  |  |  | TWG02YQ148 |  |  |  |  |  |  |  |  |  | TWG02YQ149 |  |  |  |  |  |  |  |  |  | TWG02YQ150 |  |  |  |  |  |  |  |  |  | TWG02YQ151 |  |  |  |  |  |  |  |  |  | TWG02YQ152 |  |  |  |  |  |  |  |  |  | TWG02YQ153 |  |  |  |  |  |  |  |  |  | TWG02YQ154 |  |  |  |  |  |  |  |  |  | TWG02YQ155 |  |  |  |  |  |  |  |  |  | TWG02YQ156 |  |  |  |  |  |  |  |  |  | TWG02YQ157 |  |  |  |  |  |  |  |  |  | TWG02YQ158 |  |  |  |  |  |  |  |  |  | TWG02YQ159 |  |  |  |  |  |  |  |  |  | TWG02YQ160 |  |  |  |  |  |  |  |  |  | TWG02YQ161 |  |  |  |  |  |  |  |  |  | TWG02YQ162 |  |  |  |  |  |  |  |  |  | TWG02YQ163 |  |  |  |  |  |  |  |  |  | TWG02YQ164 |  |  |  |  |  |  |  |  |  | TWG02YQ165 |  |  |  |  |  |  |  |  |  | TWG02YQ166 |  |  |  |  |  |  |  |  |  | TWG02YQ167 |  |  |  |  |  |  |  |  |  | TWG02YQ168 |  |  |  |  |  |  |  |  |  | TWG02YQ169 |  |  |  |  |  |  |  |  |  | TWG02YQ170 |  |  |  |  |  |  |  |  |  | TWG02YQ171 |  |  |  |  |  |  |  |  |  | TWG02YQ172 |  |  |  |  |  |  |  |  |  | TWG02YQ173 |  |  |  |  |  |  |  |  |  | TWG02YQ174 |  |  |  |  |  |  |  |  |  | TWG02YQ175 |  |  |  |  |  |  |  |  |  | TWG02YQ176 |  |  |  |  |  |  |  |  |  | TWG02YQ177 |  |  |  |  |  |  |  |  |  | TWG02YQ178 |  |  |  |  |  |  |  |  |  | TWG02YQ179 |  |  |  |  |  |  |  |  |  | TWG02YQ180 |  |  |  |  |  |  |  |  |  | TWG02YQ181 |  |  |  |  |  |  |  |  |  | TWG02YQ182 |  |  |  |  |  |  |  |  |  | TWG02YQ183 |  |  |  |  |  |  |  |  |  | TWG02YQ184 |  |  |  |  |  |  |  |  |  | TWG02YQ185 |  |  |  |  |  |  |  |  |  | TWG02YQ186 |  |  |  |  |  |  |  |  |  | TWG02YQ187 |  |  |  |  |  |  |  |  |  | TWG02YQ188 |  |  |  |  |  |  |  |  |  | TWG02YQ189 |  |  |  |  |  |  |  |  |  | TWG02YQ190 |  |  |  |  |  |  |  |  |  | TWG02YQ191 |  |  |  |  |  |  |  |  |  | TWG02YQ192 |  |  |  |  |  |  |  |  |  | TWG02YQ193 |  |  |  |  |  |  |  |  |  | TWG02YQ194 |  |  |  |  |  |  |  |  |  | TWG02YQ195 |  |  |  |  |  |  |  |  |  | TWG02YQ196 |  |  |  |  |  |  |  |  |  | TWG02YQ197 |  |  |  |  |  |  |  |  |  | TWG02YQ198 |  |  |  |  |  |  |  |  |  | TWG02YQ199 |  |  |  |  |  |  |  |  |  | TWG02YQ200 |  |  |  |  |  |  |  |  |  | TWG02YQ201 |  |  |  |  |  |  |  |  |  | TWG02YQ202 |  |  |  |  |  |  |  |  |  | TWG02YQ203 |  |  |  |  |  |  |  |  |  | TWG02YQ204 |  |  |  |  |  |  |  |  |  | TWG02YQ205 |  |  |  |  |  |  |  |  |  | TWG02YQ206 |  |  |  |  |  |  |  |  |  | TWG02YQ207 |  |  |  |  |  |  |  |  |  | TWG02YQ208 |  |  |  |  |  |  |  |  |  | TWG02YQ209 |  |  |  |  |  |  |  |  |  | TWG02YQ210 |  |  |  |  |  |  |  |  |  | TWG02YQ211 |  |  |  |  |  |  |  |  |  | TWG02YQ212 |  |  |  |  |  |  |  |  |  | TWG02YQ213 |  |  |  |  |  |  |  |  |  | TWG02YQ214 |  |  |  |  |  |  |  |  |  | TWG02YQ215 |  |  |  |  |  |  |  |  |  | TWG02YQ216 |  |  |  |  |  |  |  |  |  | TWG02YQ217 |  |  |  |  |  |  |  |  |  | TWG02YQ218 |  |  |  |  |  |  |  |  |  | TWG02YQ219 |  |  |  |  |  |  |  |  |  | TWG02YQ220 |  |  |  |  |  |  |  |  |  | TWG02YQ221 |  |  |  |  |  |  |  |  |  | TWG02YQ222 |  |  |  |  |  |  |  |  |  | TWG02YQ223 |  |  |  |  |  |  |  |  |  | TWG02YQ224 |  |  |  |  |  |  |  |  |  | TWG02YQ225 |  |  |  |  |  |  |  |  |  | TWG02YQ226 |  |  |  |  |  |  |  |  |  | TWG02YQ227 |  |  |  |  |  |  |  |  |  | TWG02YQ228 |  |  |  |  |  |  |  |  |  | TWG02YQ229 |  |  |  |  |  |  |  |  |  | TWG02YQ230 |  |  |  |  |  |  |  |  |  | TWG02YQ231 |  |  |  |  |  |  |  |  |  | TWG02YQ232 |  |  |  |  |  |  |  |  |  | TWG02YQ233 |  |  |  |  |  |  |  |  |  | TWG02YQ234 |  |  |  |  |  |  |  |  |  | TWG02YQ235 |  |  |  |  |  |  |  |  |  | TWG02YQ236 |  |  |  |  |  |  |  |  |  | TWG02YQ237 |  |  |  |  |  |  |  |  |  | TWG02YQ238 |  |  |  |  |  |  |  |  |  | TWG02YQ239 |  |  |  |  |  |  |  |  |  | TWG02YQ240 |  |  |  |  |  |  |  |  |  | TWG02YQ241 |  |  |  |  |  |  |  |  |  | TWG02YQ242 |  |  |  |  |  |  |  |  |  | TWG02YQ243 |  |  |  |  |  |  |  |  |  | TWG02YQ244 |  |  |  |  |  |  |  |  |  | TWG02YQ245 |  |  |  |  |  |  |  |  |  | TWG02YQ246 |  |  |  |  |  |  |  |  |  | TWG02YQ247 |  |  |  |  |  |  |  |  |  | TWG02YQ248 |  |  |  |  |  |  |  |  |  | TWG02YQ249 |  |  |  |  |  |  |  |  |  | TWG02YQ250 |  |  |  |  |  |  |  |  |  | TWG02YQ251 |  |  |  |  |  |  |  |  |  | TWG02YQ252 |  |  |  |  |  |  |  |  |  | TWG02YQ253 |  |  |  |  |  |  |  |  |  | TWG02YQ254 |  |  |  |  |  |  |  |  |  | TWG02YQ255 |  |  |  |  |  |  |  |  |  | TWG02YQ256 |  |  |  |  |  |  |  |  |  | TWG02YQ257 |  |  |  |  |  |  |  |  |  | TWG02YQ258 |  |  |  |  |  |  |  |  |  | TWG02YQ259 |  |  |  |  |  |  |  |  |  | TWG02YQ260 |  |  |  |  |  |  |  |  |  | TWG02YQ261 |  |  |  |  |  |  |  |  |  | TWG02YQ262 |  |  |  |  |  |  |  |  |  | TWG02YQ263 |  |  |  |  |  |  |  |  |  | TWG02YQ264 |  |  |  |  |  |  |  |  |  | TWG02YQ265 |  |  |  |  |  |  |  |  |  | TWG02YQ266 |  |  |  |  |  |  |  |  |  | TWG02YQ267 |  |  |  |  |  |  |  |  |  | TWG02YQ268 |  |  |  |  |  |  |  |  |  | TWG02YQ269 |  |  |  |  |  |  |  |  |  | TWG02YQ270 |  |  |  |  |  |  |  |  |  | TWG02YQ271 |  |  |  |  |  |  |  |  |  | TWG02YQ272 |  |  |  |  |  |  |  |  |  | TWG02YQ273 |  |  |  |  |  |  |  |  |  | TWG02YQ274 |  |  |  |  |  |  |  |  |  | TWG02YQ275 |  |  |  |  |  |  |  |  |  | TWG02YQ276 |  |  |  |  |  |  |  |  |  | TWG02YQ277 |  |  |  |  |  |  |  |  |  | TWG02YQ278 |  |  |  |  |  |  |  |  |  | TWG02YQ279 |  |  |  |  |  |  |  |  |  | TWG02YQ280 |  |  |  |  |  |  |  |  |  | TWG02YQ281 |  |  |  |  |  |  |  |  |  | TWG02YQ282 |  |  |  |  |  |  |  |  |  | TWG02YQ283 |  |  |  |  |  |  |  |  |  | TWG02YQ284 |  |  |  |  |  |  |  |  |  | TWG02YQ285 |  |  |  |  |  |  |  |  |  | TWG02YQ286 |  |  |  |  |  |  |  |  |  | TWG02YQ287 |  |  |  |  |  |  |  |  |  | TWG02YQ288 |  |  |  |  |  |  |  |  |  | TWG02YQ289 |  |  |  |  |  |  |  |  |  | TWG02YQ290 |  |  |  |  |  |  |  |  |  | TWG02YQ291 |  |  |  |  |  |  |  |  |  | TWG02YQ292 |  |  |  |  |  |  |  |  |  | TWG02YQ293 |  |  |  |  |  |  |  |  |  | TWG02YQ294 |  |  |  |  |  |  |  |  |  | TWG02YQ295 |  |  |  |  |  |  |  |  |  | TWG02YQ296 |  |  |  |  |  |  |  |  |  | TWG02YQ297 |  |  |  |  |  |  |  |  |  | TWG02YQ298 |  |  |  |  |  |  |  |  |  | TWG02YQ299 |  |  |  |  |  |  |  |  |  | TWG02YQ300 |  |  |  |  |  |  |  |  |  | TWG02YQ301 |  |  |  |  |  |  |  |  |  | TWG02YQ302 |  |  |  |  |  |  |  |  |  | TWG02YQ303 |  |  |  |  |  |  |  |  |  | TWG02YQ304 |  |  |  |  |  |  |  |  |  | TWG02YQ305 |  |  |  |  |  |  |  |  |  | TWG02YQ306 |  |  |  |  |  |  |  |  |  | TWG02YQ307 |  |  |  |  |  |  |  |  |  | TWG02YQ308 |  |  |  |  |  |  |  |  |  | TWG02YQ309 |  |  |  |  |  |  |  |  |  | TWG02YQ310 |  |  |  |  |  |  |  |  |  | TWG02YQ311 |  |  |  |  |  |  |  |  |  | TWG02YQ312 |  |  |  |  |  |  |  |  |  | TWG02YQ313 |  |  |  |  |  |  |  |  |  | TWG02YQ314 |  |  |  |  |  |  |  |  |  | TWG02YQ315 |  |  |  |  |  |  |  |  |  | TWG02YQ316 |  |  |  |  |  |  |  |  |  | TWG02YQ317 |  |  |  |  |  |  |  |  |  | TWG02YQ318 |  |  |  |  |  |  |  |  |  | TWG02YQ319 |  |  |  |  |  |  |  |  |  | TWG02YQ320 |  |  |  |  |  |  |  |  |  | TWG02YQ321 |  |  |  |  |  |  |  |  |  | TWG02YQ322 |  |  |  |  |  |  |  |  |  | TWG02YQ323 |  |  |  |  |  |  |  |  |  | TWG02YQ324 |  |  |  |  |  |  |  |  |  | TWG02YQ325 |  |  |  |  |  |  |  |  |  | TWG02YQ326 |  |  |  |  |  |  |  |  |  | TWG02YQ327 |  |  |  |  |  |  |  |  |  | TWG02YQ328 |  |  |  |  |  |  |  |  |  | TWG02YQ329 |  |  |  |  |  |  |  |  |  | TWG02YQ330 |  |  |  |  |  |  |  |  |  | TWG02YQ331 |  |  |  |  |  |  |  |  |  | TWG02YQ332 |  |  |  |  |  |  |  |  |  | TWG02YQ333 |  |  |  |  |  |  |  |  |  | TWG02YQ334 |  |  |  |  |  |  |  |  |  | TWG02YQ335 |  |  |  |  |  |  |  |  |  | TWG02YQ336 |  |  |  |  |  |  |  |  |  | TWG02YQ337 |  |  |  |  |  |  |  |  |  | TWG02YQ338 |  |  |  |  |  |  |  |  |  | TWG02YQ339 |  |  |  |  |  |  |  |  |  | TWG02YQ340 |  |  |  |  |  |  |  |  |  | TWG02YQ341 |  |  |  |  |  |  |  |  |  | TWG02YQ342 |  |  |  |  |  |  |  |  |  | TWG02YQ343 |  |  |  |  |  |  |  |  |  | TWG02YQ344 |  |  |  |  |  |  |  |  |  | TWG02YQ345 |  |  |  |  |  |  |  |  |  | TWG02YQ346 |  |  |  |  |  |  |  |  |  | TWG02YQ347 |  |  |  |  |  |  |  |  |  | TWG02YQ348 |  |  |  |  |  |  |  |  |  | TWG02YQ349 |  |  |  |  |  |  |  |  |  | TWG02YQ350 |  |  |  |  |  |  |  |  |  | TWG02YQ351 |  |  |  |  |  |  |  |  |  | TWG02YQ352 |  |  |  |  |  |  |  |  |  | TWG02YQ353 |  |  |  |  |  |  |  |  |  | TWG02YQ354 |  |  |  |  |  |  |  |  |  | TWG02YQ355 |  |  |  |  |  |  |  |  |  | TWG02YQ356 |  |  |  |  |  |  |  |  |  | TWG02YQ357 |  |  |  |  |  |  |  |  |  | TWG02YQ358 |  |  |  |  |  |  |  |  |  | TWG02YQ359 |  |  |  |  |  |  |  |  |  | TWG02YQ360 |  |  |  |  |  |  |  |  |  | TWG02YQ361 |  |  |  |  |  |  |  |  |  | TWG02YQ362 |  |  |  |  |  |  |  |  |  | TWG02YQ363 |  |  |  |  |  |  |  |  |  | TWG02YQ364 |  |  |  |  |  |  |  |  |  | TWG02YQ365 |  |  |  |  |  |  |  |  |  | TWG02YQ366 |  |  |  |  |  |  |  |  |  | TWG02YQ367 |  |  |  |  |  |  |  |  |  | TWG02YQ368 |  |  |  |  |  |  |  |  |  | TWG02YQ369 |  |  |  |  |  |  |  |  |  | TWG02YQ370 |  |  |  |  |  |  |  |  |  | TWG02YQ371 |  |  |  |  |  |  |  |  |  | TWG02YQ372 |  |  |  |  |  |  |  |  |  | TWG02YQ373 |  |  |  |  |  |  |  |  |  | TWG02YQ374 |  |  |  |  |  |  |  |  |  | TWG02YQ375 |  |  |  |  |  |  |  |  |  | TWG02YQ376 |  |  |  |  |  |  |  |  |  | TWG02YQ377 |  |  |  |  |  |  |  |  |  | TWG02YQ378 |  |  |  |  |  |  |  |  |  | TWG02YQ379 |  |  |  |  |  |  |  |  |  | TWG02YQ380 |  |  |  |  |  |  |  |  |  | TWG02YQ381 |  |  |  |  |  |  |  |  |  | TWG02YQ382 |  |  |  |  |  |  |  |  |  | TWG02YQ383 |  |  |  |  |  |  |  |  |  | TWG02YQ384 |  |  |  |  |  |  |  |  |  | TWG02YQ385 |  |  |  |  |  |  |  |  |  | TWG02YQ386 |  |  |  |  |  |  |  |  |  | TWG02YQ387 |  |  |  |  |  |  |  |  |  | TWG02YQ388 |  |  |  |  |  |  |  |  |  | TWG02YQ389 |  |  |  |  |  |  |  |  |  | TWG02YQ390 |  |  |  |  |  |  |  |  |  | TWG02YQ391 |  |  |  |  |  |  |  |  |  | TWG02YQ392 |  |  |  |  |  |  |  |  |  | TWG02YQ393 |  |  |  |  |  |  |  |  |  | TWG02YQ394 |  |  |  |  |  |  |  |  |  | TWG02YQ395 |  |  |  |  |  |  |  |  |  | TWG02YQ396 |  |  |  |  |  |  |  |  |  | TWG02YQ397 |  |  |  |  |  |  |  |  |  | TWG02YQ398 |  |  |  |  |  |  |  |  |  | TWG02YQ399 |  |  |  |  |  |  |  |  |  | TWG02YQ400 |  |  |  |  |  |  |  |  |  | TWG02YQ401 |  |  |  |  |  |  |  |  |  | TWG02YQ402 |  |  |  |  |  |  |  |  |  | TWG02YQ403 |  |  |  |  |  |  |  |  |  | TWG02YQ404 |  |  |  |  |  |  |  |  |  | TWG02YQ405 |  |  |  |  |  |  |  |  |  | TWG02YQ406 |  |  |  |  |  |  |  |  |  | TWG02YQ407 |  |  |  |  |  |  |  |  |  | TWG02YQ408 |  |  |  |  |  |  |  |  |  | TWG02YQ409 |  |  |  |  |  |  |  |  |  | TWG02YQ410 |  |  |  |  |  |  |  |  |  | TWG02YQ411 |  |  |  |  |  |  |  |  |  | TWG02YQ412 |  |  |  |  |  |  |  |  |  | TWG02YQ413 |  |  |  |  |  |  |  |  |  | TWG02YQ414 |  |  |  |  |  |  |  |  |  | TWG02YQ415 |  |  |  |  |  |  |  |  |  | TWG02YQ416 |  |  |  |  |  |  |  |  |  | TWG02YQ417 |  |  |  |  |  |  |  |  |  | TWG02YQ418 |  |  |  |  |  |  |  |  |  | TWG02YQ419 |  |  |  |  |  |  |  |  |  | TWG02YQ420 |  |  |  |  |  |  |  |  |  | TWG02YQ421 |  |  |  |  |  |  |  |  |  | TWG02YQ422 |  |  |  |  |  |  |  |  |  | TWG02YQ423 |  |  |  |  |  |  |  |  |  | TWG02YQ424 |  |  |  |  |  |  |  |  |  | TWG02YQ425 |  |  |  |  |  |  |  |  |  | TWG02YQ426 |  |  |  |  |  |  |  |  |  | TWG02YQ427 |  |  |  |  |  |  |  |  |  | TWG02YQ428 |  |  |  |  |  |  |  |  |  | TWG02YQ429 |  |  |  |  |  |  |  |  |  | TWG02YQ430 |  |  |  |  |  |  |  |  |  | TWG02YQ431 |  |  |  |  |  |  |  |  |  | TWG02YQ432 |  |  |  |  |  |  |  |  |  | TWG02YQ433 |  |  |  |  |  |  |  |  |  | TWG02YQ434 |  |  |  |  |  |  |  |  |  | TWG02YQ435 |  |  |  |  |  |  |  |  |  | TWG02YQ436 |  |  |  |  |  |  |  |  |  | TWG02YQ437 |  |  |  |  |  |  |  |  |  | TWG02YQ438 |  |  |  |  |  |  |  |  |  | TWG02YQ439 |  |  |  |  |  |  |  |  |  | TWG02YQ440 |  |  |  |  |  |  |  |  |  | TWG02YQ441 |  |  |  |  |  |  |  |  |  | TWG02YQ442 |  |  |  |  |  |  |  |  |  | TWG02YQ443 |  |  |  |  |  |  |  |  |  | TWG02YQ444 |  |  |  |  |  |  |  |  |  | TWG02YQ445 |  |  |  |  |  |  |  |  |  | TWG02YQ446 |  |  |  |  |  |  |  |  |  | TWG02YQ447 |  |  |  |  |  |  |  |  |  | TWG02YQ448 |  |  |  |  |  |  |  |  |  | TWG02YQ449 |  |  |  |  |  |  |  |  |  | TWG02YQ450 |  |  |  |  |  |  |  |  |  | TWG02YQ451 |  |  |  |  |  |  |  |  |  | TWG02YQ452 |  |  |  |  |  |  |  |  |  | TWG02YQ453 |  |  |  |  |  |  |  |  |  | TWG02YQ454 |  |  |  |  |  |  |  |  |  | TWG02YQ455 |  |  |  |  |  |  |  |  |  | TWG02YQ456 |  |  |  |  |  |  |  |  |  | TWG02YQ457 |  |  |  |  |  |  |  |  |  | TWG02YQ458 |  |  |  |  |  |  |  |  |  | TWG02YQ459 |  |  |  |  |  |  |  |  |  | TWG02YQ460 |  |  |  |  |  |  |  |  |  | TWG02YQ461 |  |  |  |  |  |  |  |  |  | TWG02YQ462 |  |  |  |  |  |  |  |  |  | TWG02YQ463 |  |  |  |  |  |  |  |  |  | TWG02YQ464 |  |  |  |  |  |  |  |  |  | TWG02YQ465 |  |  |  |  |  |  |  |  |  | TWG02YQ466 |  |  |  |  |  |  |  |  |  | TWG02YQ467 |  |  |  |  |  |  |  |  |  | TWG02YQ468 |  |  |  |  |  |  |  |  |  | TWG02YQ469 |  |  |  |  |  |  |  |  |  | TWG02YQ470 |  |  |  |  |  |  |  |  |  | TWG02YQ471 |  |  |  |  |  |  |  |  |  | TWG02YQ472 |  |  |  |  |  |  |  |  |  | TWG02YQ473 |  |  |  |  |  |  |  |  |  | TWG02YQ474 |  |  |  |  |  |  |  |  |  | TWG02YQ475 |  |  |  |  |  |  |  |  |  | TWG02YQ476 |  |  |  |  |  |  |  |  |  | TWG02YQ477 |  |  |  |  |  |  |  |  |  | TWG02YQ478 |  |  |  |  |  |  |  |  |  | TWG02YQ479 |  |  |  |  |  |  |  |  |  | TWG02YQ480 |  |  |  |  |  |  |  |  |  | TWG02YQ481 |  |  |  |  |  |  |  |  |  | TWG02YQ482 |  |  |  |  |  |  |  |  |  | TWG02YQ483 |  |  |  |  |  |  |  |  |  | TWG02YQ484 |  |  |  |  |  |  |  |  |  | TWG02YQ485 |  |  |  |  |  |  |  |  |  | TWG02YQ486 |  |  |  |  |  |  |  |  |  | TWG02YQ487 |  |  |  |  |  |  |  |  |  | TWG02YQ488 |  |  |  |  |  |  |  |  |  | TWG02YQ489 |  |  |  |  |  |  |  |  |  | TWG02YQ490 |  |  |  |  |  |  |  |  |  | TWG02YQ491 |  |  |  |  |  |  |  |  |  | TWG02YQ492 |  |  |  |  |  |  |  |  |  | TWG02YQ493 |  |  |  |  |  |  |  |  |  | TWG02YQ494 |  |  |  |  |  |  |  |  |  | TWG02YQ495 |  |  |  |  |  |  |  |  |  | TWG02YQ496 |  |  |  |  |  |  |  |  |  | TWG02YQ497 |  |  |  |  |  |  |  |  |  | TWG02YQ498 |  |  |  |  |  |  |  |  |  | TWG02YQ499 |  |  |  |  |  |  |  |  |  | TWG02YQ500 |  |  |  |  |  |  |  |  |  | TWG02YQ501 |  |  |  |  |  |  |  |  |  | TWG02YQ502 |  |  |  |  |  |  |  |  |  | TWG02YQ503 |  |  |  |  |  |  |  |  |  | TWG02YQ504 |  |  |  |  |  |  |  |  |  | TWG02YQ505 |  |  |  |  |  |  |  |  |  | TWG02YQ506 |  |  |  |  |  |  |  |  |  | TWG02YQ507 |  |  |  |  |  |  |  |  |  | TWG02YQ508 |  |  |  |  |  |  |  |  |  | TWG02YQ509 |  |  |  |  |  |  |  |  |  | TWG02YQ510 |  |  |  |  |  |  |  |  |  | TWG02YQ511 |  |  |  |  |  |  |  |  |  | TWG02YQ512 |  |  |  |  |  |  |  |  |  | TWG02YQ513 |  |  |  |  |  |  |  |  |  | TWG02YQ514 |  |  |  |  |  |  |  |  |  | TWG02YQ515 |  |  |  |  |  |  |  |  |  | TWG02YQ516 |  |  |  |  |  |  |  |  |  | TWG02YQ517 |  |  |  |  |  |  |  |  |  | TWG02YQ518 |  |  |  |  |  |  |  |  |  | TWG02YQ519 |  |  |  |  |  |  |  |  |  | TWG02YQ520 |  |  |  |  |  |  |  |  |  | TWG02YQ521 |  |  |  |  |  |  |  |  |  | TWG02YQ522 |  |  |  |  |  |  |  |  |  | TWG02YQ523 |  |  |  |  |  |  |  |  |  | TWG02YQ524 |  |  |  |  |  |  |  |  |  | TWG02YQ525 |  |  |  |  |  |  |  |  |  | TWG02YQ526 |  |  |  |  |  |  |  |  |  | TWG02YQ527 |  |  |  |  |  |  |  |  |  | TWG02YQ528 |  |  |  |  |  |  |  |  |  | TWG02YQ529 |  |  |  |  |  |  |  |  |  | TWG02YQ530 |  |  |  |  |  |  |  |  |  | TWG02YQ531 |  |  |  |  |  |  |  |  |  | TWG02YQ532 |  |  |  |  |  |  |  |  |  | TWG02YQ533 |  |  |  |  |  |  |  |  |  | TWG02YQ534 |  |  |  |  |  |  |  |  |  | TWG02YQ535 |  |  |  |  |  |  |  |  |  | TWG02YQ536 |  |  |  |  |  |  |  |  |  | TWG02YQ537 |  |  |  |  |  |  |  |  |  | TWG02YQ538 |  |  |  |  |  |  |  |  |  | TWG02YQ539 |  |  |  |  |  |  |  |  |  | TWG02YQ540 |  |  |  |  |  |  |  |  |  | TWG02YQ541 |  |  |  |  |  |  |  |  |  | TWG02YQ542 |  |  |  |  |  |  |  |  |  | TWG02YQ543 |  |  |  |  |  |  |  |  |  | TWG02YQ544 |  |  |  |  |  |  |  |  |  | TWG02YQ545 |  |  |  |  |  |  |  |  |  | TWG02YQ546 |  |  |  |  |  |  |  |  |  | TWG02YQ547 |  |  |  |  |  |  |  |  |  | TWG02YQ548 |  |  |  |  |  |  |  |  |  | TWG02YQ549 |  |  |  |  |  |  |  |  |  | TWG02YQ550 |  |  |  |  |  |  |  |  |  | TWG02YQ551 |  |  |  |  |  |  |  |  |  | TWG02YQ552 |  |  |  |  |  |  |  |  |  | TWG02YQ553 |  |  |  |  |  |  |  |  |  | TWG02YQ554 |  |  |  |  |  |  |  |  |  | TWG02YQ555 |  |  |  |  |  |  |  |  |  | TWG02YQ556 |  |  |  |  |  |  |  |  |  | TWG02YQ557 |  |  |  |  |  |  |  |  |  | TWG02YQ558 |  |  |  |  |  |  |  |  |  | TWG02YQ559 |  |  |  |  |  |  |  |  |  | TWG02YQ560 |  |  |  |  |  |  |  |  |  | TWG02YQ561 |  |  |  |  |  |  |  |  |  | TWG02YQ562 |  |  |  |  |  |  |  |  |  | TWG02YQ563 |  |  |  |  |  |  |  |  |  | TWG02YQ564 |  |  |  |  |  |  |  |  |  | TWG02YQ565 |  |  |  |  |  |  |  |  |  | TWG02YQ566 |  |  |  |  |  |  |  |  |  | TWG02YQ567 |  |  |  |  |  |  |  |  |  | TWG02YQ568 |  |  |  |  |  |  |  |  |  | TWG02YQ569 |  |  |  |  |  |  |  |  |  | TWG02YQ570 |  |  |  |  |  |  |  |  |  | TWG02YQ571 |  |  |  |  |  |  |  |  |  | TWG02YQ572 |  |  |  |  |  |  |  |  |  | TWG02YQ573 |  |  |  |  |  |  |  |  |  | TWG02YQ574 |  |  |  |  |  |  |  |  |  | TWG02YQ575 |  |  |  |  |  |  |  |  |  | TWG02YQ576 |  |  |  |  |  |  |  |  |  | TWG02YQ577 |  |  |  |  |  |  |  |  |  | TWG02YQ578 |  |  |  |  |  |  |  |  |  | TWG02YQ579 |  |  |  |  |  |  |  |  |  | TWG02YQ580 |  |  |  |  |  |  |  |  |  | TWG02YQ581 |  |  |  |  |  |  |  |  |  | TWG02YQ582 |  |  |  |  |  |  |  |  |  | TWG02YQ583 |  |  |  |  |  |  |  |  |  | TWG02YQ584 |  |  |  |  |  |  |  |  |  | TWG02YQ585 |  |  |  |  |  |  |  |  |  | TWG02YQ586 |  |  |  |  |  |  |  |  |  | TWG02YQ587 |  |  |  |  |  |  |  |  |  | TWG02YQ588 |  |  |  |  |  |  |  |  |  | TWG02YQ589 |  |  |  |  |  |  |  |  |  | TWG02YQ590 |  |  |  |  |  |  |  |  |  | TWG02YQ591 |  |  |  |  |  |  |  |  |  | TWG02YQ592 |  |  |  |  |  |  |  |  |  | TWG02YQ593 |  |  |  |  |  |  |  |  |  | TWG02YQ594 |  |  |  |  |  |  |  |  |  | TWG02YQ595 |  |  |  |  |  |  |  |  |  | TWG02YQ596 |  |  |  |  |  |  |  |  |  | TWG02YQ597 |  |  |  |  |  |  |  |  |  | TWG02YQ598 |  |  |  |  |  |  |  |  |  | TWG02YQ599 |  |  |  |  |  |  |  |  |  | TWG02YQ600 |  |  |  |  |  |  |  |  |  | TWG02YQ601 |  |  |  |  |  |  |  |  |  | TWG02YQ602 |  |  |  |  |  |  |  |  |  | TWG02YQ603 |  |  |  |  |  |  |  |  |  | TWG02YQ604 |  |  |  |  |  |  |  |  |  | TWG02YQ605 |  |  |  |  |  |  |  |  |  | TWG02YQ606 |  |  |  |  |  |  |  |  |  | TWG02YQ607 |  |  |  |  |  |  |  |  |  | TWG02YQ608 |  |  |  |  |  |  |  |  |  | TWG02YQ609 |  |  |  |  |  |  |  |  |  | TWG02YQ610 |  |  |  |  |  |  |  |  |  | TWG02YQ611 |  |  |  |  |  |  |  |  |  | TWG02YQ612 |  |  |  |  |  |  |  |  |  | TWG02YQ613 |  |  |  |  |  |  |  |  |  | TWG02YQ614 |  |  |  |  |  |  |  |  |  | TWG02YQ615 |  |  |  |  |  |  |  |  |  | TWG02YQ616 |  |  |  |  |  |  |  |  |  | TWG02YQ617 |  |  |  |  |  |  |  |  |  | TWG02YQ618 |  |  |  |  |  |  |  |  |  | TWG02YQ619 |  |  |  |  |  |  |  |  |  | TWG02YQ620 |  |  |  |  |  |  |  |  |  | TWG02YQ621 |  |  |  |  |  |  |  |  |  | TWG02YQ622 |  |  |  |  |  |  |  |  |  | TWG02YQ623 |  |  |  |  |  |  |  |  |  | TWG02YQ624 |  |  |  |  |  |  |  |  |  | TWG02YQ625 |  |  |  |  |  |  |  |  |  | TWG02YQ626 |  |  |  |  |  |  |  |  |  | TWG02YQ627 |  |  |  |  |  |  |  |  |  | TWG02YQ628 |  |  |  |  |  |  |  |  |  | TWG02YQ629 |  |  |  |  |  |  |  |  |  | TWG02YQ630 |  |  |  |  |  |  |  |  |  | TWG02YQ631 |  |  |  |  |  |  |  |  |  | TWG02YQ632 |  |  |  |  |  |  |  |  |  | TWG02YQ633 |  |  |  |  |  |  |  |  |  | TWG02YQ634 |  |  |  |  |  |  |  |  |  | TWG02YQ635 |  |  |  |  |  |  |  |  |  | TWG02YQ636 |  |  |  |  |  |  |  |  |  | TWG02YQ637 |  |  |  |  |  |  |  |  |  | TWG02YQ638 |  |  |  |  |  |  |  |  |  | TWG02YQ639 |  |  |  |  |  |  |  |  |  | TWG02YQ640 |  |  |  |  |  |  |  |  |  | TWG02YQ641 |  |  |  |  |  |  |  |  |  | TWG02YQ642 |  |  |  |  |  |  |  |  |  | TWG02YQ643 |  |  |  |  |  |  |  |  |  | TWG02YQ644 |  |  |  |  |  |  |  |  |  | TWG02YQ645 |  |  |  |  |  |  |  |  |  | TWG02YQ646 |  |  |  |  |  |  |  |  |  | TWG02YQ647 |  |  |  |  |  |  |  |  |  | TWG02YQ648 |  |  |  |  |  |  |  |  |  | TWG02YQ649 |  |  |  |  |  |  |  |  |  | TWG02YQ650 |  |  |  |  |  |  |  |  |  | TWG02YQ651 |  |  |  |  |  |  |  |  |  | TWG02YQ652 |  |  |  |  |  |  |  |  |  | TWG02YQ653 |  |  |  |  |  |  |  |  |  | TWG02YQ654 |  |  |  |  |  |  |  |  |  | TWG02YQ655 |  |  |  |  |  |  |  |  |  | TWG02YQ656 |  |  |  |  |  |  |  |  |  | TWG02YQ657 |  |  |  |  |  |  |  |  |  | TWG02YQ658 |  |  |  |  |  |  |  |  |  | TWG02YQ659 |  |  |  |  |  |  |  |  |  | TWG02YQ660 |  |  |  |  |  |  |  |  |  | TWG02YQ661 |  |  |  |  |  |  |  |  |  | TWG02YQ662 |  |  |  |  |  |  |  |  |  | TWG02YQ663 |  |  |  |  |  |  |  |  |  | TWG02YQ664 |  |  |  |  |  |  |  |  |  | TWG02YQ665 |  |  |  |  |  |  |  |  |  | TWG02YQ666 |  |  |  |  |  |  |  |  |  | TWG02YQ667 |  |  |  |  |  |  |  |  |  | TWG02YQ668 |  |  |  |  |  |  |  |  |  | TWG02YQ669 |  |  |  |  |  |  |  |  |  | TWG02YQ670 |  |  |  |  |  |  |  |  |  | TWG02YQ671 |  |  |  |  |  |  |  |  |  | TWG02YQ672 |  |  |  |  |  |  |  |  |  | TWG02YQ673 |  |  |  |  |  |  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[illegible]

Table 1. Cont.

| Sample                           | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ | TWG01YQ |
|----------------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Lithology                        |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |         |
| LREE/HREE                        | 7.92    | 7.90    | 7.88    | 8.44    | 8.62    | 8.77    | 8.87    | 8.86    | 8.88    | 9.11    | 8.93    | 8.87    | 8.66    | 9.19    |         |         |         |         |         |         |
| La <sub>N</sub> /Yb <sub>N</sub> | 8.05    | 7.98    | 8.06    | 8.33    | 8.15    | 8.42    | 8.89    | 8.52    | 10.58   | 11.53   | 11.04   | 10.86   | 10.22   | 11.35   |         |         |         |         |         |         |
| δEu                              | 0.86    | 0.74    | 0.85    | 0.84    | 0.83    | 0.86    | 0.80    | 0.82    | 0.83    | 0.91    | 0.85    | 0.79    | 0.74    | 0.86    |         |         |         |         |         |         |
| δCe                              | 0.96    | 0.95    | 0.94    | 0.94    | 1.01    | 0.96    | 0.95    | 0.97    | 0.97    | 0.93    | 0.95    | 0.97    | 0.96    | 0.95    |         |         |         |         |         |         |



The SiO<sub>2</sub> content of the volcanic rock samples from the Longjiang formation ranges from 58.83% to 66.28%, with an average of 63.17%. The total alkali content (Na<sub>2</sub>O+K<sub>2</sub>O) ranges from 6.50% to 8.80%, with an average of 7.29%. In the N<sub>2</sub>O+K<sub>2</sub>O-SiO<sub>2</sub> diagram (Figure 4), the samples' chemical compositions fall into the fields of trachyandesite, trachyte trachydacite, andesite, and dacite; in the SiO<sub>2</sub> vs. K<sub>2</sub>O diagram (Figure 5a), the samples mainly fall into the calc-alkaline to high-K calc-alkaline series. The aluminum-rich Al<sub>2</sub>O<sub>3</sub> content ranges from 15.26% to 18.07%, with an average of 16.75%. The aluminum saturation index A/CNK ranges from 0.90 to 1.08, with an average of 0.95. In the A/NK-A/CNK diagram (Figure 5b), the sample's chemical composition mainly falls into the sub-aluminous rock category; the TiO<sub>2</sub> content ranges from 0.55% to 1.11%, with an average of 0.79%. The Fe<sub>2</sub>O<sub>3</sub><sup>T</sup> content ranges from 4.00% to 7.37%, with an average of 5.78%. The MgO content ranges from 0.85% to 3.27%, with an average of 1.87%. The Mg<sup>#</sup> content ranges from 28.75 to 50.32, with an average of 37.85. The CaO content ranges from 2.43% to 5.08%, with an average of 3.80%. The Thorpe index σ ranges from 1.56 to 3.65, with an average of 2.96. These values indicate that the volcanic rocks of the Longjiang formation in the Lengjimanda plate are a series of intermediate basic volcanic rocks belonging to the calc-alkaline series.

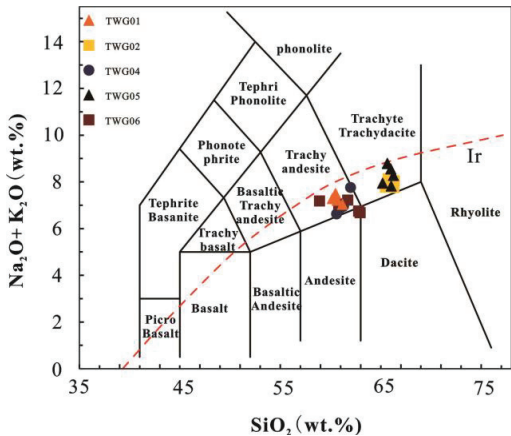


Figure 4. Diagram of (N<sub>2</sub>O+K<sub>2</sub>O) vs. SiO<sub>2</sub> of volcanic rocks of Longjiang formation [49].

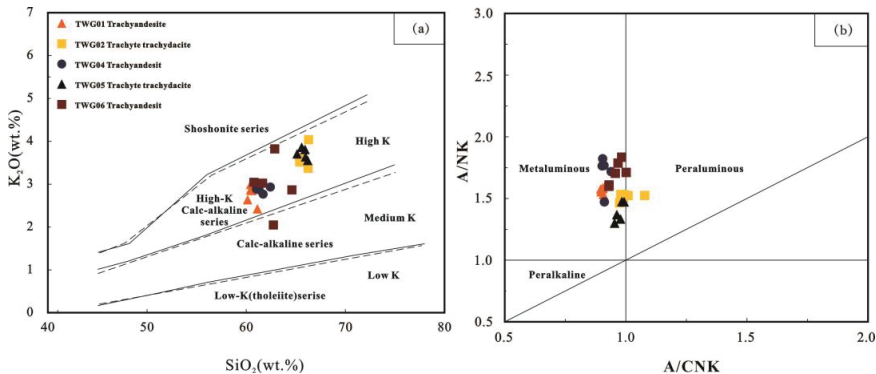
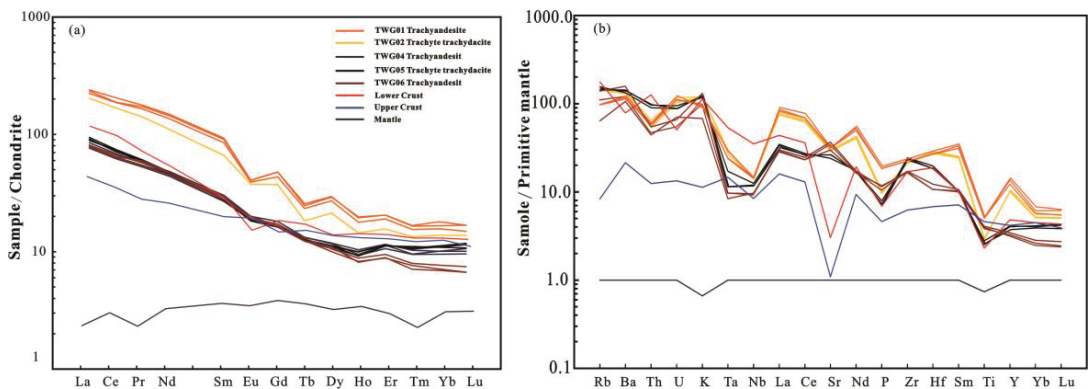


Figure 5. Major elements classification diagrams of Longjiang formation volcanic rocks, Lengjimanda plate. (a) K<sub>2</sub>O vs. SiO<sub>2</sub> diagram [50]; (b) A/NK vs. A/CNK diagram [50].

These volcanic rocks are relatively enriched in large-ion lithophile elements (such as Rb, K, Ba, U, and LREE) and depleted in high-field-strength elements (such as Nb, Ta, Zr,

Hf, and HREE). The Rb/Sr values range from 0.09 to 0.19, with an average of 0.13 (Figure 6), which is higher than the Rb/Sr values of the primitive mantle (0.03), E-MORB (0.033), and OIB (0.047), but lower than those of the crustal source magma (>0.5). The Th/Pb values range from 1.9 to 5.3, with an average of 3.17, which is between those of the crustal source rocks and the primitive mantle. The Nb/Ta values range from 8.33 to 26.03, with an average of 14.51, which is also between those of the crustal source rocks and the primitive mantle. The rocks are characterized by high Sr (average 634.22 ppm), low Y (average 31.55 ppm), low Yb (average 2.12 ppm), and high Sr/Y (average 27.59) values.



**Figure 6.** (a) Chondrite-normalized REE distribution patterns [51] and (b) primitive mantle-normalized spider diagrams [52] of the Longjiang formation volcanic rocks, Lengjimanda plate.

The total rare earth element content of these volcanic rocks from the Longjiang formation ranges from 56.23 ppm to 331.91 ppm, with an average of 184.35 ppm. The light rare earth element content ranges from 92.41 ppm to 333.91 ppm, with an average of 167.52 ppm, while the heavy rare earth element content ranges from 10.06 ppm to 28.48 ppm, with an average of 16.83 ppm. The LREE/HREE ratio ranges from 7.86 to 11.44, with an average of 9.55. The enrichment of light REEs and depletion of heavy REEs are indicated by the right-skewed distribution of REE patterns when they are normalized to chondrite (Figure 6). The fractionation of light and heavy REE is evident, with the fractionation coefficients  $(La/Yb)_N$  ranging from 7.98 to 15.23, with an average of 11.33. The  $\delta Eu$  values range from 0.54 to 1.19, and except for a few samples with positive Eu anomalies, most samples show moderately negative Eu anomalies.

#### 4.2. Zircon U–Pb Isotopic Dating

The results of the zircon U–Pb isotopic analyses of the volcanic rock samples from the Longjiang formation are shown in Table 2.

The  $^{232}Th$  content ranges from 44 ppm to 1126 ppm, while the  $^{238}U$  content ranges from 70 ppm to 1157 ppm. The  $^{232}Th/^{238}U$  ratio ranges from 0.199 to 1.711. Based on the characteristics observed in the CL images (Figure 3), it is suggested that these zircons are magmatic (Supplementary Materials).

Of the 30 analyzed points on the trachyandesite (TWG01), 27 measurement spots show good age consistency, except for 5 zircon grains with significant age anomalies. In the concordance plot of the zircon U–Pb ages (Figure 7a), all the obtained zircon U–Pb ages lie along or near the concordance line after discordant points are excluded. The  $^{206}Pb/^{238}U$  weighted mean age is  $129.1 \pm 0.65$  Ma (MSWD = 0.93,  $n = 27$ ), indicating an Early Cretaceous age.

Table 2. Zircon LA-ICP-MS U–Pb data of the volcanic rocks from Lengjiamanda plate of the Longjiang formation.

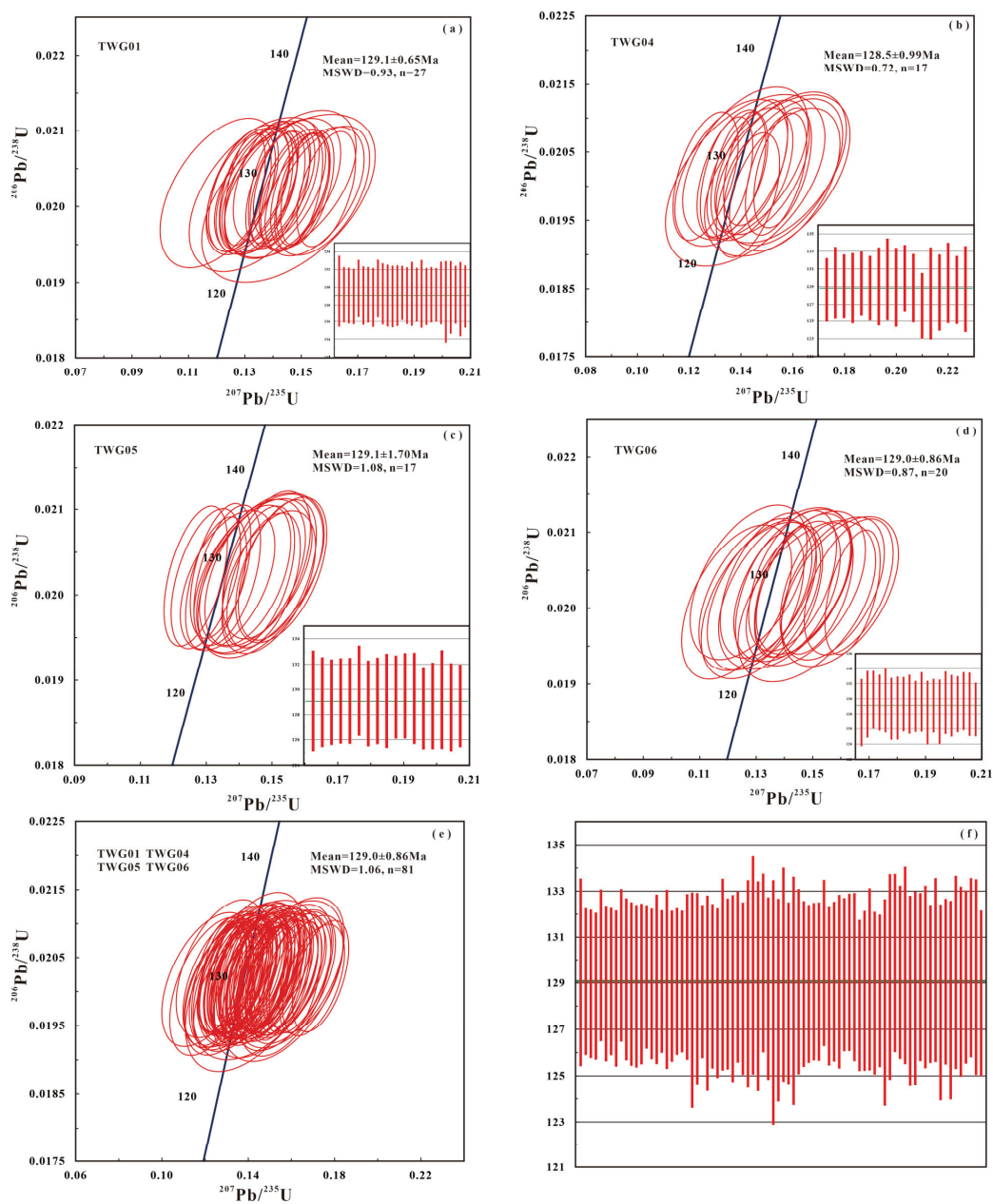
| Sample   | Lithology      | Concentration (ppm) |                  | Ratio |                                      |         |                                     | Age/Ma  |                                     |         |                                     |
|----------|----------------|---------------------|------------------|-------|--------------------------------------|---------|-------------------------------------|---------|-------------------------------------|---------|-------------------------------------|
|          |                | <sup>232</sup> Th   | <sup>238</sup> U | Th/U  | <sup>207</sup> Pb/ <sup>206</sup> Pb | ± %     | <sup>207</sup> Pb/ <sup>235</sup> U | ± %     | <sup>206</sup> Pb/ <sup>238</sup> U | ± %     | <sup>207</sup> Pb/ <sup>235</sup> U |
| TWG01-01 | Trachyandesite | 46                  | 70               | 0.657 | 0.04751                              | 0.00484 | 0.14564                             | 0.01571 | 0.0203                              | 0.00064 | 138                                 |
| TWG01-02 |                | 208                 | 591              | 0.352 | 0.05698                              | 0.00229 | 0.15885                             | 0.00687 | 0.02023                             | 0.0005  | 150                                 |
| TWG01-03 |                | 225                 | 593              | 0.379 | 0.05458                              | 0.00237 | 0.14969                             | 0.00697 | 0.02021                             | 0.0005  | 142                                 |
| TWG01-04 |                | 185                 | 351              | 0.529 | 0.04789                              | 0.0021  | 0.13013                             | 0.00608 | 0.0202                              | 0.0005  | 124                                 |
| TWG01-05 |                | 260                 | 296              | 0.878 | 0.05145                              | 0.00257 | 0.1447                              | 0.00771 | 0.02035                             | 0.00052 | 137                                 |
| TWG01-06 |                | 222                 | 301              | 0.738 | 0.04909                              | 0.00281 | 0.129                               | 0.00781 | 0.02021                             | 0.00053 | 123                                 |
| TWG01-07 |                | 775                 | 453              | 1.711 | 0.05501                              | 0.00228 | 0.15136                             | 0.00675 | 0.02024                             | 0.0005  | 143                                 |
| TWG01-08 |                | 123                 | 147              | 0.834 | 0.05014                              | 0.00297 | 0.1356                              | 0.00852 | 0.02018                             | 0.00053 | 129                                 |
| TWG01-09 |                | 57                  | 80               | 0.71  | 0.07026                              | 0.01095 | 0.19627                             | 0.03278 | 0.02025                             | 0.00093 | 182                                 |
| TWG01-10 |                | 202                 | 232              | 0.87  | 0.04973                              | 0.00259 | 0.13746                             | 0.00764 | 0.02034                             | 0.00052 | 131                                 |
| TWG01-11 |                | 98                  | 215              | 0.459 | 0.04682                              | 0.00326 | 0.13114                             | 0.00965 | 0.02024                             | 0.00055 | 125                                 |
| TWG01-12 |                | 110                 | 155              | 0.712 | 0.05788                              | 0.00384 | 0.15738                             | 0.01111 | 0.02021                             | 0.00056 | 148                                 |
| TWG01-13 |                | 111                 | 107              | 1.034 | 0.04724                              | 0.00334 | 0.13109                             | 0.00979 | 0.0202                              | 0.00055 | 125                                 |
| TWG01-14 |                | 57                  | 105              | 0.545 | 0.04748                              | 0.00319 | 0.13425                             | 0.00956 | 0.02021                             | 0.00055 | 128                                 |
| TWG01-15 |                | 251                 | 626              | 0.401 | 0.04927                              | 0.00169 | 0.13916                             | 0.00521 | 0.02026                             | 0.00049 | 132                                 |
| TWG01-16 |                | 196                 | 256              | 0.766 | 0.05052                              | 0.00249 | 0.14164                             | 0.00747 | 0.02022                             | 0.00051 | 135                                 |
| TWG01-17 |                | 46                  | 99               | 0.466 | 0.04704                              | 0.00382 | 0.13702                             | 0.01175 | 0.02025                             | 0.00058 | 130                                 |
| TWG01-18 |                | 422                 | 789              | 0.535 | 0.04594                              | 0.00153 | 0.13004                             | 0.00474 | 0.02023                             | 0.00049 | 124                                 |
| TWG01-19 |                | 43                  | 64               | 0.679 | 0.04992                              | 0.00448 | 0.14338                             | 0.01359 | 0.02024                             | 0.00061 | 136                                 |
| TWG01-20 |                | 159                 | 213              | 0.744 | 0.05181                              | 0.00261 | 0.14772                             | 0.00797 | 0.02019                             | 0.00051 | 140                                 |
| TWG01-21 |                | 265                 | 373              | 0.71  | 0.04994                              | 0.00209 | 0.14159                             | 0.00643 | 0.02023                             | 0.0005  | 135                                 |
| TWG01-22 |                | 618                 | 1157             | 0.534 | 0.05277                              | 0.00154 | 0.15015                             | 0.00491 | 0.02023                             | 0.00048 | 142                                 |
| TWG01-23 |                | 59                  | 99               | 0.6   | 0.04949                              | 0.00361 | 0.13722                             | 0.01061 | 0.02025                             | 0.00056 | 131                                 |
| TWG01-24 |                | 203                 | 259              | 0.783 | 0.04776                              | 0.00631 | 0.14546                             | 0.02029 | 0.02011                             | 0.00073 | 138                                 |
| TWG01-25 |                | 125                 | 157              | 0.798 | 0.05601                              | 0.0043  | 0.17888                             | 0.01475 | 0.02028                             | 0.00059 | 167                                 |
| TWG01-26 |                | 50                  | 77               | 0.647 | 0.04413                              | 0.00482 | 0.12089                             | 0.01383 | 0.02018                             | 0.00065 | 116                                 |
| TWG01-27 |                | 181                 | 253              | 0.716 | 0.05329                              | 0.00277 | 0.14754                             | 0.00825 | 0.02023                             | 0.00052 | 140                                 |
| TWG01-28 |                | 181                 | 192              | 0.943 | 0.04598                              | 0.00519 | 0.13447                             | 0.01598 | 0.02016                             | 0.00067 | 128                                 |
| TWG01-29 |                | 105                 | 116              | 0.912 | 0.05187                              | 0.00365 | 0.1547                              | 0.0116  | 0.0202                              | 0.00056 | 146                                 |
| TWG01-30 |                | 242                 | 205              | 1.185 | 0.06303                              | 0.00427 | 0.18018                             | 0.01313 | 0.02016                             | 0.00057 | 168                                 |

Table 2. Cont.

| Sample   | Lithology                | Concentration (ppm) |                  | Ratio |                                      |         |                                     | Age/Ma  |                                     |         |                                     |
|----------|--------------------------|---------------------|------------------|-------|--------------------------------------|---------|-------------------------------------|---------|-------------------------------------|---------|-------------------------------------|
|          |                          | <sup>232</sup> Th   | <sup>238</sup> U | Th/U  | <sup>207</sup> Pb/ <sup>206</sup> Pb | ± %     | <sup>207</sup> Pb/ <sup>235</sup> U | ± %     | <sup>206</sup> Pb/ <sup>238</sup> U | ± %     | <sup>206</sup> Pb/ <sup>235</sup> U |
| TWG04-1  | Trachyandesite           | 44                  | 48               | 0.922 | 0.15379                              | 0.00562 | 8.12828                             | 0.32538 | 0.38309                             | 0.01152 | 2091                                |
| TWG04-2  |                          | 706                 | 949              | 0.744 | 0.05827                              | 0.00192 | 0.48677                             | 0.01815 | 0.06055                             | 0.00169 | 379                                 |
| TWG04-3  |                          | 882                 | 1118             | 0.789 | 0.04837                              | 0.00227 | 0.13442                             | 0.00669 | 0.02014                             | 0.00058 | 129                                 |
| TWG04-4  |                          | 124                 | 222              | 0.56  | 0.05296                              | 0.00429 | 0.14817                             | 0.01207 | 0.02028                             | 0.00055 | 129                                 |
| TWG04-5  |                          | 545                 | 829              | 0.657 | 0.04985                              | 0.00237 | 0.13901                             | 0.00699 | 0.02021                             | 0.00058 | 129                                 |
| TWG04-6  |                          | 180                 | 264              | 0.683 | 0.05155                              | 0.0039  | 0.14345                             | 0.01095 | 0.02018                             | 0.00064 | 129                                 |
| TWG04-7  |                          | 506                 | 856              | 0.591 | 0.05584                              | 0.00246 | 0.1561                              | 0.00735 | 0.02027                             | 0.00058 | 147                                 |
| TWG04-8  |                          | 413                 | 479              | 0.862 | 0.05517                              | 0.00266 | 0.15355                             | 0.00781 | 0.02018                             | 0.00059 | 145                                 |
| TWG04-9  |                          | 132                 | 192              | 0.684 | 0.05611                              | 0.00546 | 0.15638                             | 0.01514 | 0.02021                             | 0.00071 | 148                                 |
| TWG04-10 |                          | 335                 | 343              | 0.976 | 0.0505                               | 0.00575 | 0.14168                             | 0.01599 | 0.02034                             | 0.00074 | 135                                 |
| TWG04-11 |                          | 150                 | 348              | 0.431 | 0.22667                              | 0.00849 | 1.1992                              | 0.04775 | 0.03836                             | 0.00118 | 800                                 |
| TWG04-12 |                          | 304                 | 390              | 0.777 | 0.0489                               | 0.00519 | 0.13624                             | 0.01438 | 0.0202                              | 0.00071 | 130                                 |
| TWG04-13 |                          | 507                 | 850              | 0.597 | 0.05193                              | 0.0028  | 0.14567                             | 0.00819 | 0.02035                             | 0.00061 | 138                                 |
| TWG04-14 |                          | 478                 | 761              | 0.629 | 0.04914                              | 0.00317 | 0.13669                             | 0.00903 | 0.02018                             | 0.00062 | 130                                 |
| TWG04-15 |                          | 784                 | 1083             | 0.724 | 0.05212                              | 0.00283 | 0.14269                             | 0.00807 | 0.01987                             | 0.0006  | 135                                 |
| TWG04-16 |                          | 112                 | 123              | 0.911 | 0.05116                              | 0.00744 | 0.14163                             | 0.02033 | 0.02009                             | 0.00083 | 135                                 |
| TWG04-17 |                          | 134                 | 201              | 0.667 | 0.05667                              | 0.00509 | 0.15692                             | 0.01409 | 0.0201                              | 0.00069 | 148                                 |
| TWG04-18 |                          | 340                 | 417              | 0.815 | 0.06105                              | 0.00598 | 0.17061                             | 0.01661 | 0.02028                             | 0.00073 | 160                                 |
| TWG04-19 |                          | 390                 | 686              | 0.568 | 0.04551                              | 0.00291 | 0.12634                             | 0.00831 | 0.02015                             | 0.00062 | 121                                 |
| TWG04-20 |                          | 95                  | 154              | 0.621 | 0.0586                               | 0.00676 | 0.16277                             | 0.01855 | 0.02016                             | 0.00078 | 16                                  |
| TWG05-1  | Trachyte<br>Trachydacite | 80                  | 121              | 0.661 | 0.05421                              | 0.00451 | 0.15118                             | 0.01256 | 0.02022                             | 0.00063 | 143                                 |
| TWG05-2  |                          | 103                 | 178              | 0.578 | 0.05556                              | 0.00324 | 0.15484                             | 0.00913 | 0.02021                             | 0.00056 | 146                                 |
| TWG05-3  |                          | 316                 | 371              | 0.852 | 0.04549                              | 0.00222 | 0.12682                             | 0.00636 | 0.02022                             | 0.00054 | 121                                 |
| TWG05-4  |                          | 232                 | 343              | 0.678 | 0.04889                              | 0.00233 | 0.13639                             | 0.00669 | 0.02023                             | 0.00054 | 130                                 |
| TWG05-5  |                          | 213                 | 316              | 0.673 | 0.05233                              | 0.00253 | 0.1459                              | 0.00724 | 0.02022                             | 0.00054 | 138                                 |
| TWG05-6  |                          | 128                 | 215              | 0.595 | 0.05284                              | 0.00312 | 0.14831                             | 0.00883 | 0.02035                             | 0.00057 | 140                                 |
| TWG05-7  |                          | 188                 | 269              | 0.702 | 0.04665                              | 0.00245 | 0.12989                             | 0.00697 | 0.02019                             | 0.00054 | 124                                 |
| TWG05-8  |                          | 127                 | 168              | 0.756 | 0.06221                              | 0.00303 | 0.1735                              | 0.00862 | 0.02023                             | 0.00054 | 163                                 |
| TWG05-9  |                          | 112                 | 155              | 0.723 | 0.04756                              | 0.00439 | 0.13178                             | 0.01207 | 0.0201                              | 0.00062 | 126                                 |
| TWG05-10 |                          | 77                  | 168              | 0.459 | 0.0515                               | 0.00393 | 0.14361                             | 0.01092 | 0.02022                             | 0.00059 | 136                                 |

Table 2. Cont.

| Sample   | Lithology                | Concentration (ppm) |                  |       | Ratio                                |         |                                     | Age/Ma  |                                     |         |                                     |     |                                     |     |   |
|----------|--------------------------|---------------------|------------------|-------|--------------------------------------|---------|-------------------------------------|---------|-------------------------------------|---------|-------------------------------------|-----|-------------------------------------|-----|---|
|          |                          | <sup>232</sup> Th   | <sup>238</sup> U | Th/U  | <sup>207</sup> Pb/ <sup>206</sup> Pb | ± %     | <sup>207</sup> Pb/ <sup>235</sup> U | ± %     | <sup>206</sup> Pb/ <sup>238</sup> U | ± %     | <sup>207</sup> Pb/ <sup>235</sup> U | 2σ  | <sup>206</sup> Pb/ <sup>238</sup> U | 2σ  |   |
| TWG05-11 | Trachyte<br>Trachydacite | 113                 | 157              | 0.72  | 0.06375                              | 0.00394 | 0.17798                             | 0.01101 | 0.02025                             | 0.00057 | 166                                 | 9   | 129                                 | 4   |   |
| TWG05-12 |                          | 267                 | 354              | 0.757 | 0.04806                              | 0.0021  | 0.13436                             | 0.00607 | 0.02028                             | 0.00052 | 128                                 | 5   | 129                                 | 3   |   |
| TWG05-13 |                          | 180                 | 299              | 0.602 | 0.0542                               | 0.00275 | 0.15163                             | 0.00783 | 0.02029                             | 0.00054 | 143                                 | 7   | 130                                 | 3   |   |
| TWG05-14 |                          | 101                 | 145              | 0.696 | 0.05973                              | 0.00405 | 0.16683                             | 0.0113  | 0.02026                             | 0.00057 | 157                                 | 10  | 129                                 | 4   |   |
| TWG05-15 |                          | 330                 | 406              | 0.812 | 0.04791                              | 0.00215 | 0.13301                             | 0.00612 | 0.02014                             | 0.00051 | 127                                 | 5   | 129                                 | 3   |   |
| TWG05-16 |                          | 80                  | 172              | 0.465 | 0.06122                              | 0.0034  | 0.17024                             | 0.00949 | 0.02017                             | 0.00054 | 160                                 | 8   | 129                                 | 3   |   |
| TWG05-17 |                          | 179                 | 272              | 0.658 | 0.07161                              | 0.00372 | 0.20022                             | 0.01046 | 0.02028                             | 0.00055 | 185                                 | 9   | 129                                 | 3   |   |
| TWG05-18 |                          | 70                  | 132              | 0.534 | 0.05234                              | 0.00473 | 0.14607                             | 0.01306 | 0.02025                             | 0.00062 | 138                                 | 12  | 129                                 | 4   |   |
| TWG05-19 |                          | 122                 | 241              | 0.505 | 0.05364                              | 0.00339 | 0.14898                             | 0.00942 | 0.02015                             | 0.00055 | 141                                 | 8   | 129                                 | 4   |   |
| TWG05-20 |                          | 182                 | 303              | 0.602 | 0.05304                              | 0.00261 | 0.14746                             | 0.00737 | 0.02017                             | 0.00052 | 140                                 | 7   | 129                                 | 3   |   |
| TWG06-1  |                          | Trachyandesite      | 73               | 145   | 0.504                                | 0.05341 | 0.00588                             | 0.14797 | 0.0161                              | 0.02009 | 0.0007                              | 140 | 14                                  | 128 | 4 |
| TWG06-2  |                          |                     | 62               | 131   | 0.474                                | 0.05027 | 0.00566                             | 0.14041 | 0.01565                             | 0.02026 | 0.0007                              | 133 | 14                                  | 129 | 4 |
| TWG06-3  |                          |                     | 182              | 277   | 0.658                                | 0.0509  | 0.00364                             | 0.14292 | 0.01028                             | 0.02036 | 0.00061                             | 136 | 9                                   | 130 | 4 |
| TWG06-4  |                          |                     | 80               | 141   | 0.569                                | 0.0582  | 0.00368                             | 0.1628  | 0.0104                              | 0.02028 | 0.00059                             | 153 | 9                                   | 130 | 4 |
| TWG06-5  |                          |                     | 71               | 133   | 0.531                                | 0.04539 | 0.00491                             | 0.12732 | 0.01368                             | 0.02034 | 0.00067                             | 122 | 12                                  | 130 | 4 |
| TWG06-6  |                          |                     | 97               | 156   | 0.622                                | 0.04747 | 0.00462                             | 0.13202 | 0.01278                             | 0.02017 | 0.00065                             | 126 | 11                                  | 129 | 4 |
| TWG06-7  |                          |                     | 164              | 227   | 0.723                                | 0.06413 | 0.00441                             | 0.17815 | 0.01228                             | 0.02015 | 0.00061                             | 167 | 11                                  | 129 | 4 |
| TWG06-8  |                          |                     | 85               | 118   | 0.726                                | 0.04662 | 0.00479                             | 0.12975 | 0.01323                             | 0.02018 | 0.00066                             | 124 | 12                                  | 129 | 4 |
| TWG06-9  |                          |                     | 451              | 503   | 0.896                                | 0.0542  | 0.003                               | 0.15143 | 0.00856                             | 0.02026 | 0.00057                             | 143 | 8                                   | 129 | 4 |
| TWG06-10 |                          |                     | 416              | 432   | 0.962                                | 0.06778 | 0.0026                              | 0.18953 | 0.00772                             | 0.02028 | 0.00055                             | 176 | 7                                   | 129 | 3 |
| TWG06-11 |                          |                     | 311              | 320   | 0.972                                | 0.05628 | 0.00432                             | 0.1572  | 0.01205                             | 0.02026 | 0.00062                             | 148 | 11                                  | 129 | 4 |
| TWG06-12 |                          |                     | 967              | 677   | 1.43                                 | 0.05893 | 0.00216                             | 0.16419 | 0.00645                             | 0.02021 | 0.00054                             | 154 | 6                                   | 129 | 3 |
| TWG06-13 | 85                       |                     | 149              | 0.57  | 0.03933                              | 0.00583 | 0.11011                             | 0.01614 | 0.02031                             | 0.00076 | 106                                 | 15  | 130                                 | 5   |   |
| TWG06-14 | 253                      |                     | 291              | 0.868 | 0.09994                              | 0.00652 | 0.27891                             | 0.01801 | 0.02024                             | 0.00064 | 250                                 | 14  | 129                                 | 4   |   |
| TWG06-15 | 307                      |                     | 373              | 0.823 | 0.04796                              | 0.00401 | 0.13424                             | 0.0112  | 0.0203                              | 0.00063 | 128                                 | 10  | 130                                 | 4   |   |
| TWG06-16 | 189                      |                     | 351              | 0.539 | 0.04445                              | 0.00469 | 0.12308                             | 0.01287 | 0.02008                             | 0.00067 | 118                                 | 12  | 128                                 | 4   |   |
| TWG06-17 | 289                      |                     | 423              | 0.684 | 0.05073                              | 0.00281 | 0.14148                             | 0.00798 | 0.02022                             | 0.00057 | 134                                 | 7   | 129                                 | 4   |   |
| TWG06-18 | 80                       |                     | 135              | 0.593 | 0.0475                               | 0.00508 | 0.13168                             | 0.01397 | 0.0201                              | 0.00068 | 126                                 | 13  | 128                                 | 4   |   |
| TWG06-19 | 64                       |                     | 123              | 0.519 | 0.05107                              | 0.00496 | 0.14296                             | 0.01379 | 0.0203                              | 0.00066 | 136                                 | 12  | 130                                 | 4   |   |
| TWG06-20 | 104                      |                     | 156              | 0.666 | 0.05726                              | 0.00496 | 0.15965                             | 0.01373 | 0.02022                             | 0.00065 | 150                                 | 12  | 129                                 | 4   |   |
| TWG06-21 | 179                      |                     | 220              | 0.815 | 0.05182                              | 0.00355 | 0.14473                             | 0.00997 | 0.02025                             | 0.00059 | 137                                 | 9   | 129                                 | 4   |   |
| TWG06-22 | 75                       |                     | 149              | 0.504 | 0.06617                              | 0.00556 | 0.18432                             | 0.01533 | 0.0202                              | 0.00066 | 172                                 | 13  | 129                                 | 4   |   |
| TWG06-23 | 122                      |                     | 189              | 0.648 | 0.05238                              | 0.00394 | 0.14676                             | 0.01104 | 0.02032                             | 0.00061 | 139                                 | 10  | 130                                 | 4   |   |
| TWG06-24 | 141                      |                     | 162              | 0.87  | 0.05283                              | 0.00505 | 0.14759                             | 0.01396 | 0.02026                             | 0.00067 | 140                                 | 12  | 129                                 | 4   |   |
| TWG06-25 | 265                      |                     | 360              | 0.735 | 0.04851                              | 0.00283 | 0.13479                             | 0.008   | 0.02015                             | 0.00056 | 128                                 | 7   | 129                                 | 4   |   |



**Figure 7.** Concordant and weighted diagrams of the zircon U–Pb age of the Longjiang formation volcanic rocks, Lengjimanda plate. Error ellipses are shown for 1-sigma level of uncertainty. (a) TWG01, (b) TWG04, (c) TWG05, (d) TWG06, (e) Longjiang formation volcanic rocks, (f) weighted diagrams of the Longjiang formation volcanic rocks.

Of the 20 analyzed points in the trachyandesite sample (TWG04), 17 measurement spots show good age consistency. In the concordance plot of the zircon U–Pb ages (Figure 7b), all the obtained zircon U–Pb ages lie on or near the concordance line after discor-



dant points have been excluded. The weighted mean age of  $^{206}\text{Pb}/^{238}\text{U}$  is  $128.5 \pm 0.99$  Ma (MSWD = 0.72,  $n = 17$ ), indicating an Early Cretaceous age.

Of the 20 analyzed points in the trachyte trachydacite sample (TWG05), 17 zircon measurement points show good age consistency. In the concordance plot of the zircon U–Pb ages (Figure 7c), all the obtained zircon U–Pb ages lie on or near the concordance line after discordant points are excluded. The weighted mean age of  $^{206}\text{Pb}/^{238}\text{U}$  is determined to be  $129.1 \pm 1.70$  Ma (MSWD = 1.08,  $n = 17$ ), indicating an Early Cretaceous age.

Of the 25 analyzed points in the trachyandesite sample (TWG06), 20 zircon measurement points show good age consistency. In the concordance plot of the zircon U–Pb ages (Figure 7d), all the obtained zircon U–Pb ages lie on or near the concordance line after discordant points are excluded. The weighted mean age of  $^{206}\text{Pb}/^{238}\text{U}$  is determined to be  $129.0 \pm 0.86$  Ma (MSWD = 0.87,  $n = 20$ ), indicating an Early Cretaceous age.

The volcanic rock samples from various sampling locations in the Longjiang formation have a total of 95 analytical points. Among them, 14 spots show significant deviations in their zircon surface ages due to poor separation and a complex composition, while the remaining 81 spots show good age consistency. In the concordance plot of the zircon U–Pb ages (Figure 7f), all the obtained zircon U–Pb ages lie along or near the concordance line after discordant points are excluded. The weighted mean age of  $^{206}\text{Pb}/^{238}\text{U}$  is determined to be  $129.0 \pm 0.86$  Ma (MSWD = 1.06,  $n = 81$ ), indicating an Early Cretaceous age.

4.3. Sr–Nd–Pb Isotopic Dating

The Sr–Nd–Pb isotopic compositions of the volcanic rocks of Longjiang formation volcanic rocks are shown in Table 3. The initial Sr and Nd isotopic compositions of the samples in the study area are corrected based on their corresponding zircon U–Pb ages of 129 Ma.

Table 3. Sr–Nd–Pb isotopic data of the Longjiang formation volcanic rocks.

| Sample | Age<br>Ma | Rb<br>ppm | Sr  | $^{87}\text{Rb}/^{86}\text{Sr}$ | $(^{87}\text{Sr}/^{86}\text{Sr})_i$ | Sm    | Nd    | $^{147}\text{Sm}/^{144}\text{Nd}$ | $^{143}\text{Nd}/^{144}\text{Nd}$ | $(^{143}\text{Nd}/^{144}\text{Nd})_i$ | $\varepsilon_{\text{Nd}}(t)$ | $t_{\text{DM2}}$<br>(Ma) | $^{206}\text{Pb}/^{204}\text{Pb}$ | $^{207}\text{Pb}/^{204}\text{Pb}$ | $^{208}\text{Pb}/^{204}\text{Pb}$ | $^{238}\text{U}/^{204}\text{Pb}$ | $\Delta\beta$ | $\Delta\gamma$ |
|--------|-----------|-----------|-----|---------------------------------|-------------------------------------|-------|-------|-----------------------------------|-----------------------------------|---------------------------------------|------------------------------|--------------------------|-----------------------------------|-----------------------------------|-----------------------------------|----------------------------------|---------------|----------------|
| TWG01  | 129       | 61.5      | 658 | 0.26384                         | 0.70357                             | 13.83 | 67.34 | 0.12903                           | 0.5126                            | 0.51221                               | 2.1                          | 893                      | 18.429                            | 15.537                            | 38.204                            | 9.34                             | 13.75         | 24.92          |
| TWG04  | 129       | 72.5      | 652 | 0.31428                         | 0.70352                             | 4.93  | 23.94 | 0.12943                           | 0.51277                           | 0.51221                               | 5.5                          | 621                      | 18.386                            | 15.523                            | 38.142                            | 9.32                             | 12.87         | 23.64          |
| TWG05  | 129       | 98.8      | 557 | 0.50094                         | 0.70299                             | 4.48  | 23.48 | 0.11987                           | 0.51281                           | 0.51221                               | 6.6                          | 544                      | 18.389                            | 15.519                            | 38.133                            | 9.31                             | 12.59         | 23.13          |
| TWG06  | 129       | 88.1      | 776 | 0.32055                         | 0.70352                             | 4.74  | 23.28 | 0.12786                           | 0.51274                           | 0.51221                               | 4.9                          | 671                      | 18.387                            | 15.516                            | 38.143                            | 9.3                              | 12.41         | 23.59          |

These samples have relatively low initial  $(^{87}\text{Sr}/^{86}\text{Sr})_i$  ratios, ranging from 0.70299 to 0.70357, and initial  $(^{143}\text{Nd}/^{144}\text{Nd})_i$  values ranging from 0.51260 to 0.51281, with an average of 0.512363. The  $\varepsilon_{\text{Nd}}(t)$  values are all positive, ranging from +2.1 to +6.6, and the  $t_{\text{DM1}}$  (Ma) ranges from 551 Ma to 992 Ma, while the  $t_{\text{DM2}}$  ranges from 544 Ma to 839 Ma. The Pb isotope data in the study area indicate that the  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios of the volcanic rocks of the Longjiang formation range from 18.397 to 18.429, 15.516 to 15.54, and 38.189 to 38.2, respectively, and are like the Pb isotopic compositions of the Mesozoic volcanic rocks in the southern Da Hinggan mountains [53].

4.4. Zircon Lu–Hf Isotopes Dating

The results of the zircon Lu–Hf isotope analyses of the volcanic rocks of the Longjiang formation in the Manda Banke area in the central section of the Da Hinggan mountains are listed in Table 4. The  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios of the samples in the study area range from 0.0009 to 0.0020, all of which are positive, with an average of 0.0013, which is less than 0.002. This indicates extremely low radiogenic Hf accumulation after zircon formation. Except for one sample (TWG01-5) with a negative  $\varepsilon_{\text{Hf}}(t)$ , the volcanic rocks of the Longjiang formation in the study area have positive  $\varepsilon_{\text{Hf}}(t)$  values ranging from +1.31 to +43.77, with an average of +8.47. The one-stage Hf model ages ( $t_{\text{DM1}}$ ) range from 538 Ma to 1059 Ma, with an average of 733 Ma, while the two-stage model ages ( $t_{\text{DM2}}$ ) range from 655 Ma to 1427 Ma, with an average of 893 Ma.

Table 4. Zircon Lu–Hf isotope data of Lengjimanda plate of the Longjiang formation volcanic rocks.

| Sample   | <sup>176</sup> Hf/ <sup>177</sup> Hf | 2σ       | <sup>176</sup> Lu/ <sup>177</sup> Hf | 1σ       | <sup>176</sup> Yb/ <sup>177</sup> Hf | 1σ       | Age (Ma) | ε <sub>Hf</sub> (0) | ε <sub>Hf</sub> (t) | t <sub>DM1</sub> (Ma) | t <sub>DM2</sub> (Ma) | f <sub>Lu/Hf</sub> |
|----------|--------------------------------------|----------|--------------------------------------|----------|--------------------------------------|----------|----------|---------------------|---------------------|-----------------------|-----------------------|--------------------|
| TWG01-2  | 0.283935                             | 0.000043 | 0.003236                             | 0.000004 | 0.076078                             | 0.000195 | 126      | 41.3                | 43.77               | 1059                  | 1305                  | −0.9               |
| TWG01-3  | 0.282729                             | 0.000039 | 0.00176                              | 0.000018 | 0.041094                             | 0.000427 | 130      | −1.4                | 1.31                | 751                   | 911                   | −0.95              |
| TWG01-4  | 0.282749                             | 0.000049 | 0.001616                             | 0.000012 | 0.037553                             | 0.000303 | 129      | −0.7                | 2.01                | 719                   | 874                   | −0.95              |
| TWG01-5  | 0.282444                             | 0.000034 | 0.002004                             | 0.000044 | 0.046304                             | 0.001074 | 132      | −11.5               | −8.76               | 1168                  | 1427                  | −0.94              |
| TWG01-6  | 0.282819                             | 0.000045 | 0.001756                             | 0.000009 | 0.040134                             | 0.000245 | 135      | 1.8                 | 4.6                 | 621                   | 746                   | −0.95              |
| TWG01-8  | 0.282862                             | 0.000038 | 0.001333                             | 0.000012 | 0.029231                             | 0.000249 | 130      | 3.3                 | 6.03                | 553                   | 668                   | −0.96              |
| TWG01-10 | 0.282806                             | 0.000038 | 0.000989                             | 0.000026 | 0.021776                             | 0.000614 | 129      | 1.3                 | 4.08                | 627                   | 768                   | −0.97              |
| TWG01-11 | 0.282852                             | 0.000041 | 0.001193                             | 0.000008 | 0.027001                             | 0.000203 | 127      | 2.9                 | 5.63                | 565                   | 687                   | −0.96              |
| TWG01-16 | 0.282868                             | 0.000033 | 0.000959                             | 0.000016 | 0.021678                             | 0.000368 | 130      | 3.5                 | 6.3                 | 538                   | 655                   | −0.97              |

5. Discussion

5.1. The Age of the Longjiang Formation’s Volcanic Rocks

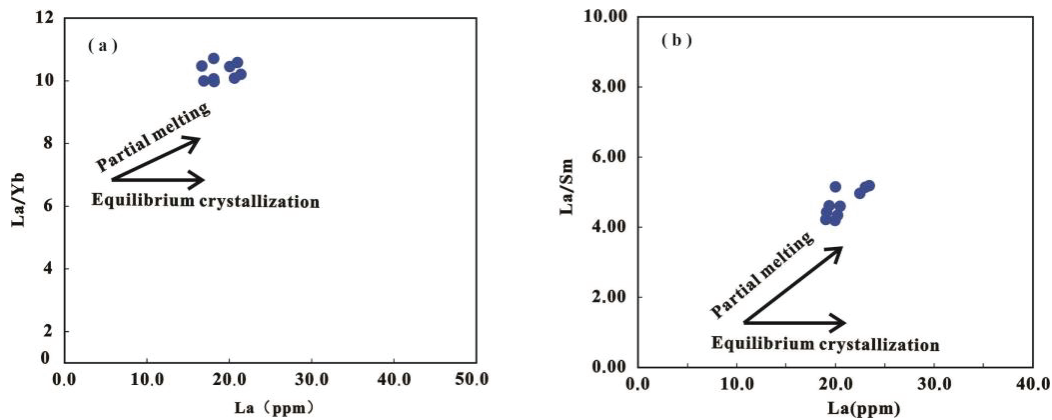
Several previous studies have determined to resolve the age of the volcanic rocks in the Longjiang formation. However, as mentioned above, these studies have mainly focused on the northern part of the Great Xing’an mountains. Li [15] used laser fusion <sup>40</sup>Ar/<sup>39</sup>Ar dating and zircon U–Pb dating to determine that the Longjiang formation in the Longjiang basin, located between the Dayangshu basin in the north and the Lujiabao depression in the south, is of an Early Cretaceous age of 122 to 126 Ma; Ye [30] obtained an age of 124.63 Ma for the Longjiang formation’s volcanic rocks in the Dongpo Xinliuzhan area of the northern section of the Da Hinggan mountains using LA-ICP-MS zircon U–Pb dating; Chen [54] obtained an age of 120.43 Ma for the volcanic rocks of the Longjiang formation in the Shiwuliquiao gold mining area, Heilongjiang province, by performing zircon U–Pb dating on andesite samples. This age belongs to the Early Cretaceous. We obtained relatively accurate ages for the volcanic rocks of the Longjiang formation.

The samples used for dating in the present study are trachyandesite (TWG01, TWG04, and TWG06) and trachyte trachydacite (TWG05). The CL images (Figure 3) show that these zircons have typical zoning structures, and the Th/U ratios range from 0.1989 to 1.7105, indicating that these zircons are of a magmatic origin. The LA-ICP-MS zircon U–Pb weighted mean age of 81 sample points is determined to be 129.0 ± 0.86 Ma (MSWD of 1.06, Figure 7f). This age is consistent with the previous dating results of 120–126 Ma [40] and is within the error range. Based on a thorough analysis of the above studies, it is concluded that the volcanic rocks of the Longjiang formation were formed during the Early Cretaceous.

5.2. The Genesis of the Longjiang Formation’s Volcanic Rocks

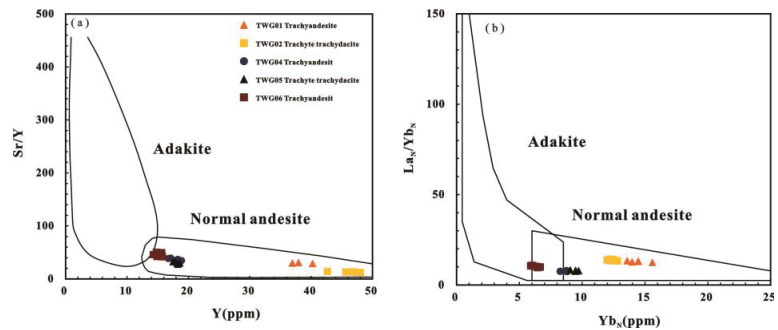
There are currently several theories of the genesis of calc-alkaline andesites: the mixing of felsic magmas from the crust and mafic magmas from the mantle [55]; the separation and crystallization of mafic magmas from the mantle [56,57]; partial melting of the mantle wedge triggered by subduction fluids or melts [58,59]; and partial melting of lower crustal material triggered by the underplating of mafic magma of a mantle origin [60,61]. Our analysis of the major and trace elements in the samples (Table 1) indicates that the dominant volcanic rocks in the study area are trachyandesite, trachyte trachydacite, and andesite. These volcanic rocks collectively form a suite of intermediate calc-alkaline volcanic rock combinations. The Mg# values (averaging 37.85), Cr content (averaging 12.11 ppm), and Ni contents (averaging 8.80 ppm) of these volcanic rocks are relatively low, much lower than the Mg# values (65–75) of mantle-derived magmas and the Cr and Nd contents (185 ppm and 16 ppm, respectively) of the crust [52,62]. Furthermore, there are no dark mafic enclaves in the volcanic rocks within the study area, indicating that their formation cannot be attributed to the mixing of crustal and mantle-derived magmas [63]. The volcanic rocks in the study area have relatively high K/Rb ratios, with an average of 342 (>110), Zr/Hf ratios with an average of 39 (>30), and Nb/Ta ratios with an average of 15 (>5) [52,64], which indicates that the studied volcanic rocks are not highly fractionated plutonic rocks (Wu et al., 2004; Li et al., 2018). In the La vs. La/Yb plot and La vs. La/Sm plot (Figure 8), the andesite samples show a partial melting trend rather than fractional crystallization,

indicating a weak fractional crystallization process. This suggests that the volcanic rocks in the study area cannot be attributed to mantle-derived magma by means of fractional crystallization [63].



**Figure 8.** Illustration of magmatic evolution of volcanic rocks in the Longjiang formation of Lengjimanda plate [65]. (a) La/Yb vs. La and (b) La/Sm vs. La.

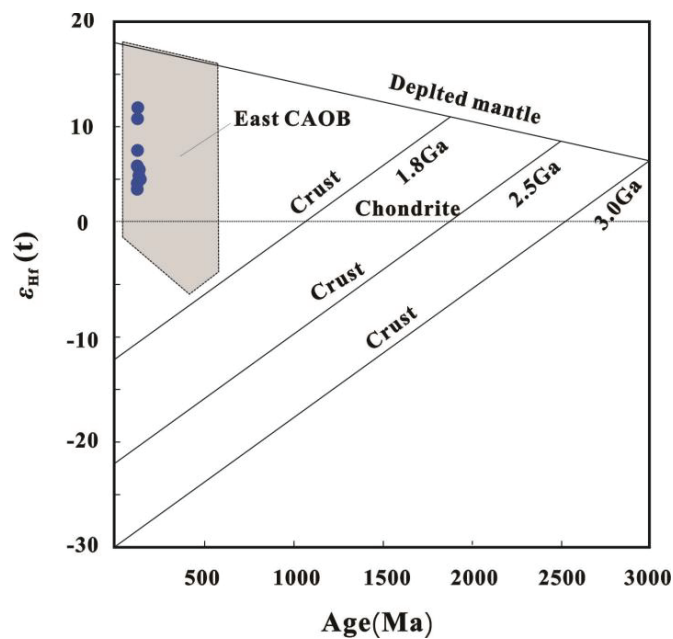
The volcanic rocks of the Longjiang formation show relatively high contents of SiO<sub>2</sub> (average 63.17%), Al<sub>2</sub>O<sub>3</sub> (average 16.75%), and K<sub>2</sub>O (average 3.22%), and low contents of MgO (average 1.87%) and Mg<sup>#</sup> (average 37.85). These characteristics are significantly different from magmas produced by the partial melting of mantle material and are closer to magmas produced by the partial melting of lower crustal material (Mg<sup>#</sup> < 40) [66]. The volcanic rocks of the Longjiang formation in the study area exhibit a moderately negative Eu anomaly, with average Sr/Y and La/Yb ratios of 27.6 and 15.8, respectively. These ratios are not consistent with the characteristics of adakite rocks (>40, >20) [67–69]. In the Sr/Y–Y diagram and the (La/Yb)<sub>N</sub> vs. (Yb)<sub>N</sub> diagram (Figure 9), all sample compositions fall within the typical island arc rock field. This indicates that the volcanic rocks of the Longjiang formation are predominantly island arc volcanic rocks rather than adakite rocks, and the volcanic rocks in question exhibit characteristics of large ion lithophile element enrichment and high-field-strength element depletion, as seen in the rare earth element distribution pattern and trace element spider diagram (Figure 6). This pattern is similar to that of the lower crust, indicating that the rocks may have originated from the partial melting of basaltic crustal materials. Additionally, the average ratios of Rb/Sr, Ti/Zr, and Ti/Y in the volcanic rock samples from the Longjiang formation in the study area are 0.13, 20.91, and 199.00, respectively. These values are significantly higher than the range of ratios found in mantle-derived magmas (0.03, <20, <100) [52,64,70]. We infer that the primary magma of the volcanic rocks in the Lengjimanda plate of the Longjiang formation originated from the partial melting of basaltic crustal materials rather than the mantle.



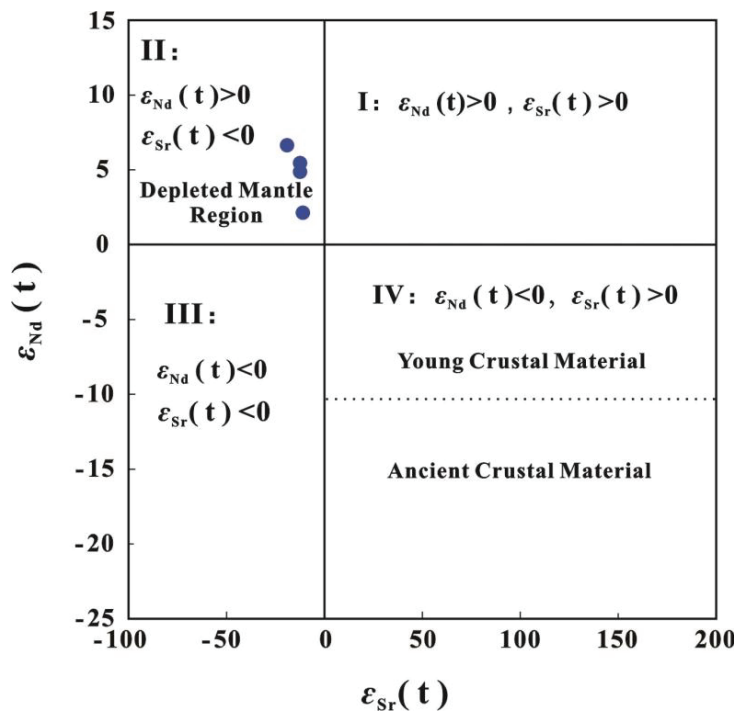
**Figure 9.** Adakite discrimination diagram of Longjiang formation volcanic rocks, Lengjimanda plate. (a) Sr/Y vs. Y diagram; (b)  $(La/Yb)_N$  vs.  $(Yb)_N$  diagram [71].

Zircon Hf isotope studies conducted in the Lengjimanda plate indicate positive  $\varepsilon_{Hf}(t)$  values ranging from +1.31 to +43.77, with an average of +8.47, except for one sample with negative values; the two-stage Hf model ages ( $t_{DM2}$ ) range from 655 to 1427 Ma. The  $\varepsilon_{Hf}(t)$  values are relatively uniform and high, indicating that the rocks are derived directly from the mantle or from basaltic crust formed by the melting of depleted mantle. The presence of a negative  $\varepsilon_{Hf}(t)$  value of −8.76 suggests the possible involvement of ancient crust in the rock formation process. In the  $\varepsilon_{Hf}(t)$  vs. age diagram (Figure 10), all the samples' compositions fall within the range of granulite meteorites and depleted mantle, which suggests that the magma may have originated from the partial melting of basaltic crustal materials that were newly generated from the depleted mantle during the Neoproterozoic to Phanerozoic period [35,72,73]. This hypothesis is consistent with the large-scale crustal accretion event that occurred in the Da Hinggan mountain region during the Neoproterozoic to Phanerozoic period, as reported by Sui [74] and Wang [75]. The Longjiang formation's volcanic rocks in the study area exhibit higher average ratios of Nb/Ta and Zr/Hf, 14.51 and 39.39, respectively, compared to the average values in the crust (13.00, 33.00) [64,76]; these values are similar to the average values in the mantle (17.50, 37.00) [52]. According to Shi [77], the magma source area is composed of recently generated crustal materials from the depleted mantle.

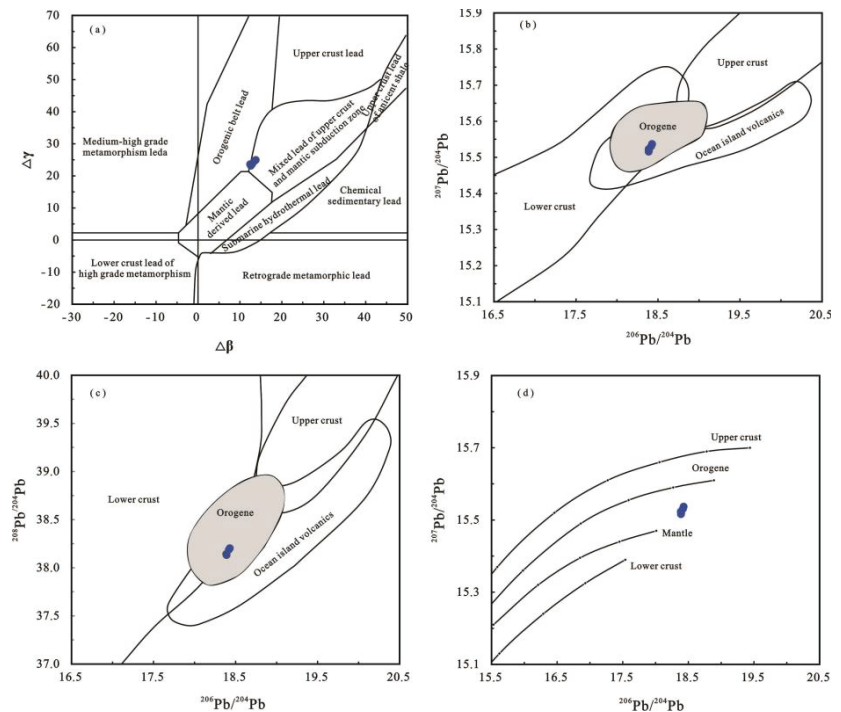
The study area's volcanic rock samples display  $^{87}Sr/^{86}Sr$  ratios ranging from 0.703 to 0.7036, all of which are below 0.705. The  $\varepsilon_{Nd}(t)$  values range from +2.1 to +6.6, and the  $\varepsilon_{Sr}(t)$  values range from −10.7 to −19.2. In Figure 11's  $\varepsilon_{Nd}(t)$  vs.  $\varepsilon_{Sr}(t)$  diagram, all the volcanic rock sample compositions from the Longjiang formation in the study area fall within quadrant II, which indicates that the magma source of the volcanic rocks in the area is related to the depleted mantle, as noted by Hou [78] and Shao [79]. The Pb isotope data from the study area indicate that the volcanic rocks of the Longjiang formation exhibit uranium lead enrichment and thorium lead depletion. The  $^{207}Pb/^{204}Pb$  ratios range from 15,516 to 15,540, which are greater than 15,530; the  $^{208}Pb/^{204}Pb$  ratios range from 38,189 to 38,200, which are lower than 39,000; and the  $^{206}Pb/^{204}Pb$  ratios range from 18,397 to 18,429, which are greater than 18,000. In the genetic classification diagram of  $\Delta\gamma$  vs.  $\Delta\beta$  (Figure 12a) by Zhu [80] and in the tectonic model diagrams of  $^{206}Pb/^{204}Pb$  vs.  $^{207}Pb/^{204}Pb$  and  $^{206}Pb/^{204}Pb$  vs.  $^{208}Pb/^{204}Pb$  (Figure 12b–d), the samples are distributed in the lead region of the subduction zone, where the crust and mantle mix; this suggests that the magma may have originated from the partial melting of basaltic crustal materials that were newly generated from the depleted mantle. This is consistent with the findings of Tan [70], Gao [81], and Jia [82] regarding the petrogenesis of Early Cretaceous volcanic rocks in the Soren and Handagai areas of the central Da Hinggan mountains.



**Figure 10.**  $\epsilon_{\text{Hf}}(t)$  vs. age diagram of Longjiang formation volcanic rocks, Lengjimanda plate. East CAOB: East Asian Orogenic Belt Eastern part [21].



**Figure 11.**  $\epsilon_{\text{Nd}}(t)$  vs.  $\epsilon_{\text{Sr}}(t)$  diagram of volcanic rocks in the Longjiang formation of Lengjimanda plate.



**Figure 12.** Pb isotope composition diagram of Longjiang formation volcanic rocks, Lengjimanda plate. Orogenic: Orogenic belt. ((a), [83]; (b,c), [84]; (d), [80]).

Based on the geochemical characteristics and zircon Hf analyses, as well as the whole-rock Sr–Nd–Pb isotopes, we conclude that the volcanic rocks of the Longjiang formation in the Lengjimanda plate region were generated through the partial melting of the lower crust, and the magma's source material is believed to be basaltic crustal material that was newly generated from the depleted mantle.

### 5.3. Tectonic Background

There are different theories regarding the tectonic environment that was responsible for the formation of the Mesozoic volcanic rocks in the Da Hinggan mountain region. They include the subduction of the ancient Pacific plate [20,85], a mantle plume origin [12,86], and the subduction of the Mongol–Okhotsk Ocean [11,87]. However, closure of the Mongol–Okhotsk Ocean and subduction of the Pacific plate have been identified as the combined cause in various studies [18,88–92].

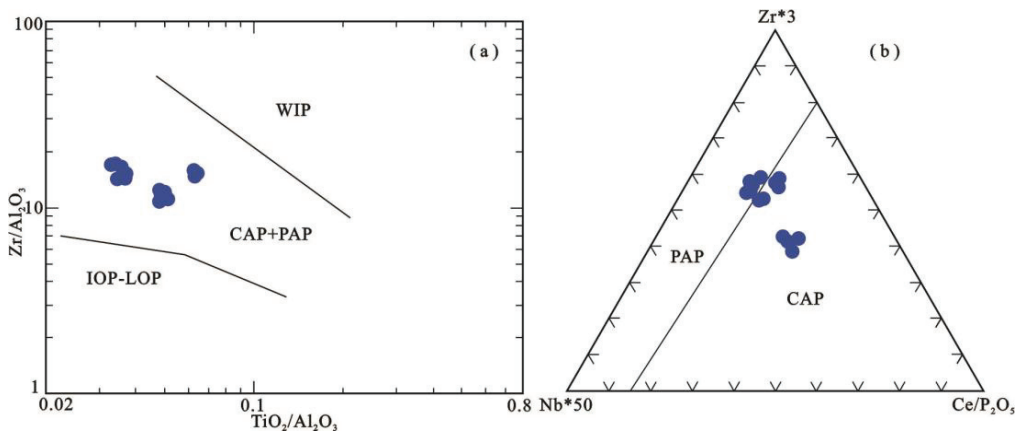
Previous data suggest that during the Mesozoic era, the Da Hinggan mountain region underwent the superposition and reformation of the ancient Pacific plate and the Mongolian–Okhotsk plate [88,92]. Early studies indicate that the Mongolian–Okhotsk Ocean closed during the Middle Late Jurassic period [93] and had little influence on the late Mesozoic magmatic activity in the Da Hinggan mountain region. Recently, researchers provided evidence for the existence of a southward subduction of the Mongolian–Okhotsk plate during the Mesozoic era; for instance, Badarch [94] divided the tectonic blocks and established a new stratigraphic column. Discovering the presence of Permo–Triassic accretionary terranes in the Mongolian–Okhotsk suture zone, Chen [95] identified Late Triassic Inner Mongolia Taipingchuan porphyry copper–molybdenum deposits. Zeng [59] obtained geochemical data and concluded that the Badaguan metamorphic complex in the Erguna area was formed due to the subduction of the Mongolian–Okhotsk Ocean towards



the Erguna block. These studies provide evidence for the southward subduction of the Mongolian-Okhotsk plate during the Mesozoic era, and many researchers believe that the Late Mesozoic magmatic activity in the Da Hinggan mountain area is related to the extensional environment after the closure of the Mongol-Okhotsk Ocean. This view is supported by Meng [87], Ying [96], Sun [97], Li [98], and Si [99]. Additionally, numerous scholars posit that the Mesozoic volcanic rocks in the Da Hinggan mountains region are closely linked to the subduction of the ancient Pacific plate. Kong conducted a study on the tectonic background of the volcanic rocks in the Khorchin area and concluded that they were primarily influenced by the subduction of the ancient Pacific plate. Tang [41] summarized the petrological composition and geochemical characteristics of Mesozoic Cenozoic volcanic rocks in the Northeast Asian margin and suggested that the ancient Pacific plate underwent low-angle subduction towards Northeast Asia in the Early Cretaceous. Yang [100] conducted research on the paleontology, regional comparisons, and chronology in the Da Hinggan mountain area and concluded that the Early Cretaceous volcanic rocks (145–110 Ma) in the Da Hinggan mountain region are generally distributed in an NNE direction, which is consistent with the mechanism of subduction of the ancient Pacific plate.

During the late Early Cretaceous period, volcanic rocks were widely distributed across the Da Hinggan mountain area, which exhibited a typical bimodal volcanic rock assemblage [101]. The region also showed an extensional environment at the regional scale [92,100,102]. The volcanic activity in the Da Hinggan mountain area during this period was influenced by the closure of the Mongol-Okhotsk suture zone [7,103] and the subduction of the ancient Pacific plate beneath the Eurasian continent [9,104,105]. Our study area's volcanic rocks consist mainly of a suite of Early Cretaceous ( $129.00 \pm 0.78$  Ma) intermediate volcanic rocks. These rocks have a high  $\text{SiO}_2$  content and are enriched in large-ion lithophile elements while being depleted in high-field-strength elements. Furthermore, there is an obvious fractionation of light and heavy rare earth elements. In the microelement tectonic environment discrimination diagram of the Longjiang formation's volcanic rocks in the study area (Figure 13), they mainly exhibit characteristics of a post-collisional environment, while some samples also show features of a continental arc environment. This indicates that the Early Cretaceous volcanic rocks in the Longjiang formation were formed in a superimposed environment of post-collision and continental arc. Combined with a regional background analysis, it is believed that the tectonic setting in the study area may be related to the closure of the Mongol-Okhotsk Ocean and the oblique subduction of the ancient Pacific plate. This view is supported by Zhang [17], Zhang [36], Zhang [106], and Xu [7], who suggested that the Da Hinggan mountain area was affected by the closure of the Mongol-Okhotsk Ocean and the oblique subduction of the ancient Pacific plate during the Early Cretaceous.

The tectonic background of the volcanic rocks formed in the Longjimanda plate of the Heilongjiang Group reflects the alternating influence of the Mongol-Okhotsk oceanic plate and the ancient Pacific plate on the Mesozoic volcanic rocks of the Da Hinggan mountains. A synthesis of previous research indicates that the Mesozoic volcanic rocks in the Greater Khingan Range were primarily influenced by the closure of the Mongol-Okhotsk Ocean during the Late Jurassic to Early Cretaceous period. During the Early Cretaceous period, the region may have been affected by the closure of the Mongol-Okhotsk Ocean and the subduction of the ancient Pacific plate. Subsequently, during the Early Cretaceous, they were primarily influenced by the subduction of the ancient Pacific plate.



**Figure 13.** Structural identification diagram of volcanic rocks in Longjiang formation, Lengjimanda plate [107]. (a) Intraplate environment (WIP), (b) continental arc environment (CAP), post-collision environment (PAP), initial ocean arc environment (IOP), late ocean arc environment (LOP).

## 6. Conclusions

The volcanic rocks of the Longjiang formation in the Lengjimanda plate in the middle section of the Da Hinggan mountains are predominantly intermediate basic volcanic rocks, comprising porphyritic rock, porphyritic andesite, and andesite. The LA-ICP-MS zircon U–Pb analysis suggested an age of  $129.0 \pm 0.86$  Ma (MSWD = 1.06,  $n = 81$ ), which suggests that these rocks were formed during the Early Cretaceous period. Petrological, geochemical, and isotopic studies of the Longjiang formation's volcanic rocks indicate that they are the result of the partial melting of the lower crust. The source material for these rocks is newly generated basaltic crustal material from a depleted mantle. These rocks are believed to have formed in a setting of post-collision and continental arc superposition. Their tectonic background may be related to the closure of the Mongolian–Okhotsk Ocean and the oblique subduction of the ancient Pacific plate, as indicated by the regional tectonic evolution history.

This study posits that the regional volcanic eruption event that occurred approximately 130 million years ago in the Lengjimanda plate coincided with the transitional period of the Da Hinggan mountains from rapid uplift to slow uplift, as well as the period of oblique subduction of the ancient Pacific plate beneath East Asia. This finding has significant implications for the analysis of the Early Cretaceous basin's evolution and stratigraphic subdivision in this region. The research on the tectonic background of the Lengjimanda plate presented in this paper demonstrates the alternating influence of the Mesozoic Mongol–Okhotsk oceanic plate and the ancient Pacific plate on the timing of the Da Hinggan mountain region. The Mesozoic volcanic rocks in the Da Hinggan mountains were significantly influenced by the closure of the Mongol–Okhotsk Ocean during the Late Jurassic to Early Cretaceous period. During the Early Cretaceous period, these rocks may have been affected by two distinct geological processes: the closure of the Mongol–Okhotsk Ocean and the subduction of the ancient Pacific plate. Subsequently, during the early Early Cretaceous, they were primarily influenced by the subduction of the ancient Pacific Ocean. This information is useful in delineating the periods in which the Mongol–Okhotsk oceanic plate and the ancient Pacific plate influenced the Da Hinggan mountains.

This article presents a petrological, zircon U–Pb geochronological, geochemical, and isotope chemical analysis of the volcanic rocks in the Longjiang formation, thereby determining the formation age of these rocks in the region. The article discusses the origin and tectonic background of the volcanic rocks, reconstructs the regional geodynamic evolution, fills the research gap concerning the Longjiang volcanic rocks, and provides reliable data

on the dynamic history of the Da Hinggan mountain region. Moreover, the study provides avenues for further geological exploration and geophysical detection in the region.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14070719/s1>, Table S1: Zircon LA-ICP-MS U–Pb data of the volcanic rocks from Lengjimanda plate of the Longjiang formation. Table S2: Major and trace element compositions of Lengjimanda plate of the Longjiang formation volcanic rocks. Table S3: Sr–Nd–Pb isotopic data of the Longjiang Formation volcanic rocks. Table S4: Zircon Lu–Hf isotope data of Lengjimanda plate of the Longjiang Formation volcanic rocks.

**Author Contributions:** Methodology, S.Z.; investigation, Z.T.; data curation, L.S.; writing—original draft preparation, S.-C.W.; writing—review and editing, Y.-J.H. All authors have read and agreed to the published version of the manuscript.

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## Article

# Origin and Geological Implications of Monzogranites and Rhyolitic Porphyries in the Wunugetu Porphyry Copper–Molybdenum Deposit, Northeast China: Evidence from Zircon U-Pb-Hf Isotopes and Whole-Rock Geochemistry

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**Abstract:** The Wunugetu deposit, a large-scale porphyry copper–molybdenum deposit, is located in the southern Erguna block. Its ore bodies are primarily found within monzogranites, granite porphyries, and biotite monzogranites. Additionally, the deposit contains late-stage intrusive dykes of rhyolitic porphyries. This study examined the deposit's monzogranites and rhyolitic porphyries using lithogeochemistry, zircon U-Pb dating, and Hf isotopic analysis. The main findings include: (1) Zircon U-Pb dating showed that the monzogranites formed around  $209.0 \pm 1.0$  Ma, whereas the rhyolitic porphyries in the northern portion formed around  $170.49 \pm 0.81$  Ma, suggesting magmatic activity in the deposit spanned from the Late Triassic to the Middle Jurassic. (2) The monzogranites exhibited high silicon content (73.16–80.47 wt.%) and relatively low aluminum content (10.98–14.37 wt.%). They are enriched in alkalis (content: 3.42–10.10 wt.%) and deficient in magnesium and sodium, with aluminum saturation indices (A/CNK) ranging from 1.1 to 2.9. In addition, the monzogranites are enriched in large-ion lithophile elements (LILEs) such as Rb, K, and Ba and deficient in high-field-strength elements (HFSEs) like Nb, P, and Ti. (3) The monzogranites have low  $Zr + Nb + Ce + Y$  contents of  $(151.3\text{--}298.6 \text{ ppm}) \times 10^{-6}$  and  $10,000 \times Ga/Al$  ratios varying between 1.20 and 2.33, suggesting that they are characteristic of I-type granites. (4) Positive zircon  $\epsilon Hf(t)$  values ranging from +0.3 to +7.6 in both rhyolitic porphyry and monzogranite samples, increasing with younger emplacement ages, imply that the deposit's rocks originated from magmatic mixing between mantle-derived mafic magmas and remelts of the juvenile crust. Considering these results and the regional geological evolution, this study proposes that the Wunugetu deposit was formed in an active continental margin setting and was influenced by the Late Triassic–Middle Jurassic southeastward subduction of the Mongol–Okhotsk Ocean.

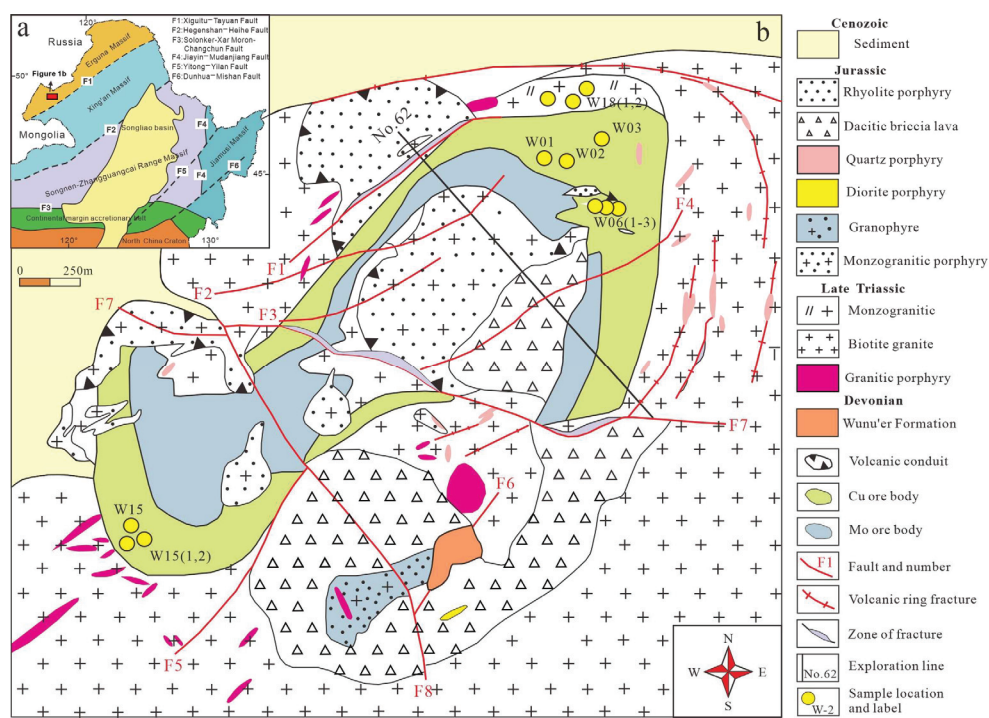
**Keywords:** Cu–Mo deposit; lithogeochemistry; I-type granite; Mongolia–Okhotsk Ocean; Wunugetu

## 1. Introduction

The Central Asian Orogenic Belt (CAOB), located between the Siberian Craton and the North China Craton, is recognized as one of the largest Phanerozoic orogenic belts globally. Its extensive geological history features the accretion of continental crust induced by oceanic subduction, the convergence of multiple plates, intracontinental orogeny, and associated multistage tectono-magmatic activity. Hence, the deep magmatic activity and

mineralization related to the CAOB's formation and evolution have garnered significant interest from geologists worldwide [1–8]. Within the CAOB, multiple world-class porphyry copper deposits, such as Oyu Tolgoi, Erdenet, and Aktogai–Aiderly, have been identified, positioning this region as a premier porphyry copper belt on a global scale, also referred to as the Central Asian Metallogenic Belt [9]. This belt, along with the Circum-Pacific and Tethyan metallogenic belts, constitutes one of the three principal global copper metallogenic provinces [10]. Situated in the eastern segment of the CAOB, Northeast China emerged from the amalgamation of various microblocks, including the Erguna, Xing'an, Songnen–Zhangguangcai Range, Jiamusi, and Xingkai blocks [11], highlighting its importance as a notable copper-bearing region in China.

The Wunugetu deposit, situated in the southern Erguna block of Northeast China (Figure 1a), represents a significant porphyry copper–molybdenum deposit within the eastern CAOB. Since its identification, the deposit has garnered considerable attention from the geological community [12–14]. Extensive studies of this deposit focus on its geological characteristics, the isotopic geochronology and lithogeochemistry of the ore-hosting surrounding rocks, and ore-forming fluids [12,15–17]. However, debates persist regarding the metallogenic periods and geodynamic setting of the Wunugetu deposit. Wang Zhitian's (1988) initial K–Ar dating of monzogranite porphyry stocks within the deposit yielded an age of 138 Ma [12], leading to the hypothesis of a Late Yanshanian origin. Qin Kezhang (1999), through Rb–Sr dating of the ore-hosting monzogranite porphyries and K–Ar dating of altered sericite, proposed that the deposit formed between 180 and 190 Ma, indicating an Early Jurassic age of this copper–molybdenum deposit [15]. Advancements in analytical methods allowed Tan Gang (2010) to determine a formation age of 177 Ma using Re–Os isotopic dating of the molybdenite [17]. These studies demonstrate that the Wunugetu deposit experienced intense magmatic activity and mineralization events during the Early Jurassic. However, there is limited information on Late Triassic and Middle Jurassic intrusions within the deposit. This study delves into the geological, ore-body, and ore characteristics of the Wunugetu deposit. Employing zircon U–Pb dating, Hf isotope analysis, and whole-rock geochemistry of the ore-hosting porphyritic monzogranites and the late-stage intrusive rhyolitic porphyries, this study aims to constrain the formation periods of ore-forming rock masses and identify the genetic types, source traits, and tectonic setting of the rock masses and late-stage dykes. Additionally, the new data can be used to effectively elucidate the geodynamic context of copper–molybdenum mineralization in the Wunugetu deposit.



**Figure 1.** (a) Tectonic location map of the Wunugetu porphyry copper-molybdenum deposit; (b) Geological map of the Wunugetu deposit showing the main lithologies and faults with a volcanic edifice [18].

2. Geological Setting

2.1. Regional Geological Setting

Located about 24 km southwest of Manzhouli City, the Wunugetu deposit is positioned in the central part of the Erguna block, nestled between the Mongol-Okhotsk suture zone (MOSZ) and the Xiguitu-Tayuan fault (Figure 1a). In the Paleozoic era, the Erguna block, influenced by the evolution of the Paleo-Asian Ocean tectonic system, experienced the complex amalgamation of several microblocks within the CAOAB [19,20]. From the Late Paleozoic to the Mesozoic, the block fell under the tectonic influence of the Mongol-Okhotsk Ocean tectonic domain [19–23]. The superposition of multiple tectonic domains has endowed this block with highly developed regional fault structures, primarily including a series of E–W- and NE–NNE-trending faults, as well as secondary faults. The oldest exposed strata within the Erguna block consist mainly of Precambrian strata, overlain by Paleozoic and Mesozoic layers. The Precambrian strata are chiefly made up of a crystalline basement composed mainly of schists, leptytes, and quartzites from the Neoproterozoic Jiageda Formation (Ptj). The Paleozoic sequence mainly comprises volcanic and terrigenous clastic rocks from the Middle Devonian Wunu’er Formation, while the Mesozoic strata encompass intermediate-mafic volcanic and pyroclastic rocks from the Middle Jurassic Tamulangou Formation, intermediate-acid volcanic rocks from the Shangkuli Formation, and acidic volcanic and pyroclastic rocks from the Upper Jurassic Marketouebo and Manitu formations. The complex process of tectonic evolution has resulted in frequent regional magmatic activity, with Mesozoic granites being the most extensively developed. The region hosts several significant deposits, including the Badaguan copper–molybdenum deposit, the Wunugetu deposit, the Jiawula and Halasheng lead–zinc–silver deposits, and

the Chaganbulagen silver–lead–zinc deposit, all of which are intimately linked to the Mesozoic magmatic activity [15,18,24,25].

## 2.2. Geological Setting of the Wunugetu Deposit

The Wunugetu deposit was discovered by the No. 706 Team of the Heilongjiang Nonferrous Metal Geological Survey in 1978. By 2006, the deposit had 1.106 million tons of copper and 0.362 million tons of molybdenum identified, establishing it as the most significant large-scale porphyry copper–molybdenum deposit within the Erguna block [13]. In 2008, the China National Gold Group Co., Ltd. (Beijing, China) acquired the Wunugetu deposit to further its exploration and production endeavors.

The exposed strata in the Wunugetu deposit encompass the Devonian Wunu'er Formation's andesites and crystalline limestones (southwest), Upper Jurassic volcanic rocks (north), and extensive Quaternary unconsolidated deposits (Figure 1b).

The Wunugetu deposit underwent two distinct magmatic phases. The first phase, during the Late Triassic, produced biotite granites, monzogranites, and granite porphyries, which together cover about 60% of the deposit's total area. The biotite granites and monzogranites, forming batholiths, extend across the deposit and its vicinity, covering an exposed area of approximately 110 km<sup>2</sup>. These rocks are crucial as the ore-hosting rock masses and surrounding rocks of the deposit.

The second magmatic phase, in the Early Jurassic, led to the formation of a volcanic edifice. The volcanic rocks mainly consist of andesitic agglomerates, while the lithologic assemblages of intrusions primarily comprise monzogranite porphyries, quartz porphyries, diorite porphyrites, and rhyolitic porphyries. The rhyolitic porphyries, intruding into the mineral-bearing monzogranite porphyries, show no signs of mineralization or alteration zones. The monzogranite porphyries are distributed in the central portion of the deposit. They are disrupted by the late-stage F7 fault, making them a key ore-hosting rock mass. Additionally, the outcrops in the deposit include minor quantities of dacitic breccias, quartz porphyries, and diorite porphyrites.

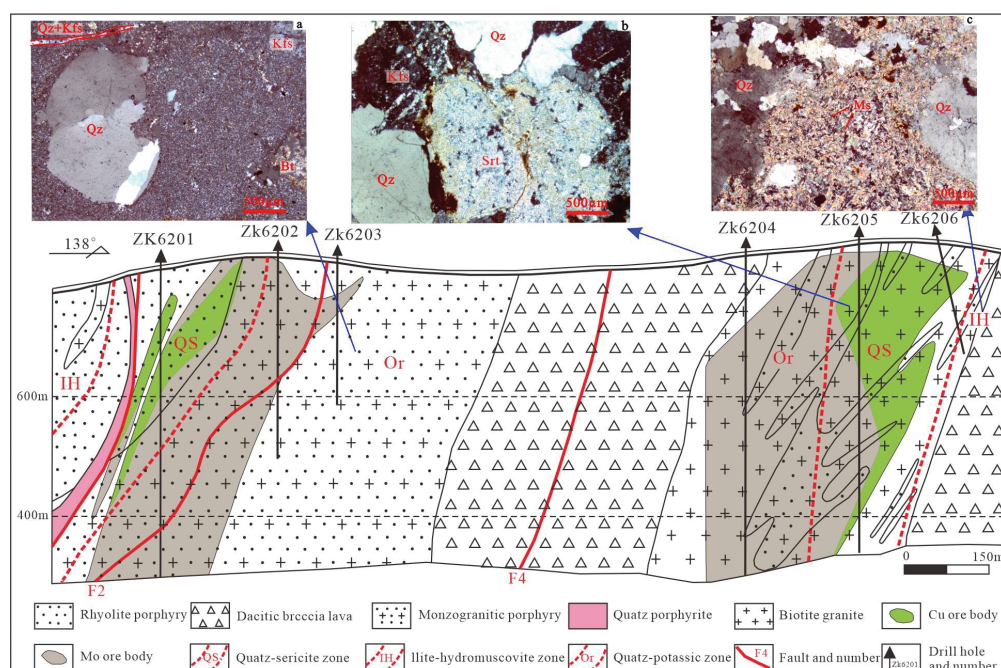
Fault structures are prominent in the Wunugetu deposit, including NE-, NNW-, and nearly E–W-trending faults, along with ring-shaped faults in volcanic areas. The NE-trending and ring-shaped faults developed during the mineralization period, whereas the NW-oriented F8 fault emerged in the later stages of mineralization. These faults cut through ore bodies, disrupting their continuity. The E–W-trending F7 fault divides the ore bodies into southern and northern segments.

## 3. Ore Body Characteristics

The ore bodies within the Wunugetu deposit are arranged in a ring-like pattern orienting NWE, with monzogranite porphyries at their core. The area of mineralization spans roughly 2600 m in length and about 1400 m in width. These ore bodies have a strike of 50° and a dip direction of WN. The F7 fault causes a horizontal displacement of approximately 700 m, thereby splitting the ore bodies into two distinct segments: the southern segment spans about 800 m in width, while the northern segment extends approximately 900 m across. Both segments are subjected to hydrothermal alteration within the deposit. The Wunugetu deposit exhibits typical alteration zones of porphyry-type mineralization, covering an area of approximately 5 km<sup>2</sup>. These zones roughly comprise potassic (Or), quartz-sericite (Qs), and illite-hydromica (IH) alteration zones [15]. The primary alterations observed include silicification, potassic feldspathization, sericitization, illitization, muscovitization, carbonatization, and kaolinization, with chloritization and epidotization being relatively less common (Figure 2).

The potassic zone (Or), centrally located within the deposit, is found predominantly in the monzogranite porphyry rock masses. The alteration minerals characteristic of this zone are mainly K-feldspar and biotite, with sericite present in smaller quantities (Figure 2a). Molybdenite is the principal type of mineralization in this zone, along with notable occurrences of chalcopyrite and pyrite mineralizations.





**Figure 2.** Northwest–southeast section (620 line) through the Wunugetu deposit showing the relationship of host monzogranitic porphyry, alteration, and mineralization [24]. Micrographs of potassium feldspathization (a), quartz-sericitization (b), and illite-hydromica (c). Bt—biotite, Qz—quartz, Pl—plagioclase, Kfs—feldspar, Srt—sericite, Ms—Muscovite.

The quartz-sericite zone (Qs) extends through the biotite granites and their contact zone with the monzogranite porphyries. This zone is rich in alteration minerals such as quartz, sericite (Figure 2b), and carbonate. The ore minerals in this zone include molybdenite, chalcopyrite, malachite, pyrite, and azurite.

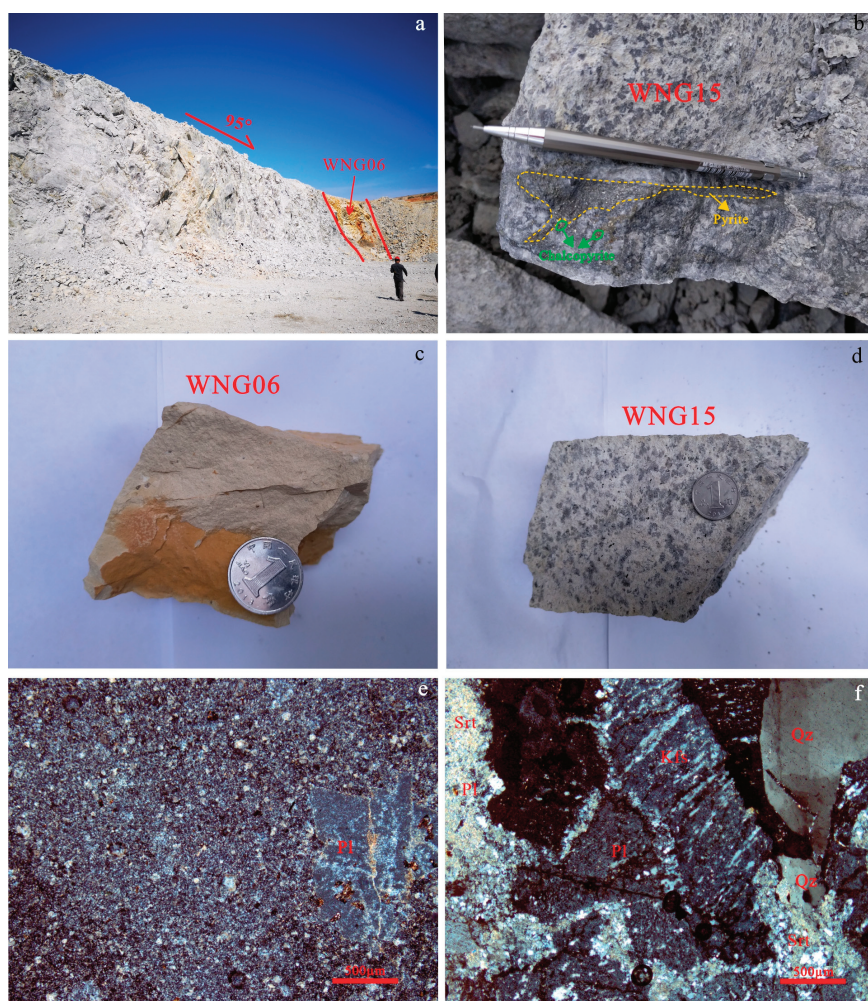
The illite-hydromica zone (IH), located within biotite granites on the periphery of the deposit and rhyolites in the northern part, features alteration minerals like illite, hydromuscovite (Figure 2c), carbonate, and kaolinite. This zone also exhibits lead and zinc mineralizations.

## 4. Sampling and Methodology

### 4.1. Sampling and Lithofacies Characteristics of Samples

A total of 14 samples were gathered, comprising three monzogranite samples (WNG01, WNG02, and WNG03), four rhyolitic porphyry samples (WNG06, WNG06-1, WNG06-2, and WNG06-3; Figure 3a) from the deposit's northern area, four monzogranite samples (WNG15-1, WNG15-2, WNG15-3, and WNG15; Figure 3b) from the southern portion, and three additional monzogranite samples (WNG18-1, WNG18-2, and WNG18-3) from the deposit's periphery. The specific sampling locations are depicted in Figure 1b.





**Figure 3.** Field outcrops, hand specimens, and microscopic photos of the monzogranites and rhyolitic porphyries in the Wunugetu deposit. Qz—quartz, Pl—plagioclase, Kfs—feldspar, Srt—sericite. (a) Field outcrops and sampling locations of rhyolitic porphyries; (b) Sampling location of monzogranite, with fine veins of pyrite and chalcopyrite; (c) Monzogranite hand specimens; (d) Rhyolitic porphyry hand specimen; (e) Microscopic photos of rhyolitic porphyry; (f) Microscopic photos of monzogranites.

#### 4.2. Zircon U-Pb Dating

Zircon monomineralic separation, target preparation, cathodoluminescence (CL) imaging, and zircon U-Pb dating were performed at the laboratory of Yandu Zhongshi Testing Technology Co., Ltd. (Beijing, China). The procedures utilized a New Wave UP213 laser ablation system and an M90 inductively coupled plasma mass spectrometer (ICP-MS) manufactured by Analytik Jena AG. Zircon reference materials 91500 and Plesovice employed exhibited the values recommended [26,27], as calculated using ZSKits software ver. 1.1.0. The quantification of trace elements in zircon utilized SRM610 and Si as the external and internal standards, respectively [28]. For U-Pb isotopic dating, zircon reference material 91500 was used as an external standard for isotopic fractionation correction. The U-Pb age concordia diagrams and the weighted average ages of the zircon samples were generated

using Isoplot/Exver3 [29]. Additionally, the correction of common lead in U-Pb analyses was performed following Andersen's (2002) method [30].

#### 4.3. In-Situ Lu-Hf Isotopes of Zircon

In-situ zircon Lu-Hf isotopic analyses were performed utilizing a Neptune Plus MC-ICP-MS manufactured by Thermo-Fisher and a New Wave UP213 laser ablation system, with the procedures and calibration methods akin to those proposed by Wu Fuyuan et al. (2007) [31]. Laser ablation was executed for 31 s at a frequency of 8 Hz and an energy density of 16 J/cm<sup>2</sup>. Considering the exceptionally low <sup>176</sup>Lu/<sup>177</sup>Hf ratios in zircon, typically below 0.002, the isotopic interference of <sup>176</sup>Lu on <sup>176</sup>Hf was deemed negligible. The isotopic fractionation factor of Yb was calculated using the average <sup>173</sup>Yb/<sup>172</sup>Yb ratios of various test points, followed by removal of the isobaric interference of <sup>176</sup>Yb on <sup>176</sup>Hf. The <sup>173</sup>Yb/<sup>172</sup>Yb ratio was established at 1.35274.

#### 4.4. Whole-Rock Major- and Trace-Element Analyses

Complete silicate analysis was performed at the laboratory of Yandu Zhongshi Testing Technology Co., Ltd. Major element analysis utilized the acid dissolution method in conjunction with a Zetium X-ray fluorescence spectrometer (XRF) from PANalytical, with analytical precision errors under 0.1%. Trace element analysis was carried out with an M90 ICP-MS from Analytik Jena AG, with analytical errors maintained below 10%.

### 5. Results

#### 5.1. Petrography

The rhyolitic porphyries, as stocks, intrude into granite porphyries, characterized by porphyritic textures and blocky structures. Their phenocrysts, making up 10% of the composition, consist of quartz (5%) and feldspar (5%), with particle sizes between 0.4 and 1.4 mm. Their matrix, constituting 90%, is mainly feldspar and quartz. It manifests felsitic textures, with radial or fan-shaped grains scattering locally (Figure 3c,e).

The monzogranites comprise plagioclase (35%), alkali feldspar (30%), and quartz (35%), with consistent mineral grain sizes ranging from 1.6 to 3.0 mm. The plagioclase is hypidiomorphic, tabular, and granular, featuring sericite alterations on their surfaces. In contrast, the alkali feldspar appears as xenomorphic grains (Figure 3d,f).

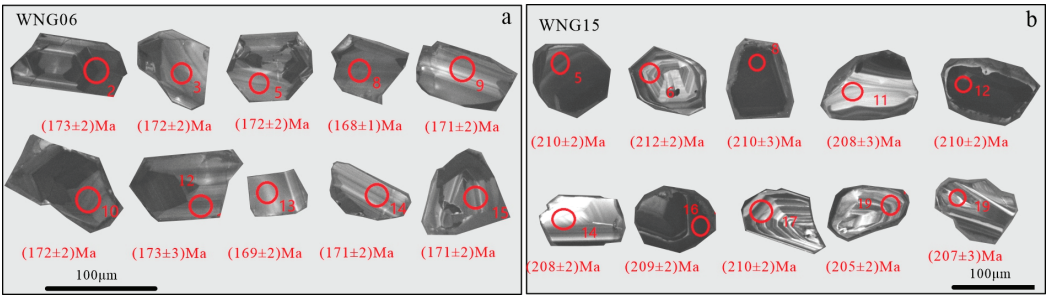
The monzogranite porphyries are composed of plagioclase (30%), alkali feldspar (30%), quartz (32%) (Figure 3d), sericite (5%), and pyrite (3%). The grains are uniform in size, ranging from 1.6 to 3.0 mm. The plagioclase is subhedral, appearing in tabular and granular shapes, with sericite pseudomorphing its surfaces. The alkali feldspar occurs as xenomorphic grains, comprising perthitic feldspar with irregularly vein-like, spotted, and patchy patterns. It exhibits weak sericitization on surfaces, with sericite replacing along the perthite (Figure 3f). The pyrite occurs mainly as euhedral to anhedral grains distributed among the minerals' intergranular spaces.

#### 5.2. Zircon U-Pb Ages

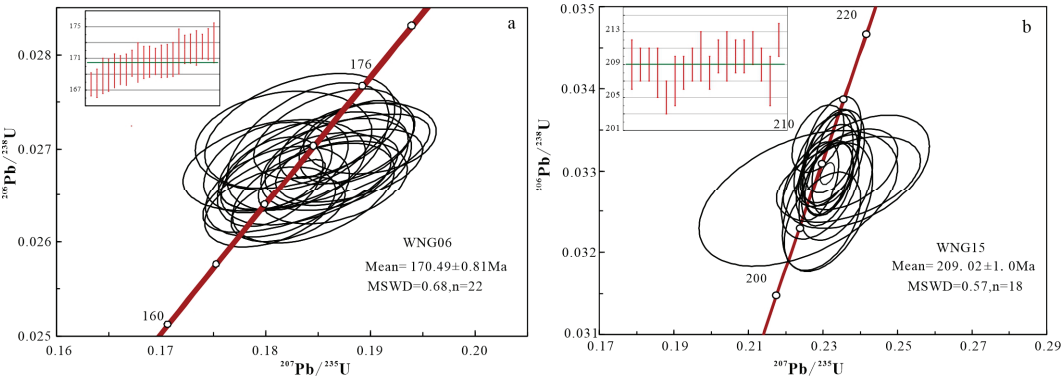
The LA-ICP-MS zircon U-Pb dating data are shown in Table 1, partial zircon CL images are illustrated in Figure 4a,b, and the concordia diagrams with weighted average age curves are presented in Figure 5a,b. Zircon grains from rhyolitic porphyry sample WNG06 ranged from idiomorphic to hypidiomorphic columnar shapes, with sizes ranging from 50 to 150 µm. These grains were primarily short columnar, followed by long columnar, with length/width ratios from 1:1 to 2.5:1 and minor fissures occasionally visible. Oscillatory zoning was observed in the CL images of these zircon grains. Their Th/U ratios spanned from 0.74 to 1.34, all above 0.1, indicating a magmatic origin for these grains. Analysis of 22 test points on this sample yielded <sup>206</sup>Pb/<sup>238</sup>U ages between 169 and 173 Ma, corresponding to weighted average ages of 170.49 ± 0.81 Ma (MSWD = 0.68).

Table 1. LA-ICP-MS zircon U-Pb dating data of Wunugetu rhyolite porphyry and monzogranites.

| Test Point Number | Th<br>( $\times 10^{-6}$ ) | U<br>( $\times 10^{-6}$ ) | Th/U | Isotope Atomic Ratio                         |                                             |                                             | Isotopic Age (Ma)                            |                                              |                                             |                                             |                                              |    |     |   |     |   |
|-------------------|----------------------------|---------------------------|------|----------------------------------------------|---------------------------------------------|---------------------------------------------|----------------------------------------------|----------------------------------------------|---------------------------------------------|---------------------------------------------|----------------------------------------------|----|-----|---|-----|---|
|                   |                            |                           |      | $^{207}\text{Pb}/^{206}\text{Pb}$ 1 $\sigma$ | $^{207}\text{Pb}/^{235}\text{U}$ 1 $\sigma$ | $^{206}\text{Pb}/^{238}\text{U}$ 1 $\sigma$ | $^{208}\text{Pb}/^{232}\text{Th}$ 1 $\sigma$ | $^{207}\text{Pb}/^{206}\text{Pb}$ 1 $\sigma$ | $^{207}\text{Pb}/^{235}\text{U}$ 1 $\sigma$ | $^{206}\text{Pb}/^{238}\text{U}$ 1 $\sigma$ | $^{208}\text{Pb}/^{232}\text{Th}$ 1 $\sigma$ |    |     |   |     |   |
| Sample WNG06      |                            |                           |      |                                              |                                             |                                             |                                              |                                              |                                             |                                             |                                              |    |     |   |     |   |
| WNG06-08          | 801                        | 724                       | 1.11 | 0.05012                                      | 0.00097 0.18207                             | 0.00359 0.02638                             | 0.00023 0.00812                              | 0.00013                                      | 200                                         | 45                                          | 170                                          | 3  | 168 | 1 | 163 | 3 |
| WNG06-26          | 1007                       | 932                       | 1.08 | 0.04959                                      | 0.00107 0.18035                             | 0.00413 0.02638                             | 0.00029 0.00808                              | 0.00022                                      | 176                                         | 51                                          | 168                                          | 4  | 168 | 2 | 163 | 4 |
| WNG06-21          | 516                        | 618                       | 0.83 | 0.05038                                      | 0.00126 0.18452                             | 0.00511 0.02653                             | 0.00036 0.00852                              | 0.00038                                      | 213                                         | 58                                          | 172                                          | 4  | 169 | 2 | 171 | 8 |
| WNG06-23          | 614                        | 689                       | 0.89 | 0.04959                                      | 0.00120 0.18107                             | 0.00453 0.02654                             | 0.00032 0.00795                              | 0.00031                                      | 176                                         | 57                                          | 169                                          | 4  | 169 | 2 | 160 | 6 |
| WNG06-13          | 722                        | 783                       | 0.92 | 0.04972                                      | 0.00148 0.18326                             | 0.00615 0.02663                             | 0.00035 0.00826                              | 0.00024                                      | 182                                         | 69                                          | 171                                          | 5  | 169 | 2 | 166 | 5 |
| WNG06-20          | 937                        | 821                       | 1.22 | 0.05074                                      | 0.00137 0.18636                             | 0.00469 0.02664                             | 0.00030 0.00824                              | 0.00038                                      | 229                                         | 62                                          | 174                                          | 4  | 169 | 2 | 166 | 8 |
| WNG06-30          | 630                        | 692                       | 0.91 | 0.04925                                      | 0.00095 0.18037                             | 0.00333 0.02665                             | 0.00032 0.00867                              | 0.00028                                      | 160                                         | 45                                          | 168                                          | 3  | 170 | 2 | 175 | 6 |
| WNG06-01          | 607                        | 624                       | 0.97 | 0.05027                                      | 0.00117 0.18590                             | 0.00398 0.02678                             | 0.00026 0.00855                              | 0.00018                                      | 208                                         | 54                                          | 173                                          | 3  | 170 | 2 | 172 | 4 |
| WNG06-22          | 475                        | 602                       | 0.79 | 0.04981                                      | 0.00140 0.18458                             | 0.00591 0.02679                             | 0.00040 0.00874                              | 0.00042                                      | 186                                         | 65                                          | 172                                          | 5  | 170 | 3 | 176 | 8 |
| WNG06-25          | 715                        | 727                       | 0.98 | 0.04887                                      | 0.00110 0.18015                             | 0.00403 0.02680                             | 0.00031 0.00860                              | 0.00031                                      | 142                                         | 53                                          | 168                                          | 3  | 170 | 2 | 173 | 4 |
| WNG06-27          | 826                        | 823                       | 1.00 | 0.04911                                      | 0.00100 0.18165                             | 0.00409 0.02682                             | 0.00031 0.00813                              | 0.00020                                      | 153                                         | 48                                          | 169                                          | 4  | 171 | 2 | 164 | 4 |
| WNG06-16          | 561                        | 598                       | 0.94 | 0.05070                                      | 0.00120 0.18792                             | 0.00463 0.02682                             | 0.00026 0.00861                              | 0.00026                                      | 227                                         | 55                                          | 175                                          | 4  | 171 | 2 | 173 | 5 |
| WNG06-14          | 457                        | 570                       | 0.80 | 0.04917                                      | 0.00155 0.18074                             | 0.00574 0.02682                             | 0.00033 0.00859                              | 0.00026                                      | 156                                         | 74                                          | 169                                          | 5  | 171 | 2 | 173 | 5 |
| WNG06-15          | 502                        | 570                       | 0.88 | 0.05059                                      | 0.00132 0.18667                             | 0.00475 0.02683                             | 0.00033 0.00805                              | 0.00025                                      | 222                                         | 61                                          | 174                                          | 4  | 171 | 2 | 162 | 5 |
| WNG06-09          | 341                        | 458                       | 0.74 | 0.05001                                      | 0.00172 0.18565                             | 0.00656 0.02686                             | 0.00034 0.00831                              | 0.00021                                      | 195                                         | 80                                          | 173                                          | 6  | 171 | 2 | 167 | 4 |
| WNG06-29          | 664                        | 701                       | 0.95 | 0.04942                                      | 0.00124 0.18396                             | 0.00511 0.02702                             | 0.00045 0.00880                              | 0.00026                                      | 168                                         | 59                                          | 171                                          | 4  | 172 | 3 | 179 | 5 |
| WNG06-03          | 589                        | 651                       | 0.90 | 0.05033                                      | 0.00105 0.18768                             | 0.00423 0.02706                             | 0.00029 0.00889                              | 0.00015                                      | 210                                         | 48                                          | 175                                          | 4  | 172 | 2 | 179 | 3 |
| WNG06-05          | 865                        | 748                       | 1.16 | 0.05059                                      | 0.00094 0.18864                             | 0.00365 0.02708                             | 0.00035 0.00868                              | 0.00013                                      | 222                                         | 43                                          | 175                                          | 3  | 172 | 2 | 175 | 3 |
| WNG06-28          | 304                        | 411                       | 0.74 | 0.04884                                      | 0.00155 0.18165                             | 0.00558 0.02709                             | 0.00035 0.00857                              | 0.00026                                      | 140                                         | 74                                          | 169                                          | 5  | 172 | 2 | 172 | 5 |
| WNG06-10          | 789                        | 765                       | 1.03 | 0.05071                                      | 0.00114 0.18990                             | 0.00419 0.02712                             | 0.00025 0.00902                              | 0.00027                                      | 228                                         | 52                                          | 177                                          | 4  | 172 | 2 | 181 | 5 |
| WNG06-02          | 2099                       | 1566                      | 1.34 | 0.04953                                      | 0.00118 0.18585                             | 0.00464 0.02717                             | 0.00031 0.00864                              | 0.00013                                      | 173                                         | 56                                          | 173                                          | 4  | 173 | 2 | 174 | 3 |
| WNG06-12          | 804                        | 740                       | 1.09 | 0.04900                                      | 0.00158 0.18321                             | 0.00601 0.02720                             | 0.00040 0.00917                              | 0.00033                                      | 148                                         | 76                                          | 171                                          | 5  | 173 | 3 | 184 | 7 |
| Sample WNG15      |                            |                           |      |                                              |                                             |                                             |                                              |                                              |                                             |                                             |                                              |    |     |   |     |   |
| WNG15-10          | 667                        | 959                       | 0.63 | 0.05252                                      | 0.00294 0.23892                             | 0.01295 0.03299                             | 0.00046 0.01035                              | 0.00012                                      | 308                                         | 131                                         | 218                                          | 11 | 209 | 3 | 208 | 2 |
| WNG15-27          | 1137                       | 2309                      | 0.47 | 0.05220                                      | 0.00287 0.23680                             | 0.01276 0.03290                             | 0.00035 0.01033                              | 0.00010                                      | 294                                         | 128                                         | 216                                          | 10 | 209 | 2 | 208 | 2 |
| WNG15-04          | 569                        | 1121                      | 0.48 | 0.05198                                      | 0.00200 0.23667                             | 0.00878 0.03302                             | 0.00033 0.01037                              | 0.00009                                      | 285                                         | 90                                          | 216                                          | 7  | 209 | 2 | 209 | 2 |
| WNG15-11          | 91                         | 236                       | 0.36 | 0.05154                                      | 0.00135 0.23341                             | 0.00653 0.03280                             | 0.00043 0.01136                              | 0.00035                                      | 265                                         | 40                                          | 213                                          | 5  | 208 | 3 | 228 | 7 |
| WNG15-18          | 201                        | 423                       | 0.45 | 0.05138                                      | 0.00148 0.22978                             | 0.00675 0.03239                             | 0.00040 0.01002                              | 0.00035                                      | 258                                         | 45                                          | 210                                          | 6  | 205 | 2 | 202 | 7 |
| WNG15-19          | 313                        | 586                       | 0.49 | 0.05129                                      | 0.00157 0.23114                             | 0.00799 0.03256                             | 0.00052 0.00972                              | 0.00041                                      | 254                                         | 50                                          | 211                                          | 7  | 207 | 3 | 196 | 8 |
| WNG15-30          | 209                        | 462                       | 0.42 | 0.05112                                      | 0.00090 0.23118                             | 0.00456 0.03284                             | 0.00034 0.01027                              | 0.00023                                      | 246                                         | 27                                          | 211                                          | 4  | 208 | 2 | 207 | 5 |
| WNG15-29          | 565                        | 1261                      | 0.43 | 0.05090                                      | 0.00075 0.23156                             | 0.00421 0.03290                             | 0.00030 0.01070                              | 0.00026                                      | 236                                         | 25                                          | 211                                          | 3  | 209 | 2 | 206 | 5 |
| WNG15-08          | 1453                       | 2266                      | 0.60 | 0.05084                                      | 0.00073 0.23251                             | 0.00365 0.03308                             | 0.00041 0.01024                              | 0.00029                                      | 233                                         | 17                                          | 212                                          | 3  | 210 | 3 | 215 | 6 |
| WNG15-14          | 233                        | 259                       | 0.85 | 0.05074                                      | 0.00144 0.22922                             | 0.00690 0.03277                             | 0.00040 0.01044                              | 0.00021                                      | 229                                         | 47                                          | 210                                          | 6  | 208 | 2 | 210 | 4 |
| WNG15-17          | 274                        | 544                       | 0.46 | 0.05076                                      | 0.00113 0.23267                             | 0.00560 0.03316                             | 0.00039 0.01080                              | 0.00038                                      | 230                                         | 34                                          | 212                                          | 5  | 210 | 2 | 217 | 8 |
| WNG15-28          | 1611                       | 2523                      | 0.60 | 0.05057                                      | 0.00087 0.23200                             | 0.00487 0.03311                             | 0.00043 0.01046                              | 0.00046                                      | 221                                         | 26                                          | 211                                          | 4  | 210 | 3 | 210 | 9 |
| WNG15-05          | 250                        | 641                       | 0.37 | 0.05054                                      | 0.00092 0.23153                             | 0.00511 0.03309                             | 0.00032 0.01065                              | 0.00041                                      | 220                                         | 23                                          | 211                                          | 4  | 210 | 2 | 214 | 8 |
| WNG15-12          | 443                        | 1048                      | 0.39 | 0.05048                                      | 0.00137 0.23097                             | 0.00583 0.03312                             | 0.00038 0.01092                              | 0.00037                                      | 218                                         | 37                                          | 211                                          | 5  | 210 | 2 | 220 | 7 |
| WNG15-24          | 425                        | 1234                      | 0.32 | 0.05048                                      | 0.00114 0.23252                             | 0.00509 0.03333                             | 0.00039 0.01015                              | 0.00047                                      | 217                                         | 30                                          | 212                                          | 4  | 211 | 2 | 204 | 9 |
| WNG15-16          | 1041                       | 1784                      | 0.56 | 0.05028                                      | 0.00068 0.22845                             | 0.00376 0.03288                             | 0.00032 0.01002                              | 0.00031                                      | 208                                         | 21                                          | 209                                          | 3  | 209 | 2 | 202 | 6 |
| WNG15-09          | 2274                       | 2216                      | 0.97 | 0.04959                                      | 0.00399 0.22341                             | 0.01758 0.03267                             | 0.00055 0.01032                              | 0.00015                                      | 176                                         | 183                                         | 205                                          | 15 | 207 | 3 | 208 | 3 |
| WNG15-06          | 339                        | 481                       | 0.67 | 0.04950                                      | 0.00086 0.22857                             | 0.00460 0.03340                             | 0.00027 0.01013                              | 0.00027                                      | 171                                         | 32                                          | 209                                          | 4  | 212 | 2 | 204 | 5 |



**Figure 4.** Cathodoluminescence images of zircons in the Wunugetu deposit. (a) Rhyolite Porphyry; (b) Monzogranite.



**Figure 5.** Zircon LA-ICP-MS U-Pb concordia diagrams from Wunugetu copper-gold deposit. (a) Rhyolitic porphyries; (b) Monzogranite.

Zircon grains from monzogranite sample WNG15 displayed shapes from idiomorphic to hypidiomorphic columnar, with sizes varying between 50 to 200 µm. These grains were predominantly short columnar and secondarily long columnar, with length/width ratios ranging between 1:1 and 3:1. Oscillatory zoning was apparent in the CL images of the zircon grains. The Th/U ratios of the zircons spanned from 0.32 to 0.97, all above the 0.1 threshold, indicating a magmatic origin. Analysis of 18 test points on this sample revealed  $^{206}\text{Pb}/^{238}\text{U}$  ages between 205 to 218 Ma, with weighted average ages of  $209.02 \pm 1.0$  Ma (MSWD = 0.57).

5.3. In-Situ Lu-Hf Isotopes of Zircon

The in-situ Lu-Hf isotopic analysis results of zircon are summarized in Table 2. The Hf isotopic data were calculated using U-Pb ages obtained from the same zircon test points. Zircon grains from samples WNG06 and WNG15 exhibited  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios within the ranges of 0.282742–0.282874 and 0.282658–0.282784, respectively, corresponding to  $\epsilon\text{Hf}(t)$  values ranging from +2.4 to +10.8 for WNG06 and from +0.3 to +4.6 for WNG15. The derived two-stage model ages ( $T_{\text{DM2}}$ ) for these samples were between 727 to 1058 Ma for WNG06 and 949 to 1227 Ma for WNG15.

Table 2. Zircon Hf isotope analysis results of Wunugetu rhyolite porphyry and monzogranites.

| Sample    | Age (Ma) | <sup>176</sup> Yb/ <sup>177</sup> Hf | 2σ       | <sup>176</sup> Lu/ <sup>177</sup> Hf | 2σ       | <sup>176</sup> Hf/ <sup>177</sup> Hf | 2σ       | ε <sub>Hf</sub> (0) | ε <sub>Hf</sub> (t) | T <sub>DM1</sub> (Ma) | T <sub>DM2</sub> (Ma) | f <sub>Lu/Hf</sub> |
|-----------|----------|--------------------------------------|----------|--------------------------------------|----------|--------------------------------------|----------|---------------------|---------------------|-----------------------|-----------------------|--------------------|
| WNG06-002 | 173      | 0.092751                             | 0.000975 | 0.002781                             | 0.000029 | 0.282836                             | 0.000023 | 2.3                 | 5.7                 | 620                   | 850                   | −0.92              |
| WNG06-003 | 172      | 0.097305                             | 0.001427 | 0.002702                             | 0.000047 | 0.282847                             | 0.000025 | 2.7                 | 6.1                 | 601                   | 823                   | −0.92              |
| WNG06-005 | 172      | 0.084428                             | 0.000322 | 0.002441                             | 0.000032 | 0.282742                             | 0.000026 | −1.1                | 2.4                 | 751                   | 1058                  | −0.93              |
| WNG06-008 | 168      | 0.087212                             | 0.001147 | 0.002416                             | 0.000046 | 0.282782                             | 0.000021 | 0.4                 | 3.8                 | 691                   | 970                   | −0.93              |
| WNG06-009 | 171      | 0.081093                             | 0.001396 | 0.002398                             | 0.000048 | 0.282865                             | 0.000025 | 3.3                 | 6.8                 | 569                   | 781                   | −0.93              |
| WNG06-010 | 172      | 0.073125                             | 0.000371 | 0.002032                             | 0.000028 | 0.282855                             | 0.000020 | 3.0                 | 6.5                 | 578                   | 800                   | −0.94              |
| WNG06-012 | 173      | 0.099545                             | 0.000903 | 0.002832                             | 0.000046 | 0.282858                             | 0.000027 | 3.0                 | 6.5                 | 587                   | 800                   | −0.91              |
| WNG06-013 | 169      | 0.093224                             | 0.000430 | 0.002751                             | 0.000027 | 0.282788                             | 0.000027 | 0.6                 | 4.0                 | 690                   | 959                   | −0.92              |
| WNG06-014 | 171      | 0.077629                             | 0.000628 | 0.002241                             | 0.000018 | 0.282889                             | 0.000027 | 4.1                 | 7.6                 | 532                   | 727                   | −0.93              |
| WNG06-015 | 171      | 0.083756                             | 0.000953 | 0.002540                             | 0.000047 | 0.282874                             | 0.000028 | 3.6                 | 7.1                 | 558                   | 762                   | −0.92              |
| WNG15-005 | 210      | 0.062887                             | 0.001353 | 0.002038                             | 0.000049 | 0.282684                             | 0.000023 | −3.1                | 1.2                 | 828                   | 1166                  | −0.94              |
| WNG15-006 | 212      | 0.081818                             | 0.002085 | 0.002546                             | 0.000050 | 0.282658                             | 0.000020 | −4.0                | 0.3                 | 877                   | 1227                  | −0.92              |
| WNG15-008 | 210      | 0.110316                             | 0.000582 | 0.003513                             | 0.000064 | 0.282673                             | 0.000028 | −3.5                | 0.6                 | 878                   | 1202                  | −0.89              |
| WNG15-011 | 208      | 0.047510                             | 0.003141 | 0.001509                             | 0.000117 | 0.282732                             | 0.000023 | −1.4                | 3.0                 | 746                   | 1053                  | −0.95              |
| WNG15-012 | 210      | 0.097143                             | 0.001717 | 0.003026                             | 0.000081 | 0.282774                             | 0.000022 | 0.1                 | 4.3                 | 716                   | 972                   | −0.91              |
| WNG15-014 | 208      | 0.092412                             | 0.002386 | 0.002985                             | 0.000046 | 0.282784                             | 0.000020 | 0.4                 | 4.6                 | 700                   | 949                   | −0.91              |
| WNG15-016 | 209      | 0.064028                             | 0.001103 | 0.001971                             | 0.000037 | 0.282751                             | 0.000016 | −0.7                | 3.6                 | 729                   | 1015                  | −0.94              |
| WNG15-017 | 210      | 0.085413                             | 0.000815 | 0.002533                             | 0.000018 | 0.282736                             | 0.000019 | −1.3                | 3.0                 | 762                   | 1052                  | −0.92              |
| WNG15-018 | 205      | 0.076844                             | 0.000813 | 0.002362                             | 0.000023 | 0.282747                             | 0.000015 | −0.9                | 3.3                 | 742                   | 1028                  | −0.93              |
| WNG15-019 | 207      | 0.070343                             | 0.000818 | 0.002212                             | 0.000025 | 0.282740                             | 0.000019 | −1.1                | 3.1                 | 750                   | 1043                  | −0.93              |

5.4. Whole-Rock Major and Trace Element Analyses

The analytical outcomes for major, trace, and rare earth elements (REEs) across 12 rock samples are compiled in Table 3. Regarding major elements, these samples contained 70.16–80.47 wt.% SiO<sub>2</sub>, 10.98–14.37 wt.% Al<sub>2</sub>O<sub>3</sub> (rhyolite), 0.17–3.77 wt.% Na<sub>2</sub>O, 2.95–9.36 wt.% K<sub>2</sub>O, 0.06–0.99 wt.% CaO, 0.14–0.37 wt.% MgO, and 3.42–10.10 wt.% Na<sub>2</sub>O + K<sub>2</sub>O, indicating high silicon content and depletion of sodium generally. The total alkali-silica (TAS) diagram shows that most samples fell within the granite field (Figure 6), in line with petrographic results.

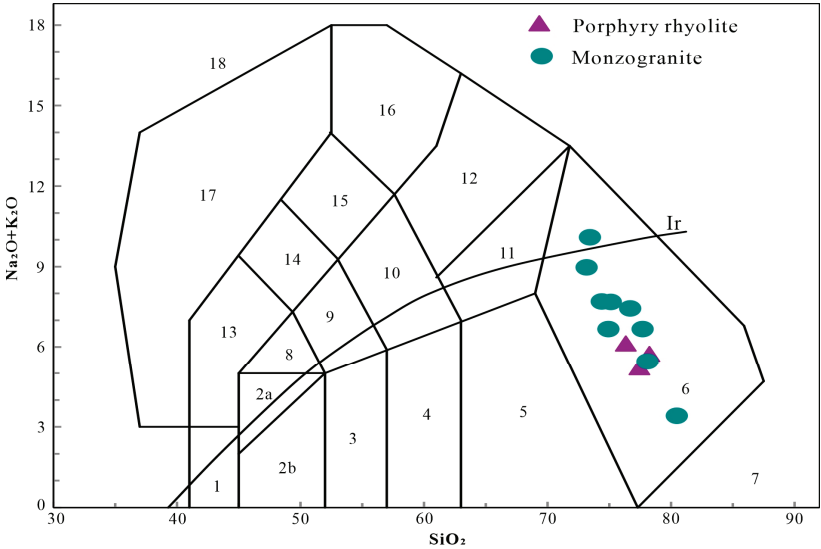
Table 3. Analysis results of major elements (wt.%), rare earth elements, and trace elements (ppm) in Wunugetu rhyolite porphyry and monzogranites.

| No.3                            | W06-1             | W06-2  | W06-3  | W01    | W02    | W03    | W15-1         | W15-2   | W15-3   | W18-1  | W18-2  | W18-3  |
|---------------------------------|-------------------|--------|--------|--------|--------|--------|---------------|---------|---------|--------|--------|--------|
| Rock Type                       | Porphyry Rhyolite |        |        |        |        |        | Monzogranites |         |         |        |        |        |
| Major element (wt.%)            |                   |        |        |        |        |        |               |         |         |        |        |        |
| SiO <sub>2</sub>                | 76.35             | 75.77  | 77.45  | 73.44  | 73.16  | 80.47  | 75.36         | 76.69   | 77.71   | 74.40  | 75.13  | 74.92  |
| Al <sub>2</sub> O <sub>3</sub>  | 12.86             | 12.87  | 12.72  | 14.25  | 14.37  | 11.38  | 13.01         | 12.89   | 10.98   | 13.52  | 13.24  | 12.81  |
| Na <sub>2</sub> O               | 0.23              | 0.23   | 0.23   | 0.74   | 0.74   | 0.17   | 0.22          | 0.30    | 1.59    | 3.77   | 3.55   | 3.73   |
| K <sub>2</sub> O                | 5.91              | 5.33   | 5.00   | 9.36   | 8.24   | 3.25   | 5.05          | 7.15    | 5.09    | 3.94   | 4.14   | 2.95   |
| CaO                             | 0.09              | 0.12   | 0.09   | 0.07   | 0.11   | 0.06   | 0.06          | 0.07    | 0.15    | 0.99   | 0.93   | 0.57   |
| P <sub>2</sub> O <sub>5</sub>   | 0.04              | 0.04   | 0.04   | 0.09   | 0.08   | 0.05   | 0.05          | 0.06    | 0.05    | 0.09   | 0.08   | 0.07   |
| TiO <sub>2</sub>                | 0.05              | 0.05   | 0.05   | 0.17   | 0.17   | 0.07   | 0.10          | 0.09    | 0.16    | 0.21   | 0.18   | 0.22   |
| MgO                             | 0.17              | 0.18   | 0.17   | 0.17   | 0.26   | 0.34   | 0.34          | 0.14    | 0.37    | 0.27   | 0.25   | 0.23   |
| MnO                             | 0.19              | 0.28   | 0.11   | 0.03   | 0.02   | 0.03   | 0.04          | 0.03    | 0.04    | 0.04   | 0.04   | 0.03   |
| TFe <sub>2</sub> O <sub>3</sub> | 1.29              | 1.93   | 1.03   | 0.54   | 0.84   | 1.44   | 2.29          | 0.51    | 1.34    | 1.43   | 1.32   | 2.89   |
| LOI                             | 2.34              | 2.82   | 2.49   | 0.77   | 1.38   | 2.11   | 2.89          | 1.46    | 1.91    | 0.73   | 0.74   | 1.39   |
| TOTAL                           | 99.51             | 99.63  | 99.38  | 99.63  | 99.36  | 99.37  | 99.40         | 99.38   | 99.38   | 99.39  | 99.58  | 99.81  |
| Trace element (ppm)             |                   |        |        |        |        |        |               |         |         |        |        |        |
| Rb                              | 62.98             | 121.78 | 113.08 | 117.95 | 113.48 | 77.48  | 146.83        | 138.72  | 171.18  | 158.50 | 166.50 | 122.31 |
| Ba                              | 203.79            | 225.28 | 839.21 | 757.42 | 606.85 | 303.08 | 696.06        | 1041.38 | 1112.03 | 604.78 | 551.03 | 916.73 |
| Th                              | 2.77              | 6.09   | 5.93   | 15.38  | 20.62  | 13.02  | 19.03         | 23.97   | 11.00   | 13.17  | 10.23  | 20.39  |
| U                               | 0.25              | 0.80   | 0.58   | 2.49   | 2.38   | 14.72  | 4.12          | 7.38    | 1.62    | 2.70   | 2.84   | 3.21   |
| Ta                              | 0.27              | 0.51   | 0.51   | 1.93   | 1.88   | 2.31   | 1.65          | 1.00    | 0.76    | 1.29   | 1.08   | 0.82   |
| Nb                              | 4.05              | 8.34   | 7.92   | 19.01  | 17.78  | 13.71  | 14.18         | 13.20   | 12.22   | 18.78  | 14.98  | 12.12  |
| Sr                              | 23.30             | 50.70  | 68.98  | 130.77 | 109.44 | 7.36   | 28.35         | 80.05   | 126.96  | 167.97 | 157.60 | 214.75 |
| Zr                              | 24.93             | 56.69  | 53.11  | 109.40 | 92.35  | 81.56  | 95.83         | 148.81  | 162.38  | 89.83  | 114.23 | 201.24 |



Table 3. Cont.

| No.3                             | W06-1             | W06-2 | W06-3 | W01           | W02    | W03    | W15-1  | W15-2  | W15-3  | W18-1 | W18-2 | W18-3  |
|----------------------------------|-------------------|-------|-------|---------------|--------|--------|--------|--------|--------|-------|-------|--------|
| Rock Type                        | Porphyry Rhyolite |       |       | Monzogranites |        |        |        |        |        |       |       |        |
| Hf                               | 1.33              | 2.56  | 2.48  | 4.19          | 3.50   | 3.63   | 3.88   | 4.74   | 4.59   | 3.38  | 3.93  | 5.30   |
| La                               | 7.21              | 15.25 | 16.25 | 23.06         | 32.07  | 29.87  | 36.42  | 46.27  | 37.12  | 10.74 | 10.88 | 54.28  |
| Ce                               | 15.21             | 32.38 | 34.44 | 46.74         | 64.09  | 60.42  | 69.61  | 82.46  | 70.73  | 20.56 | 20.21 | 74.95  |
| Pr                               | 1.77              | 4.10  | 4.44  | 5.47          | 7.29   | 6.92   | 8.00   | 9.15   | 8.63   | 2.93  | 3.28  | 7.93   |
| Nd                               | 5.76              | 13.86 | 15.31 | 17.99         | 23.33  | 22.66  | 26.14  | 32.66  | 32.29  | 10.51 | 11.63 | 23.94  |
| Sm                               | 0.99              | 2.39  | 2.63  | 3.47          | 4.18   | 3.91   | 4.13   | 5.19   | 5.83   | 2.65  | 2.87  | 3.26   |
| Eu                               | 0.18              | 0.41  | 0.56  | 0.65          | 0.67   | 0.74   | 0.74   | 0.94   | 1.12   | 0.57  | 0.57  | 0.78   |
| Gd                               | 0.78              | 1.95  | 1.99  | 3.56          | 4.66   | 4.10   | 4.04   | 5.07   | 5.53   | 2.98  | 2.81  | 3.09   |
| Tb                               | 0.10              | 0.24  | 0.21  | 0.59          | 0.79   | 0.70   | 0.56   | 0.66   | 0.83   | 0.53  | 0.48  | 0.35   |
| Dy                               | 0.46              | 1.16  | 0.92  | 3.68          | 5.03   | 4.54   | 3.01   | 3.62   | 4.79   | 3.52  | 2.95  | 1.74   |
| Ho                               | 0.09              | 0.23  | 0.19  | 0.80          | 1.15   | 1.03   | 0.65   | 0.77   | 0.97   | 0.80  | 0.64  | 0.39   |
| Er                               | 0.28              | 0.69  | 0.58  | 2.54          | 3.59   | 3.30   | 1.99   | 2.46   | 2.98   | 2.52  | 2.02  | 1.30   |
| Tm                               | 0.04              | 0.10  | 0.08  | 0.43          | 0.60   | 0.59   | 0.35   | 0.41   | 0.50   | 0.45  | 0.36  | 0.22   |
| Yb                               | 0.17              | 0.51  | 0.40  | 2.77          | 4.30   | 4.33   | 2.41   | 2.75   | 3.30   | 2.89  | 2.46  | 1.56   |
| Lu                               | 0.04              | 0.10  | 0.09  | 0.49          | 0.63   | 0.67   | 0.42   | 0.49   | 0.53   | 0.49  | 0.41  | 0.28   |
| Y                                | 2.50              | 6.25  | 5.12  | 21.35         | 30.48  | 29.67  | 18.14  | 21.48  | 26.15  | 22.18 | 17.81 | 10.26  |
| ΣREE                             | 33.08             | 73.38 | 78.07 | 112.24        | 152.37 | 143.79 | 158.48 | 192.91 | 175.14 | 62.13 | 61.57 | 174.06 |
| LREE                             | 31.13             | 68.39 | 73.63 | 97.39         | 131.62 | 124.53 | 145.03 | 176.67 | 155.71 | 47.96 | 49.44 | 165.14 |
| HREE                             | 1.95              | 4.99  | 4.44  | 14.85         | 20.76  | 19.27  | 13.45  | 16.24  | 19.43  | 14.16 | 12.13 | 8.92   |
| LREE/HREE                        | 15.96             | 13.70 | 16.59 | 6.56          | 6.34   | 6.46   | 10.78  | 10.88  | 8.01   | 3.39  | 4.08  | 18.51  |
| La <sub>N</sub> /Yb <sub>N</sub> | 31.23             | 21.48 | 29.37 | 5.97          | 5.35   | 4.95   | 10.82  | 12.07  | 8.07   | 2.67  | 3.17  | 25.01  |
| δEu                              | 0.64              | 0.58  | 0.75  | 0.57          | 0.46   | 0.57   | 0.55   | 0.56   | 0.60   | 0.62  | 0.62  | 0.75   |
| δCe                              | 1.05              | 1.00  | 0.99  | 1.02          | 1.03   | 1.03   | 1.00   | 0.98   | 0.97   | 0.90  | 0.83  | 0.89   |



**Figure 6.** TAS discrimination diagram of igneous rocks in the Wunugetu deposit. Ir—Irvine boundary [32]; above is alkaline, below is subalkaline. 1—Peridotgabbro; 2a—Alkali Gabbro; 2b—Subalkaline Gabbro; 3—Gabbroic Diorite; 4—Diorite; 5—Granodiorite; 6—Granite; 7—Quartzolite; 8—Monzogabbro; 9—Monzodiorite; 10—Monzosyenite; 11—Quartz Monzonite; 12—Syenite; 13—Foid Gabbro; 14—Foid Monzodiorite; 15—Foid Monzosyenite; 16—Foidolite Syenite; 17—Foidolite; 18—Tawite/Urtite/Italite.

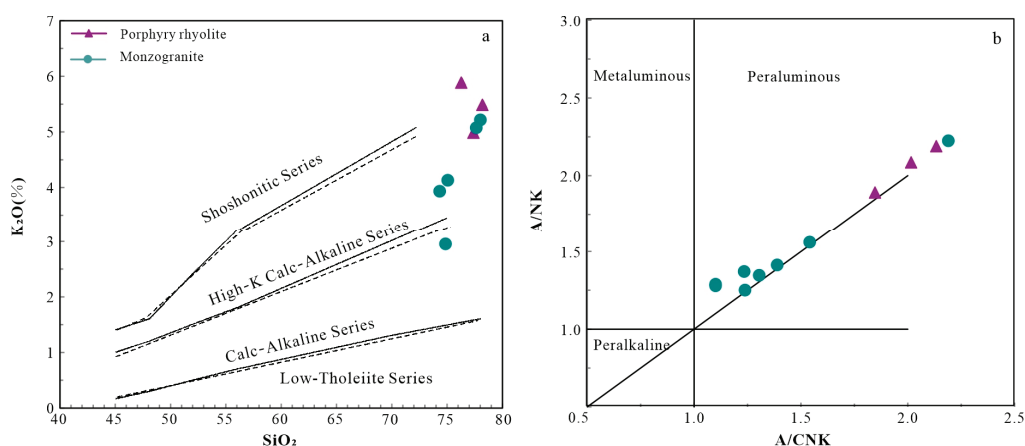
Regarding major elements, the monzogranite samples contained 73.16–80.47 wt.% SiO<sub>2</sub>, 10.98–14.37 wt.% Al<sub>2</sub>O<sub>3</sub>, 0.17–3.77 wt.% Na<sub>2</sub>O, and 2.95–9.36 wt.% K<sub>2</sub>O. Notably,



samples WNG01, WNG02, and WNG15-2 exhibited elevated  $K_2O$  levels, suggesting the potential influence of potassic feldsparization within the deposit. The  $CaO$  varied from 0.06 to 0.99 wt.%,  $MgO$  from 0.14 to 0.37 wt.%, and total alkalis ( $Na_2O + K_2O$ ) from 3.42 to 10.10 wt.%, indicating high silica and low sodium. All the samples fell within the granite field on the TAS diagram (Figure 6).

The rhyolitic porphyry samples revealed  $SiO_2$  between 75.77 wt.% and 77.45 wt.%,  $Al_2O_3$  from 10.98 to 14.37 wt.%,  $Na_2O$  at 0.23 wt.%,  $K_2O$  from 5.00 to 5.91 wt.%,  $CaO$  between 0.09 and 0.12 wt.%,  $MgO$  from 0.17 to 0.18 wt.%, and  $Na_2O + K_2O$  from 5.23 to 6.14 wt.%, also demonstrating high silica and low sodium traits. These samples fell within the granite field on the TAS diagram (Figure 6).

In the  $K_2O$ – $SiO_2$  diagram (Figure 7a), the samples fell within the high-K calc-alkaline to shoshonitic series zones, with one point in the calc-alkaline series zone, indicating the rhyolite and monzogranite samples' classification belongs to these series. All rock samples, with aluminum saturation index ( $A/CNK$ ) values from 1.1 to 2.9, fell within the peraluminous zone on the  $A/NK$  vs.  $A/CNK$  diagram (Figure 7b).



**Figure 7.**  $SiO_2$ – $K_2O$  (a) [33] and  $A/CNK$ – $A/NK$  (b) [34] diagrams of monzogranites and rhyolitic porphyries in the Wunugetu deposit.

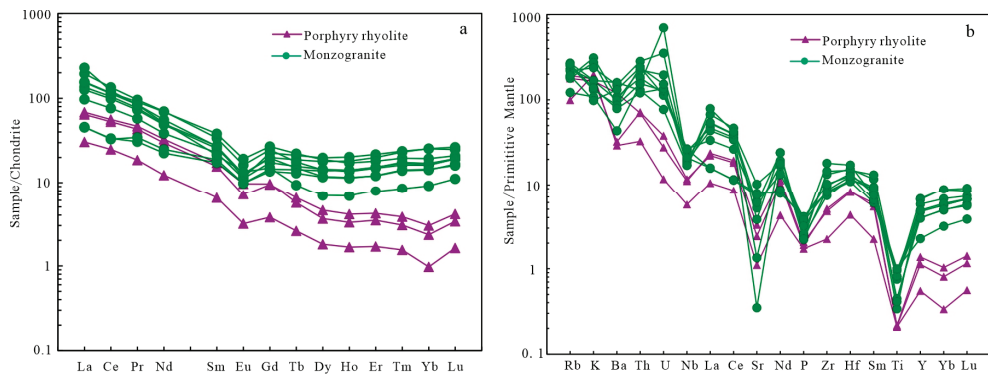
### 5.5. Rare Earth and Trace Elements

The rhyolite samples from the Wunugetu deposit showed total REE ( $\Sigma REE$ ) contents ranging from 33.08 ppm to 78.07 ppm, LREE/HREE ratios between 13.70 and 15.96, and  $(La/Yb)_N$  ratios from 21.48 to 31.23, indicating a general enrichment in light rare earth elements (LREEs) and a relative depletion in heavy rare earth elements (HREEs). Their chondrite-normalized REE patterns were rightward curves, with negative Eu anomalies ( $Eu/Eu^* = 0.58$ – $0.75$ ; Figure 8a; Table 3).

The monzogranite samples from the Wunugetu deposit yielded  $\Sigma REE$  contents from 61.57 ppm to 192.91 ppm, LREE/HREE ratios from 3.39 to 18.51, and  $(La/Yb)_N$  ratios from 2.67 to 25.01, showing an enrichment in LREEs. Their chondrite-normalized REE patterns were also rightward curves, indicative of negative Eu anomalies ( $Eu/Eu^* = 0.46$ – $0.75$ ; Figure 8a; Table 3).

As revealed by the primitive mantle-normalized profiles, both rhyolitic porphyry and monzogranite samples exhibited similar patterns, both showing significant enrichment in LILEs such as Rb, K, Ba, and elements like Th, U, La, but depletion in HFSEs like Nb, P, and Ti (Figure 8b; Table 3). Both rock types had relatively low Sm/Nd ratios (rhyolitic porphyry: 0.17; monzogranite: 0.14 to 0.19, averaging 0.19), Rb/Sr ratios (rhyolitic porphyry: 1.64 to 2.70, averaging 2.24; monzogranite: 0.90 to 10.53, averaging 2.59), and Rb/Ba ratios (rhyolitic porphyry: 0.13 to 0.54, averaging 0.33; monzogranite: 0.13 to

0.30, averaging 0.20), along with higher K/Rb ratios (rhyolitic porphyry: 363.32 to 778.55, averaging 503.03; monzogranite: 200.48 to 658.60, averaging 353.81).



**Figure 8.** Chondrite-normalized REE patterns (a) [35] and spidergram of primitive mantle-normalized REEs (b) [36] of monzogranite and rhyolitic porphyries in the Wunugetu deposit.

## 6. Discussion

### 6.1. Diagenetic and Metallogenic Epochs

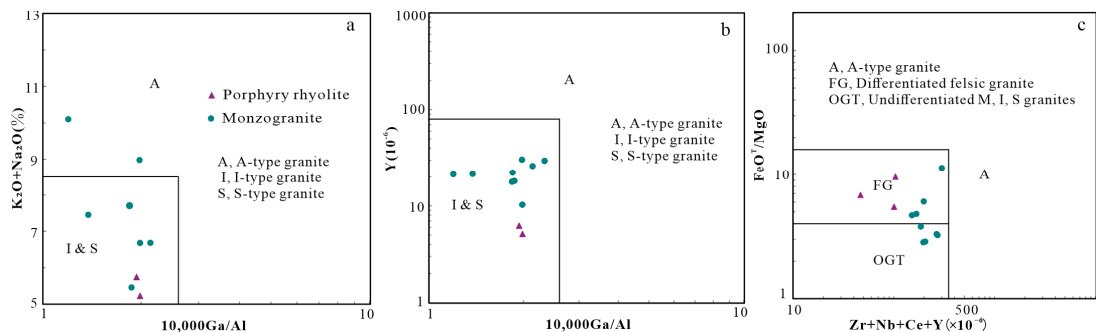
Mao Jingwen et al. (2005) proposed that metallization in eastern China predominantly occurred during the periods of 180–188 Ma, 135–144 Ma, 115–127 Ma, and 94–105 Ma [37]. Drawing from extensive isotopic dating data, Xu Wenliang et al. (2013) identified six distinct phases of mineralization-related volcanic activity in Northeast China: 220–280 Ma, 173–190 Ma, 158–166 Ma, 138–145 Ma, 106–133 Ma, and 88–97 Ma [38]. In the eastern Xing’an-Mongolia orogenic belt, principal metallization events are dated to 165–195 Ma and 110–115 Ma [39]. The Erguna block, a critical segment of the eastern CAOB, underwent notably intense Mesozoic magmatic episodes, categorized into seven stages: ~246 Ma (Late Permian to early Middle Triassic), ~225 Ma (late Middle Triassic to early Late Triassic), ~205 Ma (late Late Triassic to early Early Jurassic), ~185 Ma (Early Jurassic), ~155 Ma (Late Jurassic), ~137 Ma (early Early Cretaceous), and ~125 Ma (late Early Cretaceous) [40]. This block has revealed considerable porphyry copper mineralization, with several copper–molybdenum deposits like Badaguan, Taipingchuan, Wunugetu, and Naomingte in Mongolia being uncovered. Specifically, the Badaguan deposit’s quartz porphyries and granodiorite porphyries exhibit weighted average zircon U–Pb ages of  $217.6 \pm 2.6$  Ma and  $206.5 \pm 1.6$  Ma, respectively, while its molybdenite shows Re–Os ages of  $222.4 \pm 3.3$  Ma [41,42]. The Taipingchuan deposit’s ore-forming granodiorite porphyries have average zircon U–Pb ages of  $202.0 \pm 5.7$  Ma, with molybdenite revealing an average Re–Os age of 203 Ma [43]. In Mongolia’s Naomingte deposit, the ore-hosting granodiorites demonstrate a diagenetic age of 166 Ma. These findings suggest that the porphyry copper mineralization in the Erguna block primarily occurred from the Late Triassic to the Middle Jurassic, consistent with the Mesozoic magmatic activity timelines proposed by the aforementioned researchers.

The ore bodies in the Wunugetu deposit are primarily found within granite porphyries, monzogranites, quartz monzogranite porphyries, and biotite monzogranites, indicating a strong linkage with these rock types. Prior studies, leveraging isotopic geochronology, have suggested that the ore bodies and their encompassing rock masses share similar formation periods, highlighting Early Jurassic diagenesis and mineralization processes [13,15,44]. Contrarily, this study reveals that an ore-hosting monzogranite sample, WNG15, produced LA-ICP-MS zircon U–Pb ages of  $209.0 \pm 1.0$  Ma, pointing to a late Late Triassic formation. Additionally, rhyolitic porphyries located in the northern part of the deposit, which intrude into the ore bodies without causing mineralization or alteration, implying that they are dykes intruding in the late mineralization stage. These rhyolitic porphyries

have shown LA-ICP-MS zircon U-Pb ages of  $170.49 \pm 0.81$  Ma, indicating their formation during the early Middle Jurassic. The diverse ore features within the Wunugetu deposit imply a multi-stage mineralization process. Molybdenum mineralization predominantly occurs in joints and fissures, with the Re content in molybdenite being influenced by various factors such as lithology, paragenetic minerals, and temperature conditions [44,45]. Consequently, the molybdenite age may not precisely reflect the copper mineralization epoch. Considering the petrogenetic ages of monzogranite and rhyolitic porphyry in the deposit, along with chronological testing data on these rock masses obtained by previous researchers, the authors propose that the magmatic activity at Wunugetu Mountain spanned from 209.0 Ma to 170.5 Ma. When combined with the petrogenetic age range from 180 to 188 Ma for the ore-hosting monzogranitic porphyry in the deposit [15,17] and isochron ages of 177.4 to 179.8 Ma for the deposit's molybdenite [17,44], it can be inferred that the ore-bearing rock-bodies in the Wunugetu region were formed from the Late Triassic to the Early Jurassic, with the mineralization process predominantly occurring during the Early Jurassic.

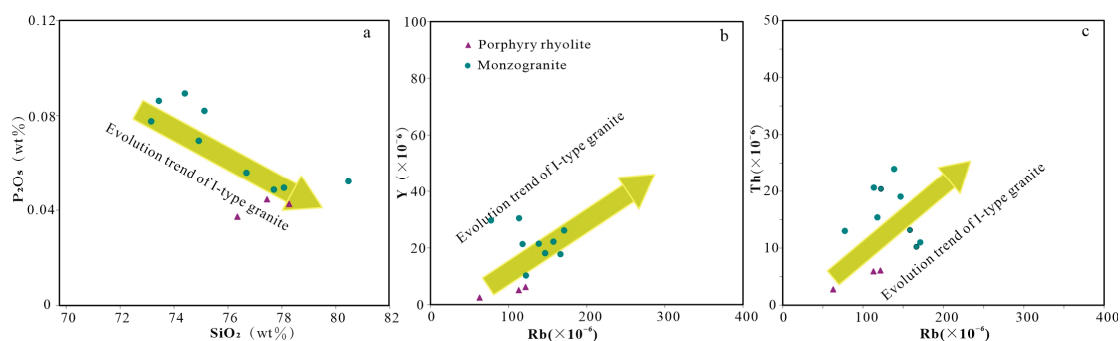
6.2. Origins of Rocks and Source Characteristics

The genetic types of magmatic rocks are pivotal for interpreting the tectonic setting related to their origin and the characteristics of their magma sources. By examining mineral compositions and elemental geochemical traits, alongside considerations such as geotectonic context, variances in magma sources, and magma evolution, it is well-recognized that granitic rocks can be categorized into M, I, S, and A types [31,46,47]. In the case of the Wunugetu deposit under study, a microscopic analysis of monzogranite samples reveals the absence of key aluminous indicator minerals like cordierite, garnet, and muscovite, ruling out their classification as S-type granites [48]. The granitic rocks within the deposit and its vicinity are characterized by high silicon levels, potassium enrichment, and relatively high Th content. M-type granites, known to result from the remelting of the oceanic crust under island arcs, typically have mantle-derived magma sources, thus featuring low  $K_2O$  and Th contents [49,50], a stark contrast to the Late Triassic to Middle Jurassic rocks found in the Wunugetu deposit. Additionally, no contemporaneous M-type granites have been identified in the study area, indicating that the Mesozoic volcanic and magmatic rocks of the Wunugetu deposit are not M-type magmatic rocks. On the discrimination diagrams for magma origin (Figure 9a–c), the samples predominantly cluster around the I- and S-type granite zones, with only a couple aligning with the A-type granite category. Nonetheless, highly differentiated I- and S-type granitic samples with  $SiO_2$  content exceeding 72% share similar geochemical characteristics to A-type magmatic rocks [47,51].



**Figure 9.** Identification of genetic types of monzogranites and rhyolitic porphyries in the Wunugetu deposit [47]. (a)  $K_2O + Na_2O$ -Ga/Al diagram; (b) Y-Ga/Al diagram; (c)  $FeO^T/MgO$ -Zr + Nb + Ce + Y diagram.

The monzogranites within the Wunugetu deposit are characterized by high silicon content (73.16–80.47 wt.%), relatively low aluminum content (10.98–14.37 wt.%), enrichment in alkalis (3.42–10.10 wt.%), and depletion in magnesium and sodium, with A/CNK ratios ( $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ ) ranging from 1.1 to 2.9. On the A/NK–A/CNK diagram, the major element composition classifies these monzogranites as peraluminous to quasi-aluminous rocks. Additionally, these rocks, with low  $\text{FeO}^T$ , MgO, and CaO contents, are enriched in Rb and Th and depleted in Ba, P, and Ti (Figure 8b), indicative of significant crystallization and differentiation from primitive magmas [52,53]. The monzogranites also display low Zr + Nb + Ce + Y content (151.3 ppm–298.6 ppm, average: 198.6 ppm) and  $10,000 \times \text{Ga}/\text{Al}$  ratios (1.20–2.33, average: 2.07), sharply contrasting with the typical characteristics of A-type granitic magmatic rocks (Zr + Nb + Ce + Y content: >400 ppm;  $10,000 \times \text{Ga}/\text{Al}$  ratios: >2.6). As illustrated in the Zr + Nb + Ce + Y– $\text{FeO}^T/\text{MgO}$  diagram (Figure 9c), most samples fell into the highly differentiated magma zone, indirectly confirming that the Wunugetu deposit's granitic rocks are highly differentiated magmatic rocks. Despite A/CNK ratios from 1.1 to 2.9 suggesting peraluminous to quasi-aluminous nature in the A/NK–A/CNK diagram, previous studies have substantiated that I-type magmatic rocks can exhibit peraluminous and even strongly peraluminous features [54,55]. As revealed by experiments, apatite exhibits low solubility and is prone to saturate undergoing fractional crystallization during magma evolution in I-type felsic magmas, with the  $\text{P}_2\text{O}_5$  content diminishing with an increase in the  $\text{SiO}_2$  content in rocks. Conversely, S-type granites have high apatite solubility, with  $\text{P}_2\text{O}_5$  content increasing with the  $\text{SiO}_2$  content [56]. Thus, the correlation between  $\text{SiO}_2$  and  $\text{P}_2\text{O}_5$  contents serves as a critical indicator for determining the type of granitic magma. As shown in the  $\text{SiO}_2$ – $\text{P}_2\text{O}_5$  diagram (Figure 10a), the magmatic rock samples from the Wunugetu deposit exhibited low  $\text{P}_2\text{O}_5$  content (0.04%–0.09%) and a negative  $\text{P}_2\text{O}_5$ – $\text{SiO}_2$  correlation, classifying them as I-type granites. For S-type felsic magmas, Th and Y contents inversely correlate with Rb content, but in I-type magmas, they increase with Rb content [57]. Therefore, the evolutionary trends of Th and Y in magmas can be used to distinguish between S- and I-type granites. The positive correlation of the Th and Y contents with Rb content in the Rb–Y (Figure 10b) and Rb–Th (Figure 10c) diagrams indicates that the deposit's magmatic rocks are characteristic of I-type granites. The aforementioned microscopic observations reveal the absence of aluminum-rich silicate minerals like muscovite, cordierite, and garnet in monzogranites. All these lead to the conclusion that the Late Triassic magmatic rocks of the Wunugetu deposit are highly differentiated I-type rocks.



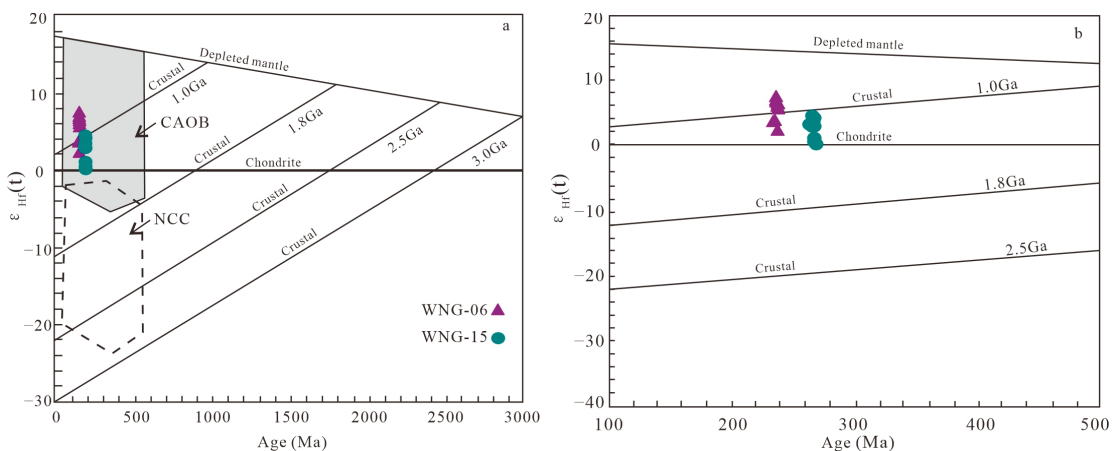
**Figure 10.** Diagrams of (a)  $\text{SiO}_2$ – $\text{P}_2\text{O}_5$ , (b) of Rb–Y, (c) and Rb–Th of monzogranites and rhyolitic porphyries in the Wunugetu deposit [57].

The Middle Jurassic rhyolitic porphyry samples from the deposit all fell into the I- and S-type granite zones in the  $10,000 \times \text{Ga}/\text{Al}$  vs.  $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ,  $10,000 \times \text{Ga}/\text{Al}$  vs. Y, and Zr + Nb + Ce + Y vs.  $\text{FeO}^T/\text{MgO}$  diagrams. The Rb–Y (Figure 10b) and Rb–Th (Figure 10c)

diagrams, where Th and Y contents show a positive correlation with the Rb content, suggest that the rhyolite porphyries also have the geochemical characteristics of I-type granites.

These Middle Jurassic rhyolitic porphyries are characterized by high silica (75.77–77.45 wt.%), elevated potassium (5.005.91 wt.%), and an A/CNK ratio of 1.85 to 2.14, all above the 1.1 threshold. Their chondrite-normalized REE patterns exhibit pronounced HREE depletion, hinting at the potential residual effects of garnet. Positioned within the I- and S-type granite zones in geochemical diagrams like  $(10,000 \times \text{Ga}/\text{Al})$  vs.  $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ ,  $(10,000 \times \text{Ga}/\text{Al})$  vs. Y, and  $(\text{Zr} + \text{Nb} + \text{Ce} + \text{Y})$  vs.  $(\text{FeO}^T/\text{MgO})$  (Figure 10b,c), the samples also displayed an increase in  $\text{P}_2\text{O}_5$  with  $\text{SiO}_2$  in the  $\text{SiO}_2$  vs.  $\text{P}_2\text{O}_5$  diagram (Figure 10a), indicating that the rhyolite porphyries in the study area exhibit geochemical traits of S-type granites.

In-situ Lu-Hf isotopic analysis of zircon from these samples revealed  $\epsilon\text{Hf}(t)$  values between +2.4 and +7.6. Moreover, all these samples fell within the zone of the  $\epsilon\text{Hf}(t)$  range for CAOBS felsic rocks as shown in the  $t$  vs.  $\epsilon\text{Hf}(t)$  diagram (Figure 11a). Their  $T_{\text{DM2}}$  ages ranged from 727 to 1058 Ma, suggesting the rhyolitic porphyries' primitive magmas originated from the partial melting of the Meso- to Neoproterozoic accreted lower crust.



**Figure 11.** Hf isotopic characteristics (a), after Yang et al., 2006 [58] and  $\epsilon\text{Hf}(t)$  vs. U-Pb ages for zircons (b) of monzonites and rhyolitic porphyries from the Wunugetu deposit.

The Late Triassic monzogranite samples from the Wunugetu deposit yielded zircon  $\epsilon\text{Hf}(t)$  values ranging from +0.3 to +4.6. On the  $t$ - $\epsilon\text{Hf}(t)$  diagram (Figure 11a), these samples clustered around the chondrite zone, displaying  $\epsilon\text{Hf}(t)$  values aligned with those of CAOBS felsic rocks. This suggests that the study area is a part of the CAOBS. The  $T_{\text{DM2}}$  ages of these samples spanned 949 to 1227 Ma, indicating that the original magma of the rhyolite porphyries in the Wunugetu deposit is derived from partial melting of the Meso- to Neoproterozoic accreted lower crust.

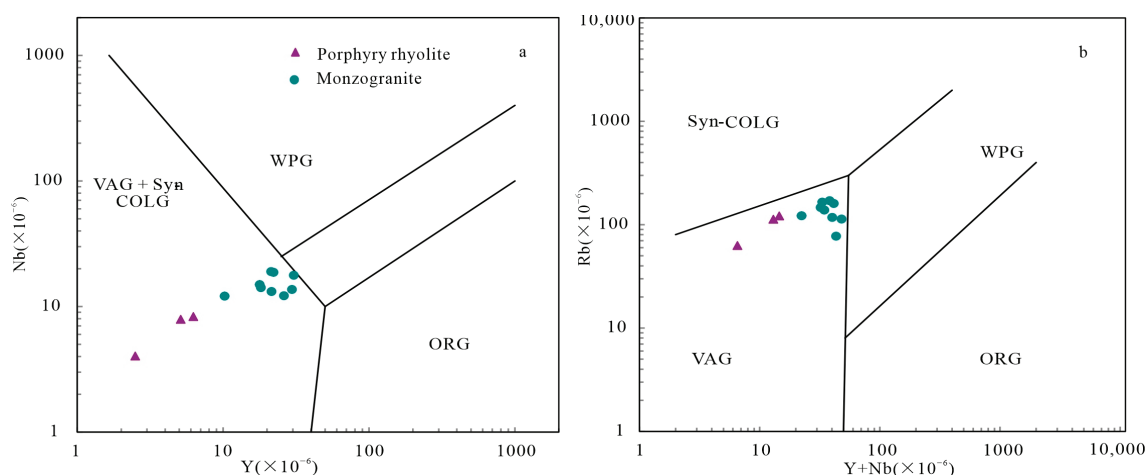
In summary, both the Late Triassic I-type granites and the Early Jurassic rhyolitic porphyries from the Wunugetu deposit demonstrate positive zircon  $\epsilon\text{Hf}(t)$  values. These values show an increasing trend with a decrease in the emplacement age, suggesting that the magmatic source for the study area's monzogranites is derived from the partial melting of the Mesoproterozoic accreted lower crust.

### 6.3. Diagenetic and Metallogenic Tectonic Settings

The Wunugetu deposit, nestled within the eastern CAOBS and the central MOSZ, is distinguished as the largest porphyry deposit in the Kherlen (Mongolia)-Erguna (China) block. Delving into the tectonic setting of rocks within this deposit is crucial for deepening our understanding of the MOSZ's tectonic evolution and contributes to the exploration

of the regional geological settings of porphyry copper mineralization and the tectonic evolution of the eastern CAOB. Previous studies on the evolution of the Mongol-Okhotsk Ocean generally indicate that this ocean evolved from the Eopaleozoic to the Mesozoic [59], undergoing bidirectional subduction toward the north and the south [22,60].

All samples of the Late Triassic magmatic rocks from the Wunugetu deposit fell within the volcanic arc-syn-collisional granite zone on the Y vs. Nb tectonic discrimination diagram (Figure 12a), with a majority situated within the volcanic arc granite zone on the Y + Nb – Rb diagram (Figure 12b). These Late Triassic magmatic rocks display the characteristics of I-type granites. It is believed that the highly differentiated I-type granites were formed in a subduction environment [61] or during the post-orogenic phase [62]. Considering their geochemical similarities with coeval magmatic rocks exposed in the northern Erguna block [40], this study posits that the study area was in an active continental margin environment subjected to subduction during the Late Triassic. This is associated with the southward subduction of the Mongol-Okhotsk Ocean sandwiched between the Neopaleozoic Siberian and Sino-Korean-Mongolian plates.

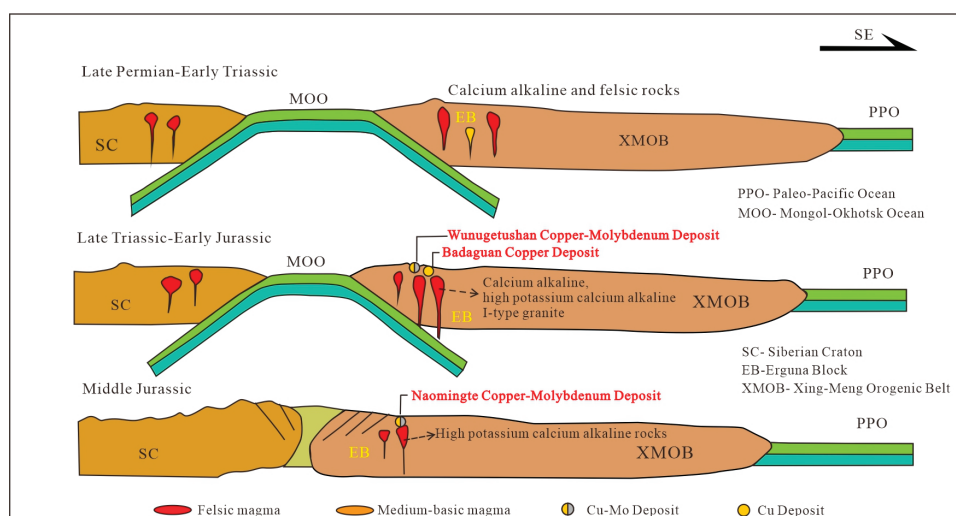


**Figure 12.** Diagrams of monzonites and rhyolitic porphyries from the Wunugetu deposit. (a) Y vs. Nb; (b) Y + Nb vs. Rb [63].

As illustrated by the Y-Nb tectonic discrimination diagram (Figure 12a), all samples of the Middle Jurassic rhyolitic porphyries from the Wunugetu deposit fall within the volcanic arc-syn-collisional granite zone. As shown in the Y + Nb vs. Rb (Figure 12b) and tectonic discrimination diagrams, these samples occupied the volcanic arc granite zone. Recent studies have unveiled a suite of Middle Jurassic (168 Ma) muscovite granites in the Sunwu area, adjacent to the study area. These granites originated from the partial melting of the thickened continental crust, resulting from the continent-continent collision during the closure of the Mongol-Okhotsk Ocean [64]. Additionally, the geochemical traits of the S-type granitic rhyolitic porphyry within the deposit suggest their formation in a continent-continent collisional context.

In summary, the geochemical characteristics of the monzogranites and rhyolitic porphyries in the Wunugetu deposit suggest that the Mongol-Okhotsk Ocean was still subjected to subduction during the Late Triassic. By the Middle Jurassic, following the ocean's closure, the ocean transitioned to a syn-collisional tectonic setting (Figure 13).





**Figure 13.** Diagram showing the evolutionary model of mineralization in the Mongolian-Okhotsk Ocean [65].

## 7. Conclusions

- (1) The formation age of the monzogranites in the Wunugetu deposit is established at  $209.02 \pm 1.0$  Ma, while the rhyolitic porphyries are dated at  $170.49 \pm 0.81$  Ma. This indicates that the deposit's magmatic activity primarily spanned from the Late Triassic to the Middle Jurassic, with the major ore-bearing intrusions dating from the Late Triassic to the Early Jurassic.
- (2) The Triassic monzogranites from the Wunugetu deposit exhibit the geochemical characteristics of I-type granites, including high silica and alkali content, enrichment in Rb and Th, and depletion in Ba, P, and Ti. The rhyolitic porphyries are characterized by high silica and potassium content, with trace elements exhibiting enrichment in LREEs and depletion in HREEs, aligning with the geochemical traits of S-type granites. Both the monzogranites and rhyolitic porphyries within the deposit exhibit positive zircon  $\epsilon_{\text{Hf}}(t)$  values, indicating their source regions underwent the partial melting of juvenile crustal materials.
- (3) The Wunugetu porphyry copper–molybdenum deposit was formed within an active continental margin context, influenced by the southeastward subduction of the Mongol-Okhotsk Ocean from the Late Triassic to the Early Jurassic. Following the Mongol-Okhotsk Ocean's closure during the Middle Jurassic, the Wunugetu region transitioned to a syn-collisional tectonic setting.

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

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**Data Availability Statement:** The data presented in this study are available in Tables 1–3.

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**Conflicts of Interest:** Qiulin Fu is an employee of Liaoning Province Institute of Geology and Mineral Resources Co., Ltd. and Xiaodan Guo is an employee of Liaoning Province Geology and Mineral Group Energy Geology Co., Ltd. We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

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## Article

# Genesis and Prospecting Potential of the Da'anhe Skarn Au Deposit in the Central of the Lesser Xing'an Range, NE China: Evidence from Skarn Mineralogy, Fluid Inclusions and H-O Isotopes

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**Abstract:** Skarn Au deposits exist in the circum-pacific metallogenic belt. Interestingly, the Da'anhe Au deposit is the only independent skarn gold deposit in the Lesser Xing'an Range. To determine the metallogenic mechanism and prospecting potential of the Da'anhe deposit, we performed skarn mineralogy, fluid inclusion (FI) and H-O isotope analyses. The results show the following: (1) The Da'anhe deposit is a calcareous reduced skarn Au deposit that formed between an Early Jurassic gabbroic diorite and the Permian Tumenling Formation marble. Its metallogenic process includes five stages: the early skarn stage (Stage I<sub>1</sub>), late skarn stage (Stage I<sub>2</sub>), early quartz-sulfide stage (Stage II<sub>1</sub>), late quartz-sulfide stage (Stage II<sub>2</sub>) and quartz-carbonate stage (Stage II<sub>3</sub>). Gold precipitated in Stage II<sub>1</sub> and Stage II<sub>2</sub>. (2) The initial ore-forming fluid was derived from magmatic water and featured a high temperature and intermediate to high salinity. After boiling and mixing, the fluid eventually changed to a low-temperature and low-salinity reducing fluid dominated by meteoric water. (3) The formation depth of the Au orebodies was 2.27–3.11 km, and the orebodies were later lifted to the surface (<500 m). The potential for finding skarn Au deposits in the study area is limited. (4) The distinctive nature of the ore-related magma (i.e., source, reducing conditions and high water content) was key to the formation of the Da'anhe skarn gold deposit.

**Keywords:** mineralization; skarn mineralogy; H-O isotopes; fluid inclusion; Da'anhe Au deposit; lesser Xing'an range



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## 1. Introduction

Skarn deposits are important sources of iron, copper, lead, zinc, molybdenum, gold, tungsten and other metal minerals worldwide. In the circum-pacific metallogenic belt, gold production from skarn deposits has exceeded 1000 tons [1,2]. Skarn gold deposits in China are distributed in various tectonic provinces and are hosted in rocks ranging in age from the Palaeoproterozoic to the Cretaceous. At least seventy deposits have been identified as gold or gold-bearing skarn deposits in China [3]. Northeastern China, located in the western circum-pacific metallogenic belt, was affected by the subduction of the



Paleo-Pacific plate and extension after the collision and orogeny between the Laurasian and Gondwanan continents. The Lesser Xing'an Range in northeastern China experienced extensive magmatism and mineralization during the Palaeozoic and Mesozoic, particularly the latter which was an important epoch for numerous skarn polymetallic deposits [4–6]. Strong tectonic-magmatic activity provided favourable conditions for the formation of skarn Au deposits in this region [7,8].

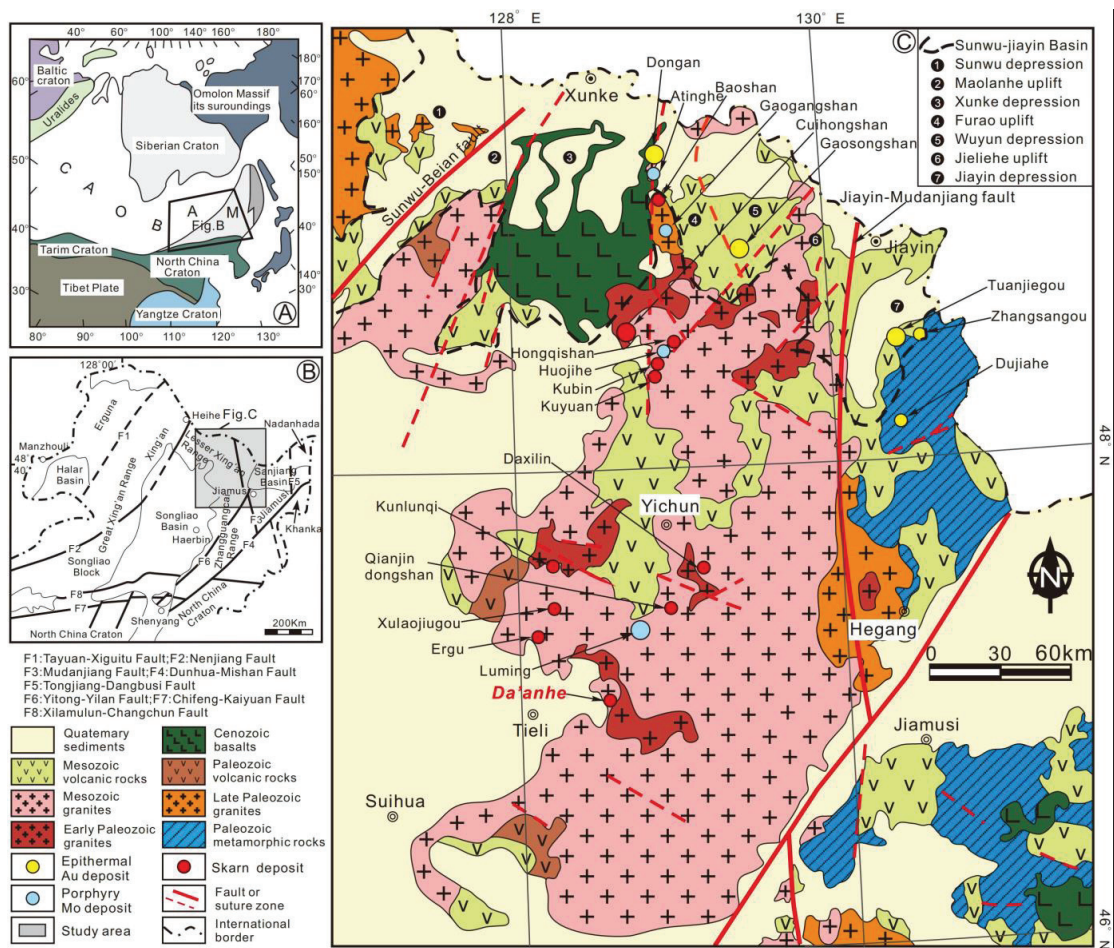
However, most of these deposits are calcareous skarn deposits that are composed mainly of iron, copper lead and zinc and are genetically related to the metasomatism of intermediate-acidic plutonic rocks and marble. Examples of such deposits include the Ergu Fe-Zn polymetallic deposit [9–12], Cuihongshan Fe-Cu-W-Mo polymetallic deposit [13–15], and Xulaojiugou Pb-Zn polymetallic deposit [16,17]. The medium-sized Da'anhe gold deposit is the only skarn Au deposit. At present, several geologists have performed detailed studies on the metallogenic mechanisms and processes of the skarn Fe-Cu-Pb-Zn deposits in this region [13,17,18], but research on the Da'anhe Au deposit has focused mainly on geological investigations and the chronologic and geochemical characteristics of plutonic rocks [19–21]. Identifying the genetic and mineralization processes of the Da'anhe deposit, and comparing them with those of the skarn Fe-Cu-Pb-Zn deposit in this region would be beneficial and is necessary for researching the metallogenic specificity of skarn deposits. Therefore, we recently carried out detailed field geological investigations, skarn mineralogy analysis, fluid inclusion (FI) analysis, coupled with H-O isotope research on the deposits, aiming to further determine the metallogenic mechanism and metallogenic process and provide a reference for prospecting for skarn Au deposits in the study area.

## 2. Regional Geological Characteristics

The Da'anhe deposit is located in the eastern section of the Xingmeng orogenic belt and is sandwiched between the Siberian, North China and Paleo-Pacific plates. This super-imposed tectonic regime has experienced the evolution of the Palaeo-Asian Ocean tectonic system and the Xingmeng orogeny in the Palaeozoic and the subduction of the Paleo-Pacific plate and Okhotsk Ocean plate in the Mesozoic [22–25] (Figure 1A,B) [26,27]. The multi-stage tectonic-magmatic activities resulted in the Lesser Xing'an Range being a typical basin-mountain region with endogenetic metal development related to tectonic-magmatic activity [28–30]. The stratigraphy in this region is dominated by the silicoferrite of the Dongfengshan Formation (821–801 Ma [31]) and overlying Cambrian–Ordovician neritic facies sedimentary rocks (limestone, dolomite marble, carbonaceous slate, etc.; ~500 Ma [32]), Permian terrigenous clastic-carbonate rocks (amphibolite, marble, tuff, felsic schist, slate, etc.; 262–286 Ma [10]), Mesozoic continental volcanic rocks, and Palaeogene fluvial and lacustrine clastic sedimentary rocks. The study area experienced at least five stages of magmatism: middle Cambrian–Late Ordovician (508–450 Ma [30]), middle-late Permian (272–260 Ma [29]), Early–Middle Triassic (252–234 Ma [29]), Late Triassic–Early Jurassic (225–197 Ma [28,29,33]) and Late Jurassic (191–175 Ma [34,35]). Voluminous Phanerozoic granitoids, including abundant I-type granites and a few A- and S-type granites are present in this region [36]. In addition to these granitoids, rare mafic-ultramafic intrusions are also present in the region. Among them, Late Triassic and Early Jurassic granites are the most developed and widely distributed. The large-scale mineralization of porphyry molybdenum and skarn deposits mainly occurred at 186–176 Ma [24], and epithermal gold mineralization mainly occurred at 110–95 Ma [24]. Many porphyry molybdenum deposits in different scales (Luming, Huojihe, Cuiling, and Gaogangshan) formed in the Mesozoic granitic complex (Figure 1C) [28]. Many skarn deposits (such as the Cuihongshan, Ergu and Xulaojiugou deposits) formed in the contact belts between Mesozoic granite and Palaeozoic carbonate strata (Figure 1C) [28]. Most epithermal deposits are located in the Mesozoic to Cenozoic basins that are composed of continental volcanic and sedimentary rocks, such as the Dong'an, Gaosongshan, Yongxin, Tuanjiogou, and Yidonglinchang deposits. In this study, the Da'anhe gold deposit is essentially consistent with the mineralization of the widely developed skarn polymetallic deposits and porphyry molybdenum deposits,



which formed during the late Triassic to Early-Middle Jurassic (203.4~179.9 Ma) [10,16,28] (Figure 1C) [28].



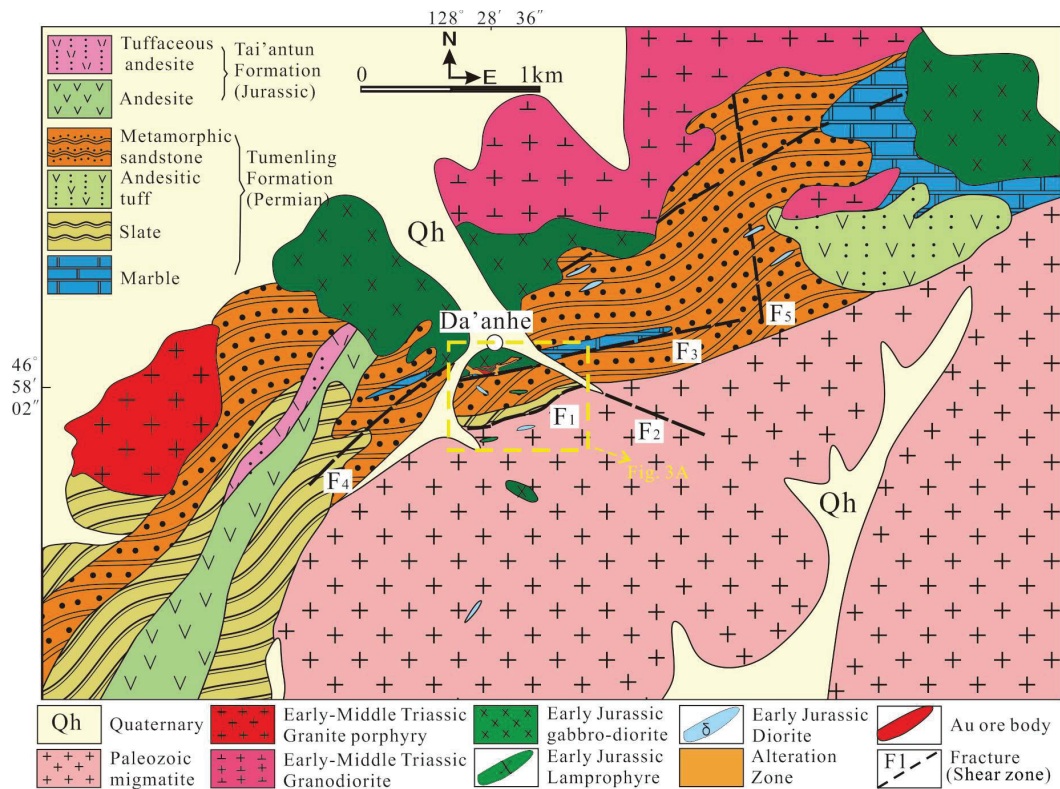
**Figure 1.** (A) Location of Northeast China with respect to the main tectonic units of China and Russia, modified after Wu et al. [26]. ‘A’ and ‘M’ represent the Altaids and Manchurids, respectively. (B) Tectonic sketch maps of Northeast China, modified after Wu et al. [27]. (C) Simplified geological map of the Lesser Xing’an range, modified after Wu et al. [28].

**3. Deposit Geology**

**3.1. Stratigraphy, Magmatism and Structure**

The Da’anhe deposit is located approximately 30 km northeast of the Tieli city, Heilongjiang Province, and is tectonically part of the southern Yichun-Yanshou magmatically and tectonically active zone [19–21]. The strata in the mining area include the Permian Tumenling Formation and the Jurassic Tai’antun Formation (Figure 2) [21]. The Tumenling Formation is distributed in the Sanjiaoshan area of the mining area in a discontinuous belt trending in the NE direction. The rock types include slate, metamorphic quartz sandstone, marble and andesitic crystal tuff. Marble is distributed in metamorphic quartz sandstone strata with lenticular or irregular shapes and surrounds Au ore bodies. The Tai’antun Formation is less exposed in the mining area and is distributed in the northeastern part of

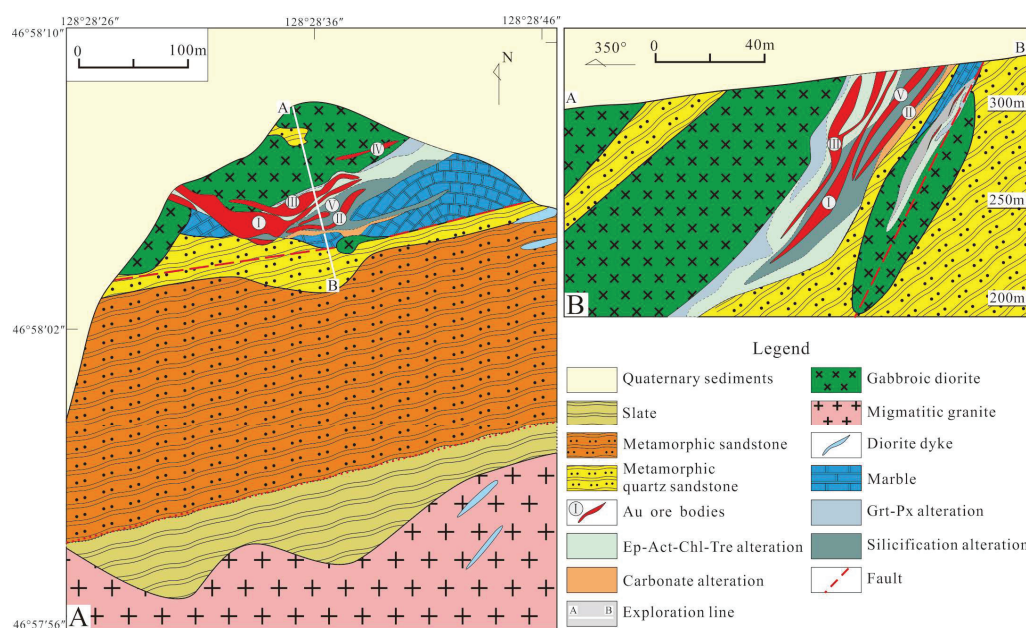
the mining area in the form of residual bodies. The rock types are mainly andesitic tuff and andesite, which unconformably overlie the Tumenling Formation.



**Figure 2.** Geological map of the Da'anhe Au deposit (Figure 2 modified according to Yang [21]. Figure 3A detailed in Figure 3).

The magmatic rocks in the mining area are mainly Palaeozoic migmatite granite and Mesozoic granodiorite, granodiorite porphyry and gabbroic diorite (Figure 2) [21]. Palaeozoic migmatite is exposed in the southern mining area in the form of a large-scale batholith. The granodiorite and granodiorite porphyry formed in the Early-Middle Triassic and were emplaced in the form of stocks in the Tumenling Formation along the NE-trending Jinniugou-Da'anhedongshan fault in the northern part of the mining area. The gabbroic diorite on both sides of the ore body has undergone significant alteration (see Section 3.2.1) and formed endoskarn, which occurs in the inner belt of the skarn, indicating a close relationship with mineralization. In addition, late lamprophyre and fine-grained diorite dikes are present in the mining area.

The structures in the mining area are mainly faults and folds. The faults in the mining area mainly include the NE-trending Jinniugou-Da'anhedongshan fault, the NW-trending Da'anhe fault and the nearly NW-trending Da'anhenanshan fault. These faults are mainly manifested as breccia zones, shear zones and schistosity zones in the mining area. The Jinniugou-Da'anhedongshan fault and Da'anhe fault intersect and become the main ore controlling structures in the mining area. The large fold in the region is the Shenshu complex anticline, and the mining area and the deposit are located on the southeastern limb of the NE-striking Sanjiaoshan syncline within the Shenshu anticlinorium (Figure 2) [21].



**Figure 3.** (A) Geological map of the Da'anhe Au deposit; (B) Profile of exploration line 4 of the Da'anhe Au deposit. ((A,B) modified according to Xue [20] and Yang [21]). Note: F1 and F3: Da'anhenanshan fault; F2: Da'anhe fault; F4: Jinniugou-Da'anhedongshan fault. Grt-garnet; Px-diopside; Ep-epidote; Act-actinolite; Tr-tremolite; Chl-chlorite.

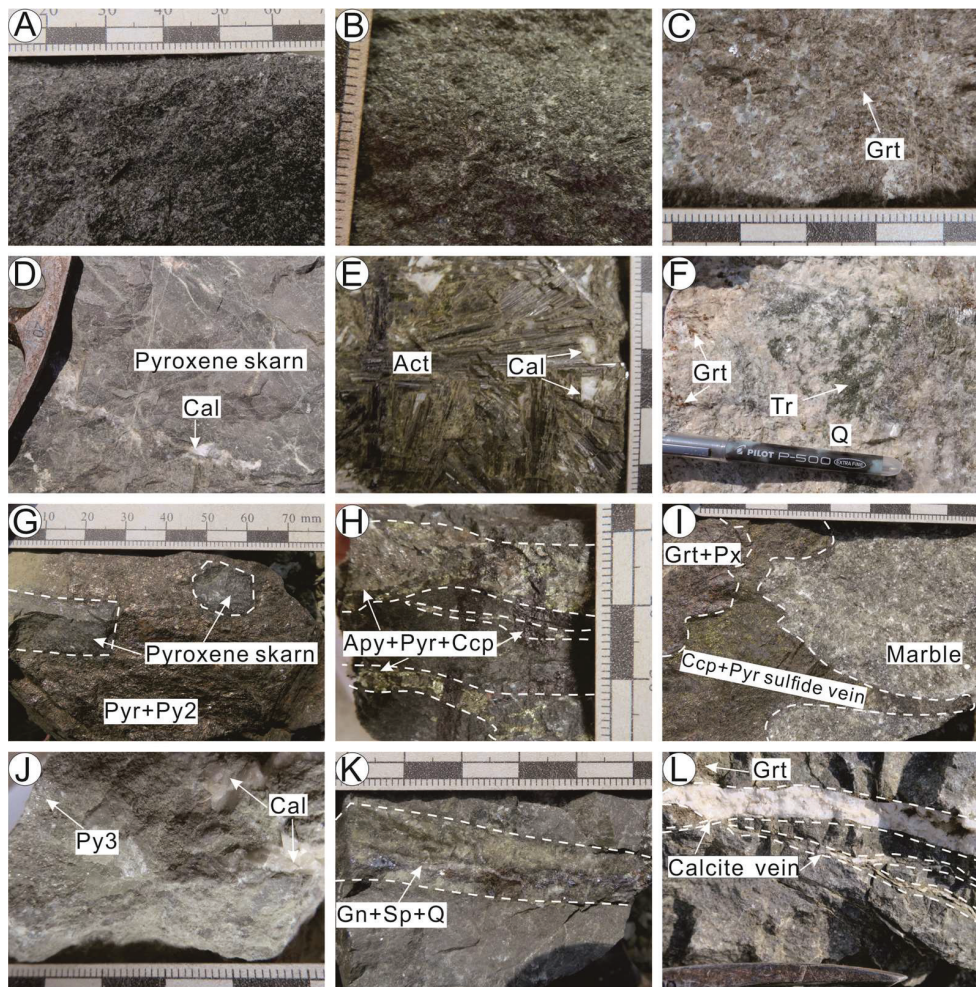
### 3.2. Mineralization

The gold orebodies in the Da'anhe deposit mainly developed in the skarn belt between the gabbroic diorite (Figures 3, 4A and 5A) and the marble of the Tumenling Formation in the central and western mining areas, and small amounts of altered gabbroic diorite and marble developed on both sides of the skarn belt. The orebodies are controlled by shear zones and occur in NE- or NW-striking lenses or veins dipping steeply between 42 and 87 degrees. The ore bodies are generally approximately 25 m long, and some ore bodies can reach lengths of up to 168 m. At present, 12 industrial orebodies have been identified in the Da'anhe deposit, and the main orebodies are the No. I, II and III orebodies. The three main orebodies occur as veins in the inner and outer belts of the skarn zone, and the average grades of gold are 11.93 g/t, 46.78 g/t and 5.93 g/t, respectively.

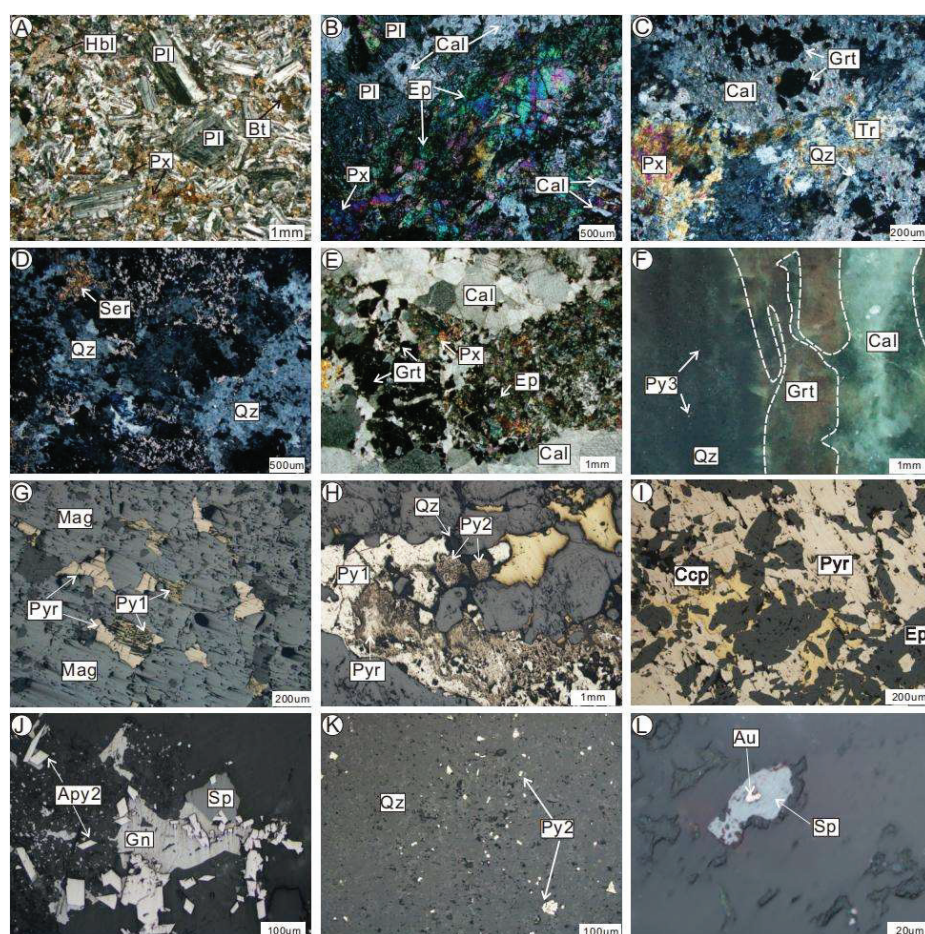
#### 3.2.1. Alteration of the Surrounding Rock

The wallrock alteration in the mining area is relatively well developed. The main alteration types are Grt-Px alteration (Figures 3 and 4B–D), Ep-Act-Chl-Tr alteration (Figures 3 and 4E,F), sericitization (Figure 4D), silicification and carbonatization (Figures 3 and 4L). Among them, Grt-Px alteration and silicification are most closely related to gold mineralization. Grt-Px alteration occurs mainly between the gabbroic diorite and the marble of the Tumenling Formation. Silicification occurs mainly in the outer belt of the skarn, and silicified veins of different colours and sizes cut through the early skarn minerals and sulfide veins. Carbonatization occurs in the late stage of mineralization and occurs in the tectonically active part in the form of veins. In addition, potassic alteration and tremolite alteration occur sporadically in the mining area.





**Figure 4.** Field geological characteristics of the Da'anhe gold deposit. (A). Unaltered gabbroic diorite; (B). Skarnized gabbroic diorite hand specimen photographs; (C). Photographs of garnet skarn hand specimens; (D). Diopside skarn was cut through by late carbonate veins; (E). Photographs of skarn hand specimens from actinolite skarn; (F). The garnet in skarn metasomatized by late tremolite and quartz began to appear; (G). The pyroxene skarn formed in the dry skarn stage was broken into a breccia shape under the influence of tectonism and cemented by late sulfide; (H). Sulfide vein penetrating skarn containing arsenopyrite pyrrhotite chalcopyrite; (I). Sulfide veins containing chalcopyrite pyrrhotite cut through garnet pyroxene skarn and marble; (J). Granular pyrite ore with good crystallinity cut through by late carbonate vein; (K). Quartz vein containing galena sphalerite; (L). The carbonate veins of the late mineralization cut through the early garnet skarn. Note: Grt-garnet; Px-diopside; Act-actinolite; Tr-tremolite; Q-quartz; Cal-calcite; Ccp-chalcopyrite; Apy-arsenopyrite; Pyr-pyrite; Py2-pyrite coexisting with quartz; Py3-pyrite coexisting with calcite; Gn-galena; Sp-sphalerite.



**Figure 5.** Microscopic characteristics of rocks and ores in the Da'anhe deposit (cross-polarized light). (A). Microphotograph of gabbroic diorite; (B). Microscopic characteristics of gabbroic diorite in skarn alteration; (C). Garnet and pyroxene were metasomatized by quartz and tremolite and were cut through by the late carbonate vein; (D). Sericitization alteration; (E). Skarn alteration of marble; (F). Garnet was replaced by pyrite bearing quartz veinlets and calcite veinlets in later stage; (G). Magnetite shows its granular structure after replacement by pyrite and pyrrhotite; (H). The early pyrite and pyrrhotite were replaced by the later pyrite and brass bearing quartz veins; (I). Chalcopyrite, pyrrhotite and epidote coexist; (J). Sphalerite and galena coexist, and metasomatic arsenopyrite; (K). Semiautomorphic pyrite particles in late mineralization; (L). Encapsulated gold developed in sphalerite. Note: Hbl-hornblende; Pl-plagioclase; Px-pyroxene; Bt-biotite; Ep-epidote; Cal-calcite; Grt-garnet; Tr-tremolite; Qz-quartz; Ser-sericite; Pyr-pyrite; Py1-early pyrite; Py2-pyrite coexisting with quartz; Py3-pyrite coexisting with calcite; Mag-magnetite; Ccp-chalcopyrite; Apy2-late arsenopyrite; Au-natural gold; Gn-galena; Sp-sphalerite.

### 3.2.2. Characteristics and Stages of Mineralization

The ore minerals in the ores are widely distributed and mainly include arsenopyrite (Figure 4H), pyrrhotite (Figure 4G–I), chalcopyrite (Figure 4H,I), pyrite (Figure 4G,J), sphalerite (Figure 4K), native gold, electrum, and small amounts of magnetite, galena (Figure 4K), malachite and bismuth telluride. Among them, gold occurs mainly in the form of native gold or electrum in skarn minerals, quartz or sulfide grains. The ore occurs in



banded (Figure 4H), vein (Figure 4I,K) and sparse disseminated (Figure 4J) forms, followed by dense massive and brecciated (Figure 4G) forms. According to the cross-cutting relationships of the veins and the mineral assemblage characteristics under the microscope, the metallogenic process of the Da'anhe deposit can be divided into skarn period and a quartz-sulfide period, with a total of five stages. (1) In the early skarn stage (Stage I<sub>1</sub>), high-temperature anhydrous skarn minerals, such as garnet and diopside minerals, formed (Figure 5B,C). (2) The late skarn stage (Stage I<sub>2</sub>) did not have a major impact on the mining area and mainly formed water-bearing skarn minerals such as actinolite, tremolite and epidote (Figure 5C,E), and a small amount of magnetite (Figure 5G). (3) In the early quartz-sulfide stage (Stage II<sub>1</sub>), skarn minerals were largely metasomatized, and gangue minerals, such as quartz, epidote, chlorite and sericite, were formed (Figure 5C,D). In addition to arsenopyrite, the ore minerals were mainly iron-copper sulfides, including pyrrhotite, pyrite and chalcopyrite (Figure 5G–K), and a small amount of native gold precipitation began in the late part of this stage. (4) The late quartz-sulfide stage (Stage II<sub>2</sub>) was the main metallogenic stage of gold. Gold precipitated as native gold or electrum between skarn minerals and quartz or metal sulfide grains (Figure 5L). In this stage, the gangue minerals are mainly quartz and calcite, and the ore minerals are mainly pyrite, galena and sphalerite (Figure 5J,K). (5) In the quartz carbonate stage (Stage II<sub>3</sub>), only small amounts of pyrite, sphalerite and other sulfides formed, and many quartz-calcite veins formed, cutting through the early skarn minerals or quartz sulfide veins (Figure 5F), signifying the end of mineralization [20,21].

#### 4. Samples and Analytical Methods

##### 4.1. Electron Probe Analysis

Initially, garnet-pyroxene skarn samples collected from the surface of the Da'anhe deposit were cut into pieces for microprobe analysis. On the basis of detailed microscopic identification, garnet and pyroxene were selected and analysed by an electron probe (EPMA-1600, Japan Shimadzu Company, Kyoto, Japan) at the Jilin University Testing and Analysis Center. Standard samples of 53 kinds of minerals were obtained from the SPI Company, Lakewood, WA, USA. The element analysis range was 5B-92U, the electron beam current was stable at  $1.5 \times 10^{-3}$  A, the accelerating voltage was 15 kV, the current was 4.5 nA, the beam spot was less than 1 µm, and the correction method was ZAF. Geokit software (GeokitPro version) was used to calculate the occupation and endmember composition of each element in the mineral [37].

##### 4.2. Temperature Measurements and Laser Raman Analysis of Fluid Inclusions (FIs)

The analysed samples consisted of garnet and pyroxene from the early skarn stage, epidote from the late skarn stage, quartz (Q<sub>1</sub>) from the early quartz-sulfide stage, quartz (Q<sub>2</sub>) from the late quartz-sulfide stage and calcite from the quartz-carbonate stage. Samples for the FI study were collected from the surface of the Da'anhe deposit. For the selected samples, first, FI thin sections (thickness ~0.3 mm) were prepared, and then the type, distribution, gas-liquid ratio and daughter minerals of FIs were carefully identified under a high-magnification microscope. From the above observations, the primary inclusions were selected for the temperature measurement experiment, and the analysis was performed in the FI laboratory at the Institute of Geology and Geophysics of the Chinese Academy of Sciences. The experiment was carried out on a THMSG 600 (Linkam Company, Salfords, UK) heating and cooling stage. The measurable temperature ranged from −196 to 600 °C, and the temperature increase and decrease rate was approximately 3 °C/min. Near the phase transition temperature, the rate was maintained at 0.2–0.4 °C/min. The measurement errors of the homogenization temperature and freezing point temperature were ±2 °C and ±0.1 °C, respectively. The analysis procedure is described in detail in Fan et al. [38]. The salinity of the salt solution was calculated using the freezing point temperature [39].

To systematically determine the fluid composition during the mineralization process, representative single FIs captured during each stage were selected for gas phase composi-



tion analysis under nondestructive conditions. The experimental instrument used was a LahnKam laser confocal Raman spectrometer (produced by Horiba Jobin Yvon, Montpellier, France), and the excitation wavelength was 532 nm. The test was performed by the authors in the FI laboratory at the Institute of Geology and Geophysics, Chinese Academy of Sciences.

#### 4.3. H-O Isotope Analysis

The samples used for H-O isotope testing were garnet (2 samples, Stage I<sub>1</sub>), epidote (1 sample, Stage I<sub>2</sub>), quartz (1 sample, Stage II<sub>2</sub>) and calcite (1 sample, Stage II<sub>3</sub>). Samples for H-O isotope analysis were collected from the surface of the Da'anhe deposit. Initially, each selected sample was crushed and ground to 40–80 mesh, and a pure sample with a purity greater than 99% was selected for analysis under a binocular microscope. The samples were tested after washing and desorbing water and secondary FIs. The test was completed at the Beijing Experimental Center of Nuclear Industry. The experimental analysis instrument was a Finnigan-MAT253 mass spectrometer. Oxygen isotope analysis was carried out using the BrF<sub>5</sub> method. Mineral oxygen was extracted by the reaction of BrF<sub>5</sub> with oxygen-containing minerals under vacuum and high-temperature conditions and converted into CO<sub>2</sub> gas by burning with a thermally resistant graphite rod. The analytical accuracy was  $\pm 0.2\text{‰}$ . The H isotopes of the FIs were analysed by the zinc method with an accuracy of  $\pm 2\text{‰}$ . The international standard for H and O isotopes was SMOW.

To calculate the  $\delta^{18}\text{O}_{\text{V-SMOW}}$  values of fluids in equilibrium with silicate minerals, the following fractionation equations were used: the garnet-water equation of Taylor [40], the epidote-water equation of Zheng [41], the quartz-water equation of Clayton et al. [42], and the calcite-water equation of Zheng [41].

### 5. Results

#### 5.1. Electron Probe Analytical Results for the Skarn Minerals

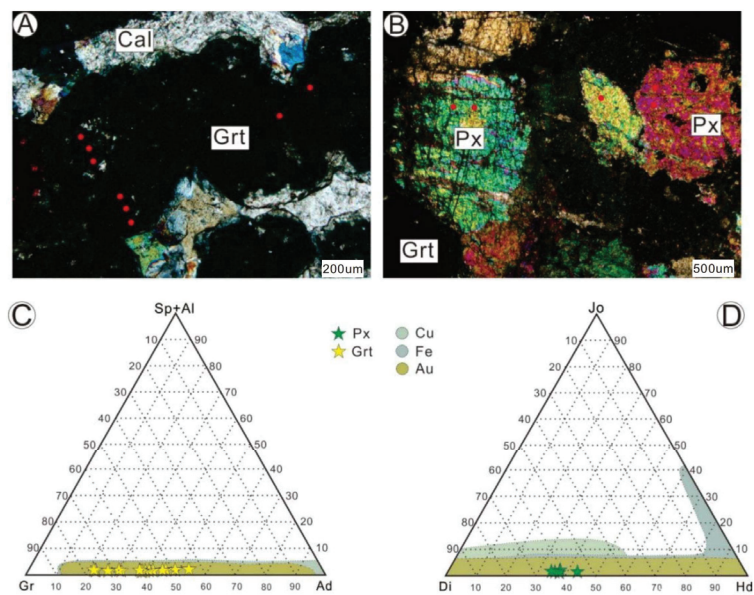
##### 5.1.1. Garnet

Only one type of garnet has been found in the Da'anhe mining area. In hand specimens, the garnet is light red to reddish-brown with particle sizes of 0.3–1.5 mm, and it is often associated with pyroxene and replaced by later minerals (Figure 6A). The garnet is homogeneous under orthogonal polarization, shows total extinction and a metasomatic residual structure, and exhibits a heteromorphic anhedral morphology. The results of the electron probe analysis of the garnet are listed in Table 1. The results show that the main components of the garnet are SiO<sub>2</sub> (average = 37.84%), CaO (average = 35.56%), FeO (average = 12.13%) and Al<sub>2</sub>O<sub>3</sub> (average = 12.20%), with small amounts of TiO<sub>2</sub>, MnO, MgO and trace Cr<sub>2</sub>O<sub>3</sub>. The garnet in the Da'anhe deposit is grossular (Gr<sub>44.93–74.76</sub>Ad<sub>21.89–52.89</sub>), with small amounts of andradite, uvarovite, pyrope and spessartite. On the garnet endmember discrimination diagram, the garnet plots within the range of typical skarn Au deposits worldwide (Figure 6C) [1].

##### 5.1.2. Pyroxene

Pyroxene is another important skarn mineral in the Da'anhe deposit that is associated with garnet and is mostly replaced by silicate minerals, quartz, calcite and other late water-bearing minerals. There is a single type of pyroxene, and the pyroxene is usually dark green in hand specimens. Bright interference colours are observed under orthogonally polarized light. The minerals exhibit high protrusions, surface cracks, and euhedral and subhedral granular textures (Figure 6B) and the particle sizes are generally 0.5–2 mm under a polarization microscope. The electron probe analytical results for pyroxene are listed in Table 2. The analytical results show that pyroxene is mainly composed of SiO<sub>2</sub> (average = 54.34%), CaO (average = 25.20%), MgO (average = 11.60%) and FeO (average = 9.05%); small amounts of Al<sub>2</sub>O<sub>3</sub>, MnO and Na<sub>2</sub>O; and trace amounts of TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O (Table 2). The pyroxene in the Da'anhe deposit is diopside rich (Di<sub>65.31–70.25</sub>Hd<sub>28.67–33.65</sub>), with small amounts of hedenbergite and johannsenite, belonging to the diopside-hedenbergite solid solution

series. In addition, on the discrimination diagram of pyroxene endmembers, the pyroxene plots in the range of typical skarn Au deposits worldwide (Figure 6D).



**Figure 6.** (A,B): Skarn mineral microscopic characteristics of the Da'anhe gold deposit (cross-polarized light); (C,D): Composition of garnet (data taken from Table 1) and pyroxene (data taken from Table 2) from gold skarn deposits in the study area and comparison with garnet and pyroxene from other types of skarn deposits in the world [1]. The red dot represents the testing location.

**Table 1.** Electron microprobe analyses of garnet from the Da'anhe deposits.

| Sample                         | Unit | 1-1   | 1-2   | 1-3   | 1-4   | 2-1   | 2-2   | 2-3   | 2-4   | 1-4-1 | 1-4-2 | 1-4-3 | 1-4-4 | 2-1-1 | 2-1-2 | 2-1-3 | 2-1-4 |
|--------------------------------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| SiO <sub>2</sub>               | wt.% | 37.60 | 38.45 | 38.10 | 37.29 | 36.85 | 36.84 | 37.82 | 37.68 | 38.09 | 37.89 | 38.05 | 39.06 | 38.14 | 38.48 | 38.36 | 38.14 |
| TiO <sub>2</sub>               | wt.% | 0.79  | 0.56  | 0.64  | 0.76  | 1.01  | 0.69  | 0.94  | 0.70  | 0.59  | 0.35  | 0.96  | 0.12  | 1.01  | 0.80  | 0.87  | 0.91  |
| Al <sub>2</sub> O <sub>3</sub> | wt.% | 11.25 | 13.24 | 12.79 | 11.24 | 9.10  | 9.72  | 11.99 | 12.48 | 13.21 | 11.76 | 12.55 | 14.98 | 14.35 | 16.02 | 15.79 | 15.87 |
| Cr <sub>2</sub> O <sub>3</sub> | wt.% | 0.07  | 0.00  | 0.09  | 0.04  | 0.17  | 0.01  | 0.06  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.18  | 0.12  | 0.18  | 0.21  |
| FeO                            | wt.% | 13.51 | 10.50 | 11.50 | 12.88 | 15.75 | 14.98 | 12.35 | 11.57 | 11.44 | 13.60 | 12.08 | 9.41  | 8.15  | 6.94  | 6.97  | 6.83  |
| MnO                            | wt.% | 0.19  | 0.16  | 0.22  | 0.19  | 0.33  | 0.28  | 0.16  | 0.29  | 0.12  | 0.26  | 0.11  | 0.25  | 0.17  | 0.19  | 0.17  | 0.15  |
| MgO                            | wt.% | 0.18  | 0.14  | 0.11  | 0.13  | 0.23  | 0.16  | 0.21  | 0.13  | 0.07  | 0.09  | 0.11  | 0.03  | 0.59  | 0.60  | 0.56  | 0.68  |
| CaO                            | wt.% | 35.47 | 36.04 | 35.82 | 35.95 | 34.30 | 35.41 | 35.64 | 35.89 | 35.78 | 35.11 | 36.00 | 35.84 | 35.07 | 35.48 | 35.80 | 35.45 |
| Na <sub>2</sub> O              | wt.% | 0.10  | 0.05  | 0.02  | 0.04  | 0.02  | 0.07  | 0.05  | 0.03  | 0.00  | 0.02  | 0.02  | 0.04  | 0.10  | 0.08  | 0.06  | 0.05  |
| K <sub>2</sub> O               | wt.% | 0.02  | 0.03  | 0.01  | 0.00  | 0.00  | 0.03  | 0.00  | 0.01  | 0.01  | 0.00  | 0.01  | 0.00  | 0.03  | 0.12  | 0.00  | 0.04  |
| Total                          | wt.% | 99.17 | 99.15 | 99.28 | 98.52 | 97.76 | 98.20 | 99.21 | 98.78 | 99.31 | 99.08 | 99.88 | 99.74 | 97.77 | 98.82 | 98.75 | 98.33 |
| Based on 12 oxygen atoms       |      |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Si                             | apfu | 2.97  | 3.01  | 2.99  | 2.97  | 2.98  | 2.96  | 2.98  | 2.98  | 2.98  | 2.99  | 2.97  | 3.02  | 3.01  | 2.99  | 2.98  | 2.98  |
| Ti                             | apfu | 0.05  | 0.03  | 0.04  | 0.05  | 0.06  | 0.04  | 0.06  | 0.04  | 0.03  | 0.02  | 0.06  | 0.01  | 0.06  | 0.05  | 0.05  | 0.05  |
| Al                             | apfu | 1.05  | 1.22  | 1.18  | 1.06  | 0.87  | 0.92  | 1.11  | 1.16  | 1.22  | 1.09  | 1.15  | 1.36  | 1.33  | 1.47  | 1.45  | 1.46  |
| Cr                             | apfu | 0.00  | 0.00  | 0.01  | 0.00  | 0.01  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.01  | 0.01  | 0.01  | 0.01  |
| Fe3+                           | apfu | 0.89  | 0.69  | 0.75  | 0.86  | 1.06  | 1.01  | 0.81  | 0.76  | 0.75  | 0.90  | 0.79  | 0.61  | 0.54  | 0.45  | 0.45  | 0.45  |
| Fe2+                           | apfu | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| Mn                             | apfu | 0.01  | 0.01  | 0.01  | 0.01  | 0.02  | 0.02  | 0.01  | 0.02  | 0.01  | 0.02  | 0.01  | 0.02  | 0.01  | 0.01  | 0.01  | 0.01  |
| Mg                             | apfu | 0.02  | 0.02  | 0.01  | 0.02  | 0.03  | 0.02  | 0.02  | 0.01  | 0.01  | 0.01  | 0.01  | 0.00  | 0.07  | 0.07  | 0.06  | 0.08  |
| Ca                             | apfu | 3.01  | 3.02  | 3.01  | 3.07  | 2.97  | 3.05  | 3.01  | 3.04  | 3.00  | 2.97  | 3.01  | 2.97  | 2.96  | 2.95  | 2.98  | 2.97  |
| Ura                            | wt.% | 0.22  | 0.00  | 0.28  | 0.13  | 0.53  | 0.03  | 0.20  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.56  | 0.38  | 0.55  | 0.63  |
| Ad                             | wt.% | 44.12 | 33.82 | 37.23 | 41.57 | 52.89 | 48.92 | 40.09 | 37.34 | 37.24 | 44.90 | 39.03 | 30.54 | 26.49 | 22.28 | 22.22 | 21.89 |
| Pyr                            | wt.% | 0.69  | 0.52  | 0.43  | 0.51  | 0.90  | 0.63  | 0.81  | 0.49  | 0.26  | 0.37  | 0.44  | 0.13  | 2.27  | 2.27  | 2.10  | 2.59  |
| Spe                            | wt.% | 0.41  | 0.34  | 0.48  | 0.41  | 0.75  | 0.61  | 0.35  | 0.62  | 0.25  | 0.58  | 0.23  | 0.55  | 0.37  | 0.42  | 0.37  | 0.33  |
| Gro                            | wt.% | 54.55 | 65.32 | 61.57 | 57.37 | 44.93 | 49.81 | 58.56 | 61.55 | 62.24 | 54.14 | 60.30 | 68.79 | 70.32 | 74.66 | 74.76 | 74.56 |
| Alm                            | wt.% | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |

**Note:** Ura-Uvarovite; Ad-Andradite; Pyr-Pyroxene; Spe-Spessartite; Gro-Grossular; Alm-Almandine.

Table 2. Electron microprobe analyses of pyroxene from the Da’anhe deposits.

| Sample                         | Unit | DAH-1-1 | DAH-1-2 | DAH-1-3 | DAH-1-4 | DAH-1-5 |
|--------------------------------|------|---------|---------|---------|---------|---------|
| SiO <sub>2</sub>               | wt.% | 54.11   | 54.22   | 53.95   | 54.59   | 54.84   |
| TiO <sub>2</sub>               | wt.% | 0.00    | 0.00    | 0.04    | 0.03    | 0.01    |
| Al <sub>2</sub> O <sub>3</sub> | wt.% | 0.15    | 0.34    | 0.34    | 0.14    | 0.16    |
| Cr <sub>2</sub> O <sub>3</sub> | wt.% | 0.03    | 0.05    | 0.08    | 0.03    | 0.02    |
| FeO                            | wt.% | 8.62    | 8.72    | 10.10   | 8.62    | 9.21    |
| MnO                            | wt.% | 0.33    | 0.13    | 0.31    | 0.33    | 0.35    |
| MgO                            | wt.% | 11.88   | 11.79   | 11.05   | 11.90   | 11.40   |
| CaO                            | wt.% | 25.51   | 25.24   | 24.99   | 25.28   | 24.98   |
| Na <sub>2</sub> O              | wt.% | 0.11    | 0.18    | 0.16    | 0.08    | 0.10    |
| K <sub>2</sub> O               | wt.% | 0.05    | 0.00    | 0.01    | 0.00    | 0.04    |
| Total                          | wt.% | 100.78  | 100.68  | 101.02  | 100.99  | 101.11  |
| Based on 6 oxygen atoms.       |      |         |         |         |         |         |
| Al(iv)                         | apfu | 0.00    | 0.00    | 0.00    | 0.00    | 0.00    |
| Al(vi)                         | apfu | 0.01    | 0.01    | 0.01    | 0.01    | 0.01    |
| Ti                             | apfu | 0.00    | 0.00    | 0.00    | 0.00    | 0.00    |
| Cr                             | apfu | 0.00    | 0.00    | 0.00    | 0.00    | 0.00    |
| Fe <sup>3+</sup>               | apfu | 0.00    | 0.00    | 0.00    | 0.00    | 0.00    |
| Fe <sup>2+</sup>               | apfu | 0.27    | 0.27    | 0.32    | 0.27    | 0.29    |
| Mn                             | apfu | 0.01    | 0.00    | 0.01    | 0.01    | 0.01    |
| Mg                             | apfu | 0.66    | 0.65    | 0.61    | 0.66    | 0.63    |
| Ca                             | apfu | 1.02    | 1.01    | 1.00    | 1.00    | 0.99    |
| Na                             | apfu | 0.01    | 0.01    | 0.01    | 0.01    | 0.01    |
| K                              | apfu | 0.00    | 0.00    | 0.00    | 0.00    | 0.00    |
| Di                             | wt.% | 70.21   | 70.25   | 65.31   | 70.21   | 67.83   |
| Hd                             | wt.% | 28.67   | 29.30   | 33.65   | 28.70   | 30.99   |
| Jo                             | wt.% | 1.12    | 0.45    | 1.04    | 1.09    | 1.18    |
| Mn/Fe                          | —    | 0.02    | 0.01    | 0.02    | 0.02    | 0.02    |

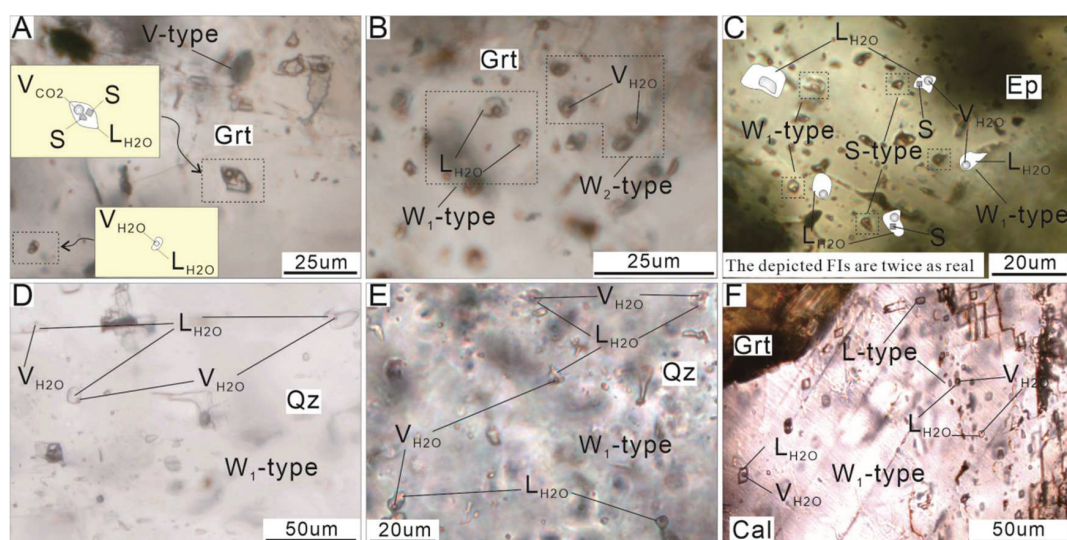
Note: Di-Diopside; Hd-Hedenbergite; Jo-Johannsenite.

5.2. Results of FI Analysis

5.2.1. Petrographic and Microthermometric Results for FIs

In this study, a petrographic microscope was used to observe the FIs in garnet, diopside, epidote, quartz and calcite in the Da’anhe mining area. Among them, the FIs in quartz and calcite were the most common, followed by those in garnet and diopside, and the FIs in epidote were the least common. Most of the FIs were primary FIs, with a small number of secondary FIs developed along mineral fissures. The sizes of the FIs vary and are concentrated in the range of 3~15 μm, and the maximum size is more than 20 μm. The morphologies are mainly elliptical and irregular, with minor long strip and spindle morphologies. According to the phase characteristics of FIs at room temperature, the FIs in the Da’anhe gold deposit can be divided into five types: daughter mineral-bearing three-phase FIs (S type), liquid-rich FIs (W1 type), gas-rich FIs (W2 type), pure gas FIs (PV) and pure liquid FIs (PL).

- (1) S-type FIs: S-type FIs developed in the early skarn stage and late skarn stage and those that exhibit oval, spindle or irregular shapes. These FIs in garnet are larger (Figure 7A), and the FIs in epidote are smaller. The overall sizes range from 3~20 μm, and the gas-liquid ratios vary from 15% to 35%. Combined with the morphology of transparent daughter minerals in FIs and the findings of previous research [20,21], we believe that the crystalline minerals are mainly halite and sylvinite. These FIs are generally less common, accounting for approximately 10% of the total number of inclusions, and coexist with the W1-, W2- and PV-type inclusions (Figure 7A,C).



**Figure 7.** Microscopic photographs of fluid inclusions in the Da'anhe deposit. (A): W1-, S- and PV-type FIs coexist in garnet; (B): W1- and W2-type FIs coexist in garnet; (C): W1- and S-type FIs coexist in epidote; (D): W1-type FIs in early quartz-sulfide stage; (E): W1-type FIs in quartz of late quartz-sulfide stage; (F): W1- and PL-type FIs coexist in calcite of quartz-carbonate stage.

- (2) W1-type FIs: These FIs formed throughout the metallogenic stage and are observed in garnet, diopside, epidote, quartz and calcite, especially in quartz. Most of the FIs are oval and irregularly shaped, range from 3~18 μm, and account for approximately 60% of the total number of FIs. The gas-liquid ratios of W1-type inclusions vary greatly from 5%~40%, and the gas-liquid ratios in the early quartz-sulfide stage inclusions are the lowest (Figure 7A–F).
- (3) W2-type FIs: These FIs developed during all stages, except the quartz-carbonate stage, and appear in large quantities in quartz. The FIs are mostly uniform in size, with oval and irregular shapes and a small number of long strips, range in size from 5 to 15 μm, and account for approximately 25% of the total number of inclusions. The gas-liquid ratios of the W2 inclusions range between 65% and 80% (Figure 7B).
- (4) PV-type and PL-type FIs: These two types of inclusions are less common in each mineralization stage and account for approximately 5% of the total number of inclusions. Among them, the PV-type FIs mainly developed during the skarn stage, while the PL-type FIs mainly developed during the quartz carbonate stage of late mineralization. The FIs are mostly elliptical and cuboid shaped, and a few are irregular or long strips, with sizes ranging from 2 to 15 μm (Figure 7A,F).

On the basis of petrographic observations, temperature measurements during the heating and cooling stages were carried out for the FIs in each mineralization. Most of the FIs used for these temperature measurement stages appear in groups, indicating that they are primary FIs. A total of 164 uniform temperature data points were obtained. The test results are listed in Table 3.

Table 3. Microscopic thermometry results of fluid inclusions in the Da’anhe gold deposit.

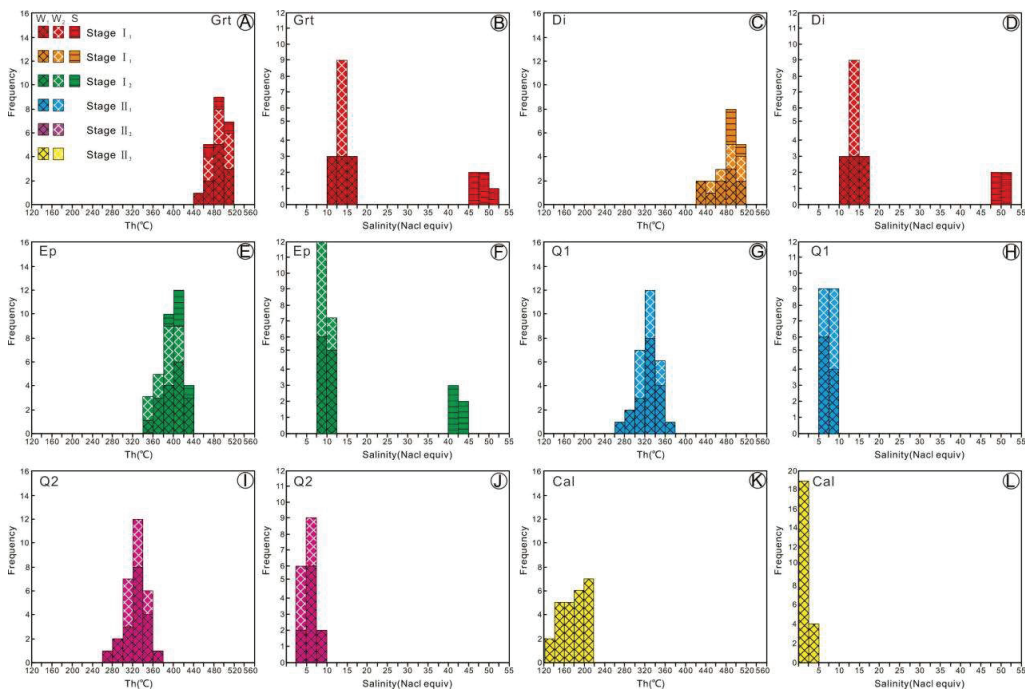
| Stage           | Sample | Minerals       | Type | Gas-Liquid Ratio | $T_d$                  | $T_{m-ice}$            | $T_h$                  | Salinity           | Density                    | Number | Pressure  | Depth     |
|-----------------|--------|----------------|------|------------------|------------------------|------------------------|------------------------|--------------------|----------------------------|--------|-----------|-----------|
|                 |        |                |      | ( $V_G/V_T\%$ )  | ( $^{\circ}\text{C}$ ) | ( $^{\circ}\text{C}$ ) | ( $^{\circ}\text{C}$ ) | (wt.% NaCl Equiv.) | ( $\text{g}/\text{cm}^3$ ) |        | (MPa)     | (Km)      |
| I <sub>1</sub>  | DAH-1  | Grt            | W1   | 10~35            |                        | −12.7~−7.8             | 447~515                | 11.5~16.7          | 0.56~0.61                  | 11     | 49.5~64.1 | 5.60~6.46 |
|                 |        |                | W2   |                  |                        | −10.8~−8.8             | 468~511                | 12.7~14.8          | 0.55~0.59                  | 8      | 52.5~60.8 | 5.79~6.27 |
|                 |        |                | S    | 15~30            | 393~431                |                        | 477~503                | 46.7~51.0          | 1.56~1.70                  | 5      |           |           |
|                 | DAH-1  | Di             | W1   | 15~40            |                        | −13.1~−8.5             | 420~520                | 12.3~17.1          | 0.57~0.66                  | 11     | 46.7~65.3 | 5.43~6.52 |
|                 |        |                | W2   |                  |                        | −11.7~−7.6             | 453~511                | 11.2~15.8          | 0.57~0.58                  | 6      | 48.7~62.2 | 5.56~6.35 |
|                 |        |                | S    | 15~30            | 409~431                |                        | 481~505                | 38.0~42.0          | 1.62~1.70                  | 4      |           |           |
| I <sub>2</sub>  | DAH-2  | Ep             | W1   | 10~35            |                        | −8.5~−5.8              | 358~431                | 8.94~12.3          | 0.64~0.72                  | 17     | 35.6~47.9 | 3.56~5.51 |
|                 |        |                | W2   |                  |                        | −7.3~−5.7              | 356~418                | 8.81~10.9          | 0.63~0.72                  | 12     | 35.2~43.6 | 3.52~5.24 |
|                 |        |                | S    | 10~30            | 336~366                |                        | 385~428                | 41.1~43.9          | 1.45~1.50                  | 5      |           |           |
| II <sub>1</sub> | DAH-3  | Q <sub>1</sub> | W1   | 15~35            |                        | −6.3~−3.7              | 279~366                | 5.99~9.60          | 0.71~0.80                  | 19     | 24.5~37.3 | 2.45~3.73 |
|                 |        |                | W2   | 55~60            |                        | −6.4~−4.4              | 305~357                | 7.01~9.73          | 0.73~0.78                  | 10     | 28.2~36.5 | 2.82~3.65 |
| II <sub>2</sub> | DAH-4  | Q <sub>2</sub> | W1   | 10~30            |                        | −5.7~−2.5              | 226~305                | 4.17~8.81          | 0.80~0.87                  | 15     | 18.0~30.2 | 1.8~3.02  |
|                 |        |                | W2   | 60~70            |                        | −4.2~−2.5              | 247~300                | 4.17~5.62          | 0.78~0.84                  | 11     | 20.0~27.2 | 2.0~2.72  |
| II <sub>3</sub> | DAH-5  | Cal            | W1   | 15~25            |                        | −2.0~−0.5              | 137~247                | 0.87~3.37          | 0.82~0.94                  | 30     | 9.25~18.8 | 0.93~1.88 |

**Note:** Grt-Garnet; Di-Diopside; Ep-Epidote; Q<sub>1</sub>-Quartz from early quartz sulfide stage; Q<sub>2</sub>-Quartz from late quartz sulfide stage; Cal-Calcite.  $T_d$ -disappearance temperature of daughter minerals;  $T_{m-ice}$ -freezing point temperatures;  $T_h$ -homogenization temperature;  $V_G$ -Volume of gas;  $V_T$ -Total Volume.

Early skarn stage: The FIs used for temperature measurements during the heating and cooling stages include garnet and diopside. The FIs are mainly W1- and S-type FIs, with a small number of W2- and PL-type FIs. In the same field of view, W1-, S- and PV-type FIs coexist (Figure 7A), indicating that the fluid underwent boiling during the evolution process. When the W1-type FIs are heated to 420~520 °C, they homogenize to the liquid phase (homogenization temperature,  $T_h$ ). The freezing point temperatures ( $T_{m-ice}$ ) of this type of inclusion vary from −13.1 °C to −7.8 °C and are obtained by cooling. After calculation, the corresponding salinities range from 11.5~17.1 wt.% NaCl equiv., and the densities range from 0.56~0.66 g/cm<sup>3</sup>. When the W2-type FIs are heated to 453~511 °C, they uniformly transform to the gas phase. The  $T_{m-ice}$  values of the W2-type FIs vary from −11.7 to −7.6 °C and are obtained by cooling. The salinities of the corresponding fluids range from 11.2~15.8 wt.% NaCl equiv. and the densities range from 0.55~0.59 g/cm<sup>3</sup>. The daughter minerals in the S-type FIs disappear when heated to 393~431 °C (disappearance temperature of daughter minerals,  $T_d$ ) and homogenize to the liquid phase when heated to 477~503 °C. Based on these results, the salinities and densities of the fluids are 38.0~51.0 wt.% NaCl equiv. and 1.56~1.70 g/cm<sup>3</sup>, respectively (Figures 7 and 8A–D).

Late skarn stage: The FIs used for temperature measurements using the heating and cooling stage are from epidote. The FIs that developed in this stage were mainly W1, W2 and S-type FIs. The coexistence of different types of FIs in the same field of view is observed in epidote (Figure 7C), indicating that fluid boiling also occurred during this stage. When the W1-type FIs homogenize into the liquid phase, the temperature is 358~431 °C, the freezing point temperatures vary from −8.5 to −5.8 °C, the corresponding salinities are 8.94~12.3 wt.% NaCl equiv., and the densities are 0.64~0.72 g/cm<sup>3</sup> (Figures 7 and 8E,F). W2-type FIs homogenize into the gas phase at temperatures of 356~418 °C, the freezing point temperature varies from −7.3 to −5.7 °C, and their corresponding salinities are 8.81~10.9 wt.% NaCl equiv. and the density is 0.63~0.72 g/cm<sup>3</sup>. The daughter minerals in the S-type inclusions disappear at 336~366 °C, and they homogenize into the liquid phase at 385 to 428 °C. After calculation, their corresponding salinities range from 41.1~43.9 wt.% NaCl equiv., and their densities are 1.45~1.50 g/cm<sup>3</sup> (Figures 7 and 8E,F).





**Figure 8.** Histograms of total homogenization temperatures ( $T_h$ ) and salinities of FIs in different stages. (A–D): Stage I<sub>1</sub>; (E,F): Stage I<sub>2</sub>; (G,H): Stage II<sub>1</sub>; (I,J): Stage II<sub>2</sub>; (K,L): Stage II<sub>3</sub>.

**Early quartz-sulfide stage:** The FIs used for temperature measurements using the heating and cooling stage are from quartz. The FIs are mainly W1 and W2 type FIs, and no S-type FIs are found (Figure 7). The W1-type FIs were heated and homogenized to the liquid phase. The homogenization temperatures range from 279 to 366 °C, the freezing point temperatures vary from −6.3 to −3.7 °C, the calculated corresponding salinities are 5.99–9.60 wt.% NaCl equiv., and the densities are 0.71–0.80 g/cm<sup>3</sup>. For the W2-type FIs, the homogenization temperatures, freezing point temperatures, and corresponding salinities and densities are 305–357 °C, −6.4–−4.4 °C, 7.01–9.73 wt.% NaCl equiv., and 0.73–0.78 g/cm<sup>3</sup>, respectively (Figure 8G,H).

**Late quartz-sulfide stage:** The FIs used for temperature measurements using the heating and cooling stage are from quartz. Petrography revealed that the types of FIs in this stage are similar to those in the early quartz-sulfide stage, i.e., mainly W1- and W2-type FIs (Figure 7E). In this stage, the W1-type FIs were heated and homogenized to the liquid phase. The homogenization temperatures range from 226 to 305 °C, and the freezing point temperatures vary from −5.7 to −2.5 °C. After calculation, their corresponding salinities range from 4.17–8.81 wt.% NaCl equiv., and their densities range from 0.80–0.87 g/cm<sup>3</sup>. For the W2-type FIs, the homogenization temperatures range from 247–300 °C, the freezing point temperatures vary from −4.2 to −2.5 °C, their corresponding salinities are 4.17–5.62 wt.% NaCl equiv., and their densities are 0.78–0.84 g/cm<sup>3</sup> (Figure 8I,J).

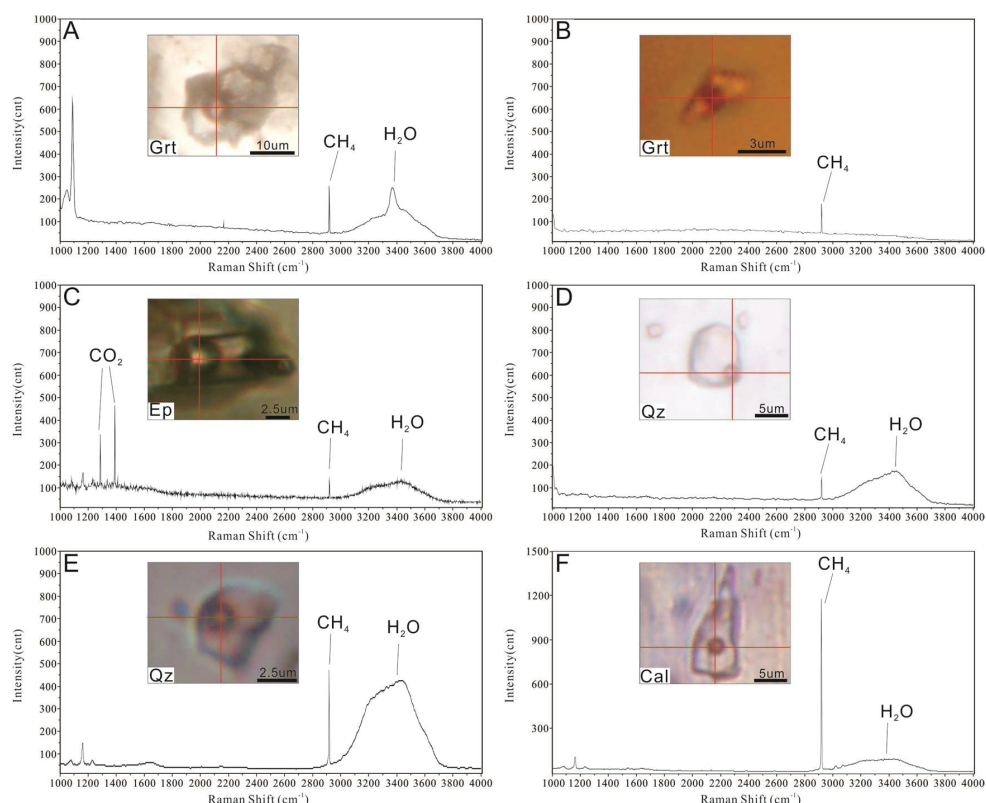
**Quartz-carbonate stage:** The FIs developed in calcite veins were selected for microscopic analysis. The petrography shows that only W1- and PL-type FIs developed during this stage. The homogenization temperatures of the W1-type FIs range from 137 to 247 °C, and the freezing point temperatures vary from −2.0–−0.5 °C. After calculation, their corresponding salinities are 0.87–3.37 wt.% NaCl equiv., and their fluid densities are 0.82–0.94 g/cm<sup>3</sup> (Figure 8K,L).



### 5.2.2. Laser Raman Spectral Analysis Results

To further understand the compositions of the FIs, the authors of this paper selected representative FIs from different mineralization stages of the Da'anhe gold deposit for Laser Raman spectral analysis. Because W2-type FIs are not well developed, W1-type FIs were used.

The Laser Raman spectral results show that the gas phase components of the W1-type FIs in the early skarn stage are  $\text{CH}_4$  and  $\text{H}_2\text{O}$  (Figure 9A,B). The  $\text{CH}_4$  and  $\text{H}_2\text{O}$  peaks of the W1-type FIs in the late skarn stage are weaker than those in the early skarn stage, and  $\text{CO}_2$  is present (Figure 9C). The gas phase composition of the W1-type FIs in the early quartz-sulfide stage is mainly  $\text{H}_2\text{O}$  with a small amount of  $\text{CH}_4$  (Figure 9D). In the late quartz-sulfide stage and quartz-carbonate stage, the gas phase components in the W1-type FIs are  $\text{CH}_4$  and  $\text{H}_2\text{O}$ , and the peak intensity of  $\text{CH}_4$  gradually increases (Figure 9E,F).



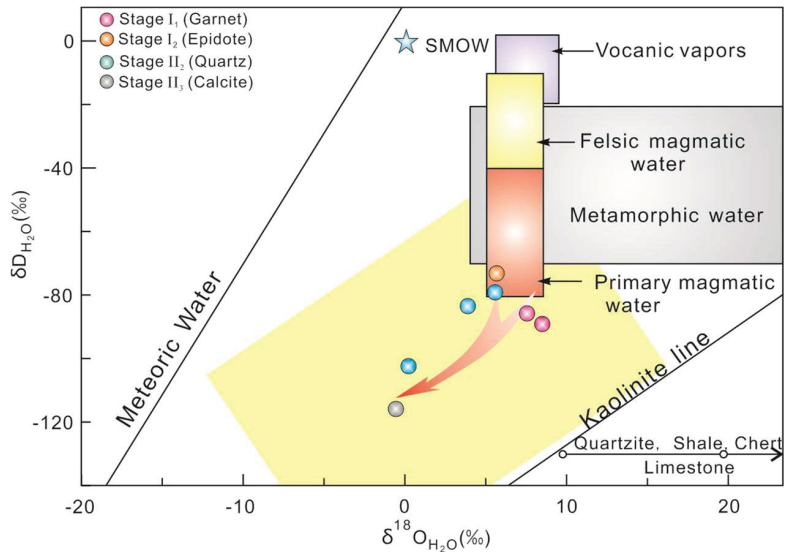
**Figure 9.** Representative Laser Raman spectra of FIs in garnet, epidote, quartz and calcite grains of different stages from the Da'anhe deposit. (A,B): Spectrum for vapor phase of W1-type FIs hosted in garnet grain of the dry skarn stage; (C): Spectrum for vapor phase of W1-type FIs hosted in epidote grain of the wet skarn stage; (D): Spectrum for vapor phase of W1-type FIs hosted in quartz grain of the early quartz sulfide stage; (E): Spectrum for vapor phase of W1-type FIs hosted in quartz grain of the late quartz sulfide stage; (F): Spectrum for vapor phase of W1-type FIs hosted in calcite grain of the quartz-carbonate stage.

In general, the gas components in the ore-forming fluid of the Da'anhe deposit are mainly  $\text{CH}_4$ ,  $\text{H}_2\text{O}$  and a small amount of  $\text{CO}_2$ . The process of mineralization is commonly accompanied by a transition from an oxidizing environment to a reducing environment. Therefore, we suggest that the large amount of  $\text{CH}_4$  present during the skarn stage was

provided by carbonate rocks, and that the CO<sub>2</sub> in the fluid may have escaped in large quantities. As the mineralization entered the early quartz sulfide stage, the abundance of CH<sub>4</sub> gradually decreased, and that of CO<sub>2</sub> gradually increased. During the late quartz sulfide stage and quartz carbonate stage, a large amount of CO<sub>2</sub> in the fluid was consumed, the ore-forming system transformed into a reducing environment, and large amounts of CH<sub>4</sub> accumulated. Therefore, the initial ore-forming fluid was a H<sub>2</sub>O-CO<sub>2</sub>-NaCl system (Figure 9).

5.3. H-O Isotope Analytical Results

The results of mineral H-O isotope tests for different metallogenic stages in the Da'anhe gold deposit (Figure 10, Table 4) [2,43] reveal that the  $\delta D_{H_2O}$  values of garnet samples in the early skarn stage vary from  $-89.1\text{‰}$  to  $-85.9\text{‰}$ , and the  $\delta^{18}O_{V-SMOW}$  values vary from  $6.1\text{‰}$  to  $7.0\text{‰}$ . Combined with the results of FI temperature measurements (the average value is  $490\text{ }^{\circ}\text{C}$ ), the  $\delta^{18}O_{H_2O}$  values of the fluid are calculated and vary from  $7.57\text{‰}$  to  $8.47\text{‰}$ . In the late skarn stage, the  $\delta D_{H_2O}$  value of epidote is  $-73.3\text{‰}$ , and the  $\delta^{18}O_{V-SMOW}$  value is  $5.4\text{‰}$ . After calculation, the  $\delta^{18}O_{H_2O}$  value of the fluid is  $5.71\text{‰}$  ( $T_h$  is  $393\text{ }^{\circ}\text{C}$ ). The  $\delta D_{H_2O}$  values of the quartz samples in the late quartz-sulfide stage vary from  $-79.3\text{‰}$  to  $-102.5\text{‰}$ , and the  $\delta^{18}O_{V-SMOW}$  values range from  $8.7\text{‰}$  to  $14.1\text{‰}$ . After recalculation, the  $\delta^{18}O_{H_2O}$  values of the fluid vary from  $0.25\text{‰}$  to  $5.65\text{‰}$  ( $T_h$  is  $261\text{ }^{\circ}\text{C}$ ). The  $\delta D_{H_2O}$  values of calcite samples in the quartz-carbonate stage are concentrated at  $-116\text{‰}$ , and the  $\delta^{18}O_{V-SMOW}$  value is  $11.6\text{‰}$ . The calculated  $\delta^{18}O_{H_2O}$  value of the fluid is  $-0.77\text{‰}$  ( $T_h$  is  $190\text{ }^{\circ}\text{C}$ ).



**Figure 10.** Hydrogen and oxygen isotopic compositions of the ore-forming fluid in the Da'anhe deposit (data taken from Table 4, modified after Hedenquist and Lowenstern [2]).

**Table 4.** Hydrogen and oxygen isotopic compositions of fluids from the Da’anhe Au deposit.

| Sample  | Mineral | Th (°C) | $\delta^{18}\text{O}_{\text{V-SMOW}}$<br>(‰) | $\delta^{18}\text{O}_{\text{H}_2\text{O}}$<br>(‰) | $\delta\text{D}_{\text{H}_2\text{O}}$<br>(‰) | Data<br>Sources |
|---------|---------|---------|----------------------------------------------|---------------------------------------------------|----------------------------------------------|-----------------|
| 19DAH-2 | Garnet  | 490     | 6.1                                          | 7.57                                              | −85.9                                        | This study      |
| 19DAH-3 |         |         | 7.0                                          | 8.47                                              | −89.1                                        |                 |
| 19DAH-3 | Epidote | 393     | 5.4                                          | 5.71                                              | −73.3                                        |                 |
| 19DAH-7 | Quartz  | 261     | 8.7                                          | 0.25                                              | −102.5                                       |                 |
| DKDA3   |         |         | 12.4                                         | 3.95                                              | −83.4                                        | [43]            |
| DKDA4   |         |         | 14.1                                         | 5.65                                              | −79.3                                        |                 |
| 19DAH-7 | Calcite | 190     | 11.6                                         | −0.77                                             | −116                                         | This study      |

6. Discussion

6.1. Implications of Skarn Minerals for Mineralization

The chemical composition of skarn minerals can be characterized by physical and chemical conditions, such as temperature, pressure, depth, pH and oxygen fugacity during their formation, which can provide important information on the formation environment of deposits [44–46]. It is generally believed that andradite and magnesium-rich diopside are formed in high-temperature environments with strong oxidation reactions and weak acidity, while grossular and hedenbergite are often formed in environments with high temperature, weak oxidation, reduction and alkalinity [45,47,48]. The garnet in the Da’anhe gold deposit is mainly grossular (Figure 6C), and pyroxene belongs to the diopside-hedenbergite solid solution series (Figure 6D). Both coexist in the outer belt of the skarn, and the pyroxene content is greater than the garnet content. The above results show that the Da’anhe deposit formed in a reducing environment related to an intrusive body and is a typical calcareous reduced skarn Au deposit. In addition, our team conducted electron probe analysis on the hornblende and biotite in the gabbroic diorite, and the results showed that the gabbro-diorite magma related to mineralization had reducing characteristics ( $\Delta\text{FMQ} = -0.95\sim-0.60$ , with an average value of 0.17;  $\log(f\text{O}_2) = -15.65\sim-14.68$ , with an average value of  $-15.11$  [49]), which indicates that the Da’anhe deposit is a reduced skarn gold deposit.

6.2. Source of the Ore-Forming Materials

Previous studies have shown that skarn deposits in the Lesser Xing’an Range generally lack sulfate minerals [49]. Therefore, the  $\delta^{34}\text{S}$  values of the metal sulfide minerals in the ore can be used to represent the  $\delta^{34}\text{S}$  values of the ore-forming fluid of the deposit [50]. To determine the source of ore-forming materials in the Da’anhe gold deposit, S-Pb isotope data from metal sulfides in the Da’anhe gold deposit were collected and are listed in Tables 5 and 6. The S-Pb isotope data show that the  $\delta^{34}\text{S}$  values of pyrrhotite in the Da’anhe deposit vary from  $-0.6\text{‰}$  to  $0.5\text{‰}$  (with an average of  $0.10\text{‰}$ ), the  $\delta^{34}\text{S}$  values of pyrite vary from  $-2.9\text{‰}$  to  $-0.6\text{‰}$  (with an average of  $-3.07\text{‰}$ ), and the arithmetic average of the sulfides is  $-0.83\text{‰}$ . The  $\delta^{34}\text{S}$  values of sulfides in the Da’anhe deposit are within the range of typical porphyry-skarn deposits ( $-5.0\text{‰}$  to  $5.0\text{‰}$ , [51]) (Figure 11) [50,52], indicating that the sulfur in the Da’anhe deposit may have mainly come from the magmatic system. The Pb isotope values of the metal sulfides in the Da’anhe deposit vary greatly, and the  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios are  $18.099\sim18.568$ ,  $15.532\sim15.580$  and  $37.909\sim38.176$ , respectively. In the  $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$  projection (Figure 12) [53], the sample points are mainly located in the lower crust area. According to the  $^{208}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$  diagram, the sample points are located mainly on both sides of the orogenic belt evolution line, and some of them are located on the upper crust evolution line, which indicates that the Pb in the Da’anhe sulfide has the characteristics of mixed lead. These results imply that the ore-forming materials may have been derived from crust-mantle mixing. The Sr-Nd isotopes of the medium-grained gabbroic diorite related to the mineral-

ization of the Da'anhe gold deposit have been studied by Yang et al. [54] ( $\epsilon\text{Nd}(t) = 0.8\sim1.9$ ,  $\epsilon\text{Sr}(t) = 75.9\sim77.2$ , and  $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.70962\sim0.70972$ ,  $T_{\text{DM2}} = 815\sim1076$  Ma); their results indicate that the mineralization originated from Neoproterozoic lower crust metasomatized by fluids or weakly enriched mantle and that the ascending material was contaminated by young crustal materials during the process of ascent and emplacement [54]. This result further shows that the ore-forming material of the Da'anhe deposit was derived from gabbro-dioritic magma.

Table 5. Sulfur isotopic composition of sulfides from the Da'anhe Au deposit.

| Sample   | Mineral | $\delta^{34}\text{S}\text{‰}$ | Data Sources |
|----------|---------|-------------------------------|--------------|
| Dah4-Pyr | Pyr     | 0.5                           | [21]         |
| Dah5-Pyr | Pyr     | 0.5                           |              |
| Dah7     | Pyr     | −0.6                          |              |
| Dah4-Py  | Py      | −0.6                          |              |
| Dah5-Py  | Py      | −2.9                          |              |
| Dah6-Py  | Py      | −2.7                          |              |
| Dah6-Pyr | Pyr     | 0                             |              |

Note: Pyr-Pyrrhotite; Py-Pyrite.

Table 6. Lead isotopic composition of sulfides from the Da'anhe Au deposit.

| Sample   | Mineral | $^{206}\text{Pb}/^{204}\text{Pb}$ | $^{207}\text{Pb}/^{204}\text{Pb}$ | $^{208}\text{Pb}/^{204}\text{Pb}$ | Data Sources |
|----------|---------|-----------------------------------|-----------------------------------|-----------------------------------|--------------|
| Dah4-Pyr | Pyr     | 18.308                            | 15.543                            | 38.139                            | [21]         |
| Dah4-Py  | Py      | 18.508                            | 15.578                            | 38.176                            |              |
| Dah5-Pyr | Pyr     | 18.303                            | 15.536                            | 38.125                            |              |
| Dah5-Py  | Py      | 18.099                            | 15.556                            | 38.071                            |              |
| Dah6Py   | Py      | 18.317                            | 15.532                            | 38.098                            |              |
| Dah6Pyr  | Pyr     | 18.568                            | 15.580                            | 37.909                            |              |
| Dah7     | Pyr     | 18.455                            | 15.577                            | 38.103                            |              |

Note: Pyr-Pyrrhotite; Py-Pyrite.

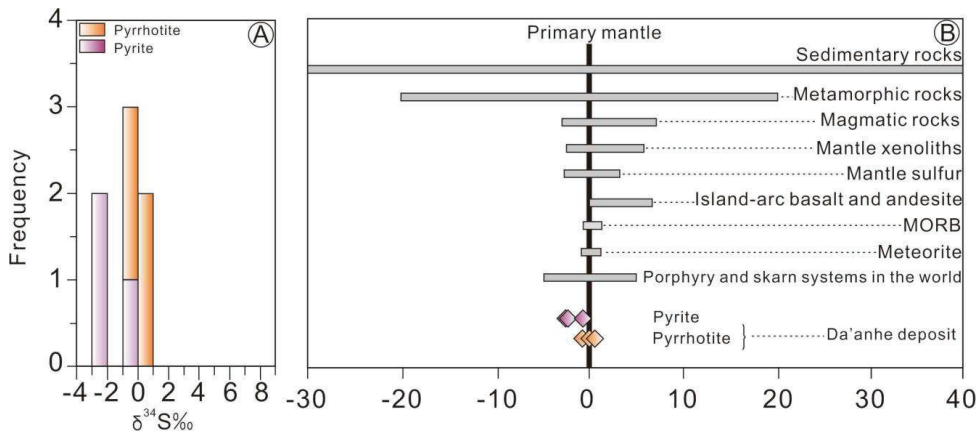
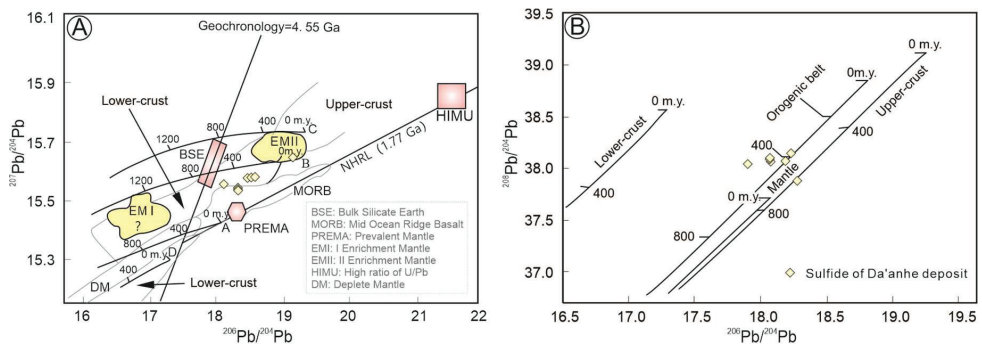


Figure 11. (A) Histogram of the sulfur isotopic compositions of sulfides from the Da'anhe deposit; (B) Ranges of  $\delta^{34}\text{S}$  values of selected geologically important sulfur reservoirs [50,52] and the Da'anhe deposit (data taken from Table 5). The orange and purple squares represent magnetite and pyrite, respectively. The gray squares represent different geologically important sulfur reservoirs.



**Figure 12.** Diagram of lead isotopic compositions of the Da'anhe deposit. (A)— $^{207}\text{Pb}/^{204}\text{Pb}$  v.s.  $^{206}\text{Pb}/^{204}\text{Pb}$ ; (B)— $^{208}\text{Pb}/^{204}\text{Pb}$  v.s.  $^{206}\text{Pb}/^{204}\text{Pb}$  (data taken from Table 6, modified after Zartman and Doe [53]).

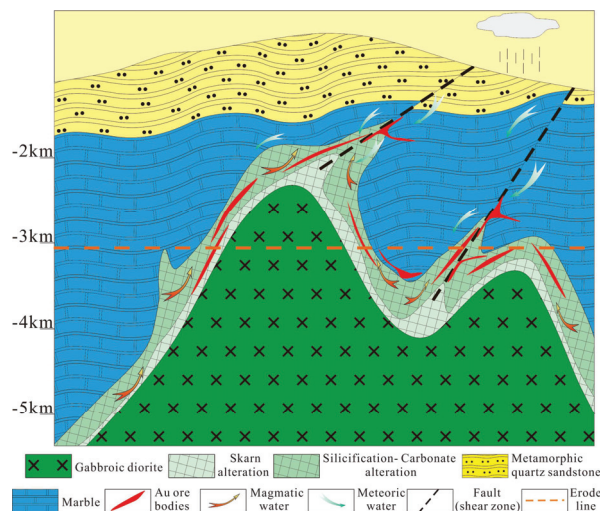
### 6.3. Source and Evolution of Ore-Forming Fluids

For the source of ore-forming fluids in skarn deposits, magmatic water is generally the dominant source, followed by meteoric water [55,56], and the duration and amount of meteoric water can vary according to the geological characteristics of different deposits. Several geologists [55,57] have suggested that the different alteration characteristics of the early skarn stage and late skarn stage reflect the dominant roles of magmatic water and meteoric water, respectively. Meinert et al. [58,59] suggested that these two processes may be the result of the evolution of a single magmatic hydrothermal system. The FIs in the skarn minerals of the Da'anhe gold deposit are mainly W1- and W2-type FIs and a small number of S-type FIs. According to the crystal form, the daughter crystals are mainly halite and sylvinites. Laser Raman spectroscopy shows that the gas phases involved in the early skarn stage were  $\text{H}_2\text{O}$  and  $\text{CH}_4$  and that  $\text{CO}_2$ -containing FIs began to appear in the late skarn stage. The homogenization temperatures of the FIs that developed in the early skarn and late skarn stages are  $393\sim 515^\circ\text{C}$  and  $336\sim 431^\circ\text{C}$ , respectively, and their corresponding salinities are 11.2~51.0 wt.% NaCl equiv. and 8.81~43.9 wt.% NaCl equiv., respectively. The above characteristics indicate that the initial ore-forming fluid was an  $\text{H}_2\text{O}$ -NaCl- $\text{CO}_2$  system with a high temperature and high salinity. The main types of FIs in the quartz-sulfide period are W1 and W2. Laser Raman analysis revealed that the gas phases in the FIs are mainly  $\text{H}_2\text{O}$  and  $\text{CH}_4$ . The homogenization temperatures of the FIs from the early to late stages are  $279\sim 366^\circ\text{C}$ ,  $226\sim 305^\circ\text{C}$  and  $137\sim 247^\circ\text{C}$ . The corresponding salinities are 5.99~9.73 wt.% NaCl equiv., 4.17~8.81 wt.% NaCl equiv. and 0.87~3.37 wt.% NaCl equiv., respectively. The above characteristics indicate that the ore-forming fluids in this period were part of a medium- to low temperature and low salinity  $\text{H}_2\text{O}$ - $\text{CH}_4$  system. The H-O isotope data show that the  $\delta\text{D}_{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values ( $\delta\text{D}_{\text{H}_2\text{O}} = -89.1\text{‰} \sim -73.3\text{‰}$ ;  $\delta^{18}\text{O}_{\text{H}_2\text{O}} = 5.71\text{‰} \sim 8.47\text{‰}$ ) of the skarn minerals are close to the range of magmatic water during the skarn subperiod (Figure 10) [2], and the  $\delta\text{D}_{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values ( $\delta\text{D}_{\text{H}_2\text{O}} = -79.3\text{‰} \sim -116\text{‰}$ ;  $\delta^{18}\text{O}_{\text{H}_2\text{O}} = -0.77\text{‰} \sim 5.65\text{‰}$ ) of quartz in the quartz-sulfide period show a trend of gradual migration towards those of meteoric water (Figure 10) [2]. These results indicate that the initial ore-forming fluid of the Da'anhe gold deposit was derived from magmatic water that dissolved into the gabbro-dioritic magma. With continuous mineralization, the fluid mixed with meteoric water during the early stage of the quartz-sulfide period, and the mixing proportion gradually increased during the subsequent mineralization process until the end of mineralization at which point the system was dominated by meteoric water.

#### 6.4. Metallogenic Pressure and Depth Estimation

To better understand the physical and chemical conditions involved in the mineralization process of the Da'anhe deposit, we calculated the pressure and depth at each stage.

Previous studies [60,61] have suggested that the trapping pressure can be estimated only when the exact trapping temperature is known or when FIs are trapped during phase separation. The coexistence of S-type, W1-type and W2-type FIs with similar temperature ranges occurred during the skarn period of the Da'anhe gold deposit, indicating that fluid immiscibility occurred during the early stage of mineralization. Previous studies have shown that cooling to a temperature below 400 °C leads to a transition from ductile to brittle rock behaviour, and therefore causes a change from lithostatic to hydrostatic pressure conditions [62]. The FIs in the quartz-sulfide period formed below 400 °C (137–366 °C), which indicates that the metallogenic system changed from lithostatic to hydrostatic pressure conditions. Therefore, the trapping pressures and depth were estimated using FIncor software [60]. The calculated results show that the metallogenic pressures during each mineralization stage (I<sub>1</sub>, I<sub>2</sub>, II<sub>1</sub>, II<sub>2</sub> and II<sub>3</sub>) in the Da'anhe deposit were 46.7–65.3 MPa, 35.2–47.9 MPa, 24.5–37.3 MPa, 18.0–30.2 MPa and 9.25–18.8 MPa, corresponding to mineralization depths of 5.43–6.52 km (average of 6.03 km), 3.52–5.51 km (average of 4.44 km), 2.45–3.73 km (average of 3.11 km), 1.80–3.02 km (average of 2.27 km) and 0.93–1.88 km (average of 1.36 km), respectively. As mentioned above, gold precipitated mainly during the quartz sulfide stage, so the depth of gold deposit formation ranged from 2.27–3.11 km. At present, the orebodies are close to the surface (<500 m), indicating strong uplift and denudation after the mineralization period. This result also corresponds to the denudation depth of approximately 3.0 km in the Lesser Xing'an Range since the Jurassic [6]. Based on the above characteristics, we suggest that the Da'anhe deposit has undergone severe erosion, making it difficult to identify industrial ore bodies at depth (Figure 13).



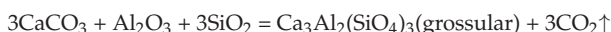
**Figure 13.** Simplified sketch that metallogenic model of the Da'anhe Au deposit.

#### 6.5. Metallogenic Mechanism and Process

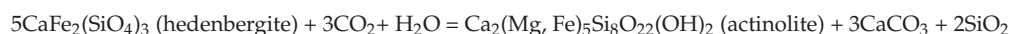
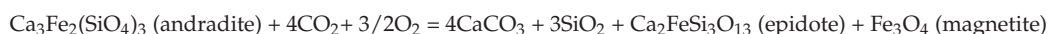
In magmatic-hydrothermal metallogenic systems, fluid boiling and fluid mixing are considered the most effective ways to restrict metal enrichment and precipitation [63]. The S-Pb isotopic characteristics of the metal sulfides and the H-O isotopic characteristics of the gangue minerals indicate that the initial ore-forming materials and ore-forming fluids of the Da'anhe gold deposit originated from gabbro-dioritic magma related to mineralization (Figures 10–12). The temperature of the magma chamber in the deep part of the Da'anhe deposit was very high, and the surrounding rock exhibited ductile



characteristics, thereby preventing interactions between the magma solution fluid and the external fluid. [62]. When the initial ore-bearing fluid rose to the shallow part of the upper crust along with the magma and met the carbonate (approximately 6.03 km), ore-bearing fluids with high temperatures ( $T = 393\sim 520\text{ }^{\circ}\text{C}$ ) and intermediate to high salinities ( $S = 11.2\%\sim 51.0\%$  NaCl equiv.) coexisted, and the reducing fluid underwent double metasomatism with the carbonate to form grossular and diopside (Stage I<sub>1</sub>) (Figure 4C,D). The chemical reactions are as follows:



Garnet and pyroxene contain three types of FIs (Figure 7A,B): S-type, W1-type and W2-type FIs, indicating that immiscibility caused by fluid boiling occurred in the early stage of mineralization. This process resulted in phase separation and the coexistence of different types of FIs in similar temperature ranges (Figure 8A–D) [64–66]. In the late skarn stage (Stage I<sub>2</sub>), the ore-bearing hydrothermal solution continued to rise (reaching approximately 4.44 km). Although the overall temperature of the hydrothermal solution decreased during this time, it was still part of the hydrothermal system with high temperatures ( $T = 336\sim 431\text{ }^{\circ}\text{C}$ ) and high salinities ( $S = 2.06\%\sim 43.9\%$  NaCl equiv.) (Figure 8E,F). The FI evidence indicates that the ore-forming fluid began to shift to a subcritical state during this stage, and anhydrous skarn minerals, such as garnet and pyroxene, which formed during the early stage, underwent degenerative alteration and were replaced by water-bearing skarn minerals, such as epidote (Figure 5B,E), tremolite (Figures 4F and 5C), actinolite (Figure 4E) and chlorite. This process was accompanied by the precipitation of a small amount of magnetite (Figure 5G). The equations for the reactions in the late skarn stage is as follows [67]:



Studies have shown that the process of skarn formation produces a large amount of free space, resulting in the release of pressure in the metallogenic system as well as boiling [10]. We found that the skarn minerals that formed early in the mining area were broken into breccia and cemented by quartz, chalcopyrite and pyrite (Figure 4G), indicating a sudden release of pressure during the skarn period. The petrographic study of FIs in the Da'anhe deposit shows that different types of FIs in skarn minerals (garnet, pyroxene and epidote) developed during the skarn stage (Figure 7A–C). According to the Th-salinity correlation diagram of FIs, high- and low-salinity FIs coexist within similar temperature intervals (Figure 8A–F), indicating that the ore-forming fluids experienced boiling [61].

The quartz-sulfide stage (Stage II<sub>1</sub> and Stage II<sub>2</sub>) was the gold mineralization stage (Figures 4I and 5L). When the gold started to precipitate, the ore-forming fluid was part of a medium- to high-temperature and medium- to low-salinity reducing system ( $T = 226\sim 366\text{ }^{\circ}\text{C}$ ;  $S = 4.17\%\sim 9.73\%$  NaCl equiv., with  $\text{CH}_4$  and  $\text{H}_2\text{O}$  as the main gases) (Figures 8G–J and 9D,E). The ranges of temperature and pressure were relatively large. Studies have shown that gold migrates mainly in the form of chloride complexes in low- to high-temperature hydrothermal systems [68,69], and contributes to the control of the stability of metal complexes in ore-forming fluids because a decrease in temperature leads to the decomposition of metal chlorides and the precipitation of minerals [61,70]. Therefore, the solubility of Au in an ore-bearing fluid gradually decreases as the ore-forming fluid temperature decreases, and Au gradually precipitates in the ore-forming system.

In addition, fluid boiling during the skarn period caused the  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{HCl}$  and  $\text{CO}_2$  components in the gas phase from escape to the original uniform fluid phase; this process

resulted in an increase in the pH of the fluid, an increase in the concentrations of reduced sulfur and metal elements, and a decrease in the chloride ion concentration [71–73]. In addition, the fluid that separated from the magma underwent a water-rock reaction with the surrounding rock (Figure 10), causing  $\text{CH}_4$  to enter the mineralization system, leading to a continued decrease in the oxygen fugacity of the fluid [74–76]. Changes in the physical and chemical conditions of ore-forming fluids can promote the decomposition of metal complexes and eventually lead to the reaction of  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and other metal ions with  $\text{HS}^-$  ions in solution, forming small amounts of metal sulfides (pyrite, pyrrhotite, chalcopyrite, sphalerite, etc.) [69,77].

In the quartz-carbonate stage (Stage II<sub>3</sub>), after boiling, mixing and water-rock reactions in the previous stages, the initial ore-bearing hydrothermal fluid changed to a low-temperature and low-salinity system ( $T = 137\text{--}247\text{ }^\circ\text{C}$ ;  $S = 0.87\%\text{--}3.37\%$  NaCl equiv.) (Figure 8K,L). At this time, meteoric water entered and dominated the metallogenic system (Figure 10), and large amounts of quartz and calcite began to precipitate from the fluid, forming quartz-carbonate veins and cutting through skarns and orebodies (Figure 4L) and marking the end of mineralization.

Overall, the mineralization in the Da'anhe deposit experienced an evolutionary process from high temperatures and intermediate to high salinities to low temperatures and low salinities. Fluid boiling and mixing were the mechanisms driving gold precipitation.

#### 6.6. Significant Indicators for Identifying Different Types of Skarn Deposits

Numerous skarn deposits have developed in NE China, and skarn gold deposits are mainly associated with copper deposits (such as the Laozuoshan Cu-Au deposit and Yuejinshan Cu-Au deposit). The Da'anhe deposit is the only independent skarn gold deposit in this region. By analysing the genesis and mineralization characteristics of the skarn deposits in the region, we suggest that the reasons for the formation of the Da'anhe independent skarn gold deposit are as follows.

Skarn deposits in northeastern China mainly formed in the late Permian-Early Triassic period (Baoshan Cu deposit [10]; Laozuoshan Cu-Au deposit [78]), Jurassic (Cuihongshan Fe-polymetallic deposit [14]; Ergu Fe-Zn polymetallic deposit [12]), and Early Cretaceous (Huanggangliang Fe-Sn deposit [79]; Haobugao Pb-Zn deposit [48]; Xieertala Fe-Zn deposit [80]; Tongshan Cu-Mo deposit [81]), while independent skarn gold deposits formed only in the Early Jurassic period (184–203 Ma, [19,20,43]. From the perspective of magmatic properties related to mineralization, the gabbro-dioritic magma related to the mineralization of the Da'anhe deposit originated from lower crust or mantle wedge metasomatized by subduction fluid, and such magmas are characterized by reducing conditions and a high water content ( $\Delta\text{FMQ} = 0.17$ ,  $\log(f\text{O}_2) = -15.11$ , water content = 6.80 wt.%, [49]). The magmas related to the mineralization of the skarn Fe-Cu-Pb-Zn-Ag-W-Sn deposit were mostly felsic magmas (Chaobuleng Fe-polymetallic deposit [82]; Xulaojiugou Pb-Zn deposit [16]) or highly differentiated alkaline granitic magmas (Cuihongshan Fe-polymetallic deposit [14]), which were mainly derived from partial melting of the crust. These magmas were typically weakly oxidized to oxidized and had a high water content (Xieertala Fe-Zn deposit [80]; Ergu Fe-Cu polymetallic deposit [49]). In terms of the temperature during metal precipitation, the temperature during the precipitation of skarn Fe-Cu deposits is relatively high, corresponding to medium- to high-temperature mineralization (235–402  $^\circ\text{C}$ , Ergu Fe-Cu polymetallic deposit [11]; 200–350  $^\circ\text{C}$ , Handagai Fe-Cu deposit [83]). The temperature during the precipitation of skarn Pb-Zn-Ag deposits varies significantly (Xiaoxilin Pb-Zn deposit, 188.6–398.3  $^\circ\text{C}$  [43]; Baiyinnuoer, ~350  $^\circ\text{C}$  [84]). The temperature at which gold precipitated in the Da'anhe deposit was mainly in the medium temperature range (226–305  $^\circ\text{C}$ ). Therefore, we propose that the properties of the magma and ore-forming fluids may contribute to the specific mineralization of skarn deposits, which has guiding significance for identifying different types of skarn deposits.

## 7. Conclusions

- (1) The Da'anhe deposit is a calcareous reduced skarn Au deposit related to the metasomatism of gabbro-dioritic magma and marble in the middle-deep part of the crust. The metallogenic process involved skarn and quartz-sulfide periods. Gold precipitated mainly in the late quartz sulfide stage and to a lesser extent in.
- (2) The initial ore-forming fluid of the Da'anhe deposit was derived from the gabbro-dioritic magma. Boiling and mixing were the main mechanisms driving gold and sulfide precipitation. The ore-forming material was mainly derived from the gabbro-dioritic magma.
- (3) The Da'anhe deposit was formed at depths ranging from 2.27 to 3.11 km, and is a medium to deep skarn gold deposit. Combined with regional observations, the rocks in the study area have been uplifted to the shallow surface (<500 m), and its prospecting potential is limited.
- (4) The distinctive nature of the ore-forming magma (source, reducing conditions and high water content,  $\Delta\text{FMQ} = 0.17$ ,  $\log(f\text{O}_2) = -15.11$ , water content = 6.80 wt.%) was key to the formation of the Da'anhe skarn gold deposit.

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## Article

# Geochemistry, Chronology and Tectonic Implications of the Hadayang Schists in the Northern Great Xing'an Range, Northeast China

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**Abstract:** The Late Paleozoic tectonic evolution of the Xing'an block in the eastern Central Asian orogenic belt has long been the subject of debate. In this paper, a comprehensive study of U–Pb zircon ages, Lu–Hf isotopes and whole-rock elemental analyses was carried out on Hadayang schists. Representative samples of the epidote-biotite-albite schist and biotite-albite schist yielded the weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $360 \pm 2$  Ma and  $355 \pm 3$  Ma, respectively. This indicated the presence of Late Devonian–Early Carboniferous intermediate-basic rocks in the eastern Xing'an block. The Hadayang schists exhibited a Na-rich, tholeiitic and calc-alkaline affinity in composition with low Mg# (35.2–53.0), Cr (23.7–86.5 ppm), Ni (21.1–40.0 ppm) and Co (12.1–30.6 ppm). They were characterized by enrichment of LILEs, depletion of HFSEs and highly positive zircon  $\varepsilon_{\text{Hf}}(t)$  values (the average values were +8.93 and +9.29, respectively). The magma source of the Hadayang schists was a mantle that consisted of both spinel and garnet lherzolite, with a partial melting degree of 1%–5%, and it had undergone fractional crystallization of olivine, orthopyroxene and plagioclase. The Hadayang schists, together with other Late Devonian–Early Carboniferous intermediate-basic magmatic rocks in the eastern Xing'an block, were formed in an intracontinental extension tectonic setting similar to that of the North American Basin and Range basalt. Moreover, Late Devonian–Early Carboniferous ophiolite under a similar tectonic background in the western Xing'an block has been reported. We believe that the Xing'an block would have been in the stage of intracontinental extension during the Late Devonian–Early Carboniferous.

**Keywords:** eastern Xing'an block; late Devonian–early Carboniferous; Hadayang schists; petrogenesis; tectonic implications

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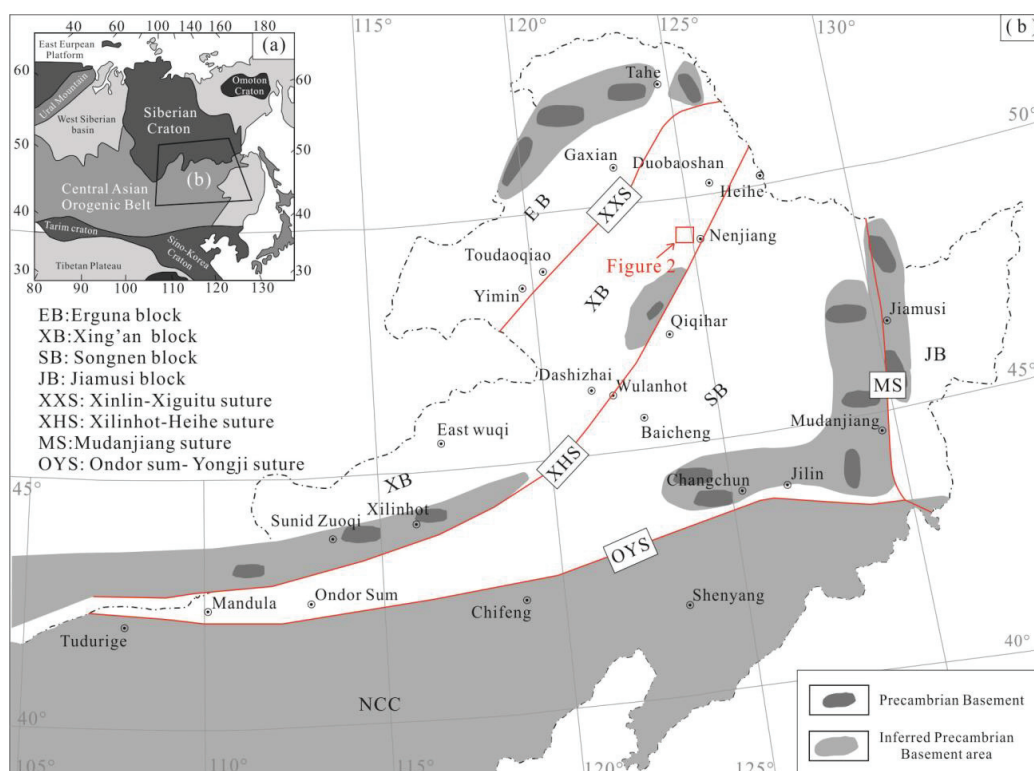


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## 1. Introduction

The Central Asian orogenic belt (CAOB) is located between the Siberian craton and the Sino-Korean craton, and is composed of a series of micro-continental blocks and suture zones [1–5] (Figure 1a). The Xing'an–Mongolia orogenic belt (XMOB) is located in the eastern section of the CAOB, and is made up of several microcontinents, including the Erguna, Xing'an, Songnen and Jiamusi–Khanka blocks [6–11] (Figure 1b). Although much progress has been made in the study area of the tectonic pattern and evolutionary history of the XMOB in recent years, there are still many controversies, among which the dating of the integration of the Xing'an (XB) and Songnen blocks (SB) is the most prominent. For example, Xu et al. [6] argued that the XB and SB combined along the Angin Sum–Xilinhot–Heihe line before the Devonian [7,12]; Liu et al. [8] proposed that these two blocks closed along the Hegenshan–Moguqi–Heihe line during the late Early Carboniferous and early Late Carboniferous [9,13–15]; Xu et al. [11] believed that the XB and SB combined along the Xilinhot–Ulanhot–Nenjiang–Heihe line, and the time limit was the late Early Carboniferous [16]. In addition, the time limit of convergence is also dated

to the Late Devonian to Early Carboniferous [17,18], to before the Permian [19,20] and to the Triassic [21,22].



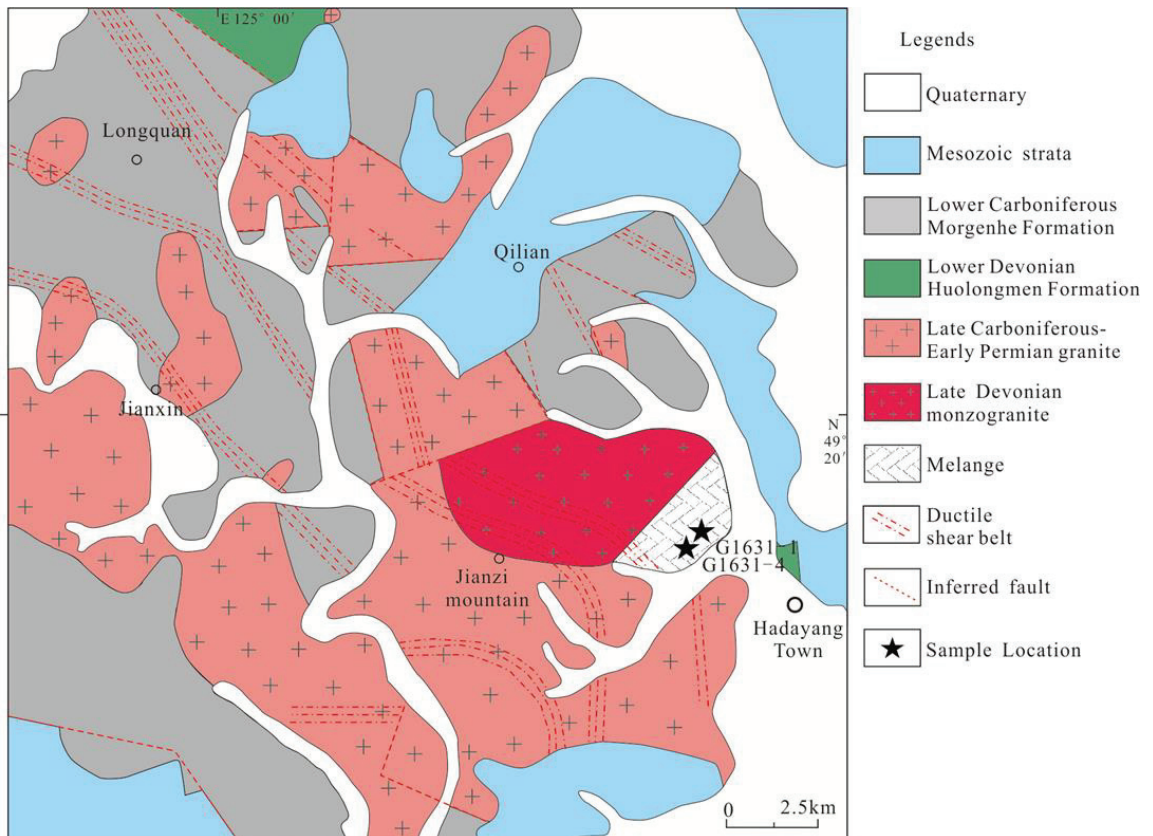
**Figure 1.** Pre-Devonian blocks in XMOB, northeast China: (a) location of the CAOB; (b) blocks in the XMOB (modified after [7]).

Through the analysis of the above different views, it can be found that one of the focuses of the debate is whether there was subduction in the ocean basin between the XB and the SB in the late Paleozoic, and the study of the tectonic background of the late Paleozoic igneous rock in the XB can provide important evidence for solving the above problems. Compared with granitic rocks, mafic magmatic rocks originate directly from partial melting of mantle and the geochemistry is less affected by late transformation, so they become ideal objects for the derivation of mantle source characteristics and regional tectonic background [23]. Therefore, we report zircon U-Pb geochronology, Hf isotopes and whole-rock geochemistry studies on late Devonian–early Carboniferous metamorphic intermediate-basic volcanic rocks in the southern XB, to determine their origins and tectonic setting. This study provides a more detailed understanding of the evolution history of the XB and SB in the late Paleozoic. Furthermore, it provides important constraints for the study of the tectonic evolution of the XMOB.

## 2. Geological Settings and Sampling

The study area was located in the Hadayang area of Molidawa Banner in the eastern part of the Inner Mongolia Autonomous Region and it tectonically belongs to the southern part of the XB (Figure 2). As the oldest block in the XMOB, the Precambrian record of the EB is well developed, and the oldest rock exposed is a set of Neoproterozoic–Paleoproterozoic granitic gneiss [24–27]. The Xinghuadukou Group, which was previously considered to be of Paleo–Mesoproterozoic age, may have formed in the Neoproterozoic [27–31].

In addition, Neoproterozoic magmatism is also well developed in the EB [31–34]. The XB is traditionally based on Precambrian strata such as the Xinghuadukou Group, the Jiageda Formation and the Wolegen Group, but recent research shows that these strata were formed in the Paleozoic [35–37]. In recent years, a series of Neoproterozoic–Paleoproterozoic magmatic rocks [38–42] and metamorphic rock series [43] have been identified in the Ulanhot–Longjiang area, suggesting the existence of Precambrian basement in the XB. After the convergence of the EB and XB along the XXS in the early Paleozoic [44–49] (Figure 1b), the Erguna–Xing’an block (EXB) was covered by the Early Paleozoic–Lower Permian marine and continental alternative deposition, the Upper Permian continental sedimentary strata and the Mesozoic volcanoclastic rocks, and developed multistage Paleozoic–Mesozoic magmatic intrusion. The SB is located in the southeast of the EXB, which is bounded by the XHS (Figure 1b). The Dongfengshan Group and Tadong Group in the eastern SB, which are traditionally considered as “Paleoproterozoic”, were formed in the Neoproterozoic [50–52], accompanied by contemporaneous magmatic intrusions [53–56]. The western SB is mostly covered by late Mesozoic–Cenozoic volcanoclastic sediments.



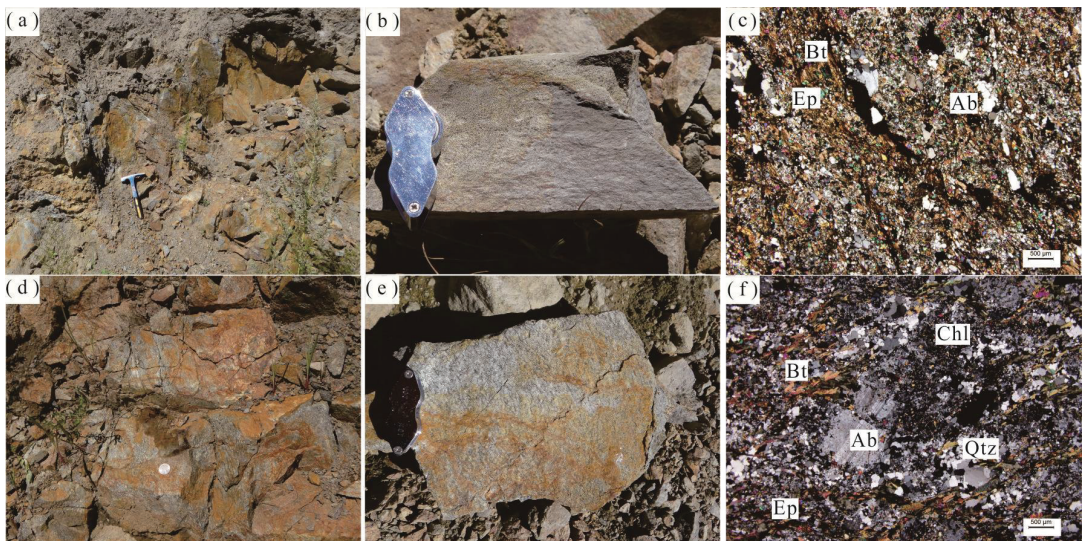
**Figure 2.** Simplified geological map of Hadayang area and locations of samples used in this study.

The late Paleozoic strata in the study area include the Lower Devonian Huolongmen Formation and the Lower Carboniferous Morgenhe Formation (Figure 2). The Lower Devonian Huolongmen Formation is mainly composed of clastic sedimentary rocks with a small amount of intermediate volcanic rocks, and is affected by a poorly developed ductile deformation. The formation age of chlorite muscovite schist (protolith is volcanic rock) is 414 Ma [57]. The Lower Carboniferous Morgenhe Formation is mainly composed of



weakly metamorphic intermediate-acid volcanic rocks, which are generally mylonitic. The zircon U-Pb age of the volcanic rocks is 353 to 352 Ma [58,59]. Late Paleozoic intrusive rocks include Late Devonian mylonitic syenite granite [60], Late Carboniferous–Early Permian granodiorite, syenogranite and alkali feldspar granite. The above are mostly covered by Mesozoic volcanic rocks and Cenozoic detrital sedimentary rocks. In addition to the above features, there is also a Hadayang melange developed in the study area [61,62]. The matrix in the melange is mainly composed of schist, while blocks consist of schist, mafic–ultramafic rocks and meta-acidic volcanic rocks [62].

Two samples were collected from the blocks of Hadayang melange for age dating, and the sample locations are shown in Figure 2. At each of these two sites, six additional samples were collected for geochemical and petrological analysis. Sample G1631-1, an epidote-biotite-albite schist ( $49^{\circ}18'28''$  N,  $125^{\circ}06'33''$  E, Figures 2 and 3a–b), showed porphyroblastic, lepidoblastic texture and schistose structure (Figure 3c). The mineral assemblage consisted of albite (~27%), biotite (~30%), chlorite (~8%), epidote (~20%), quartz (~8%) and opaque mineral (~7%) (Figure 3c). The content of the remaining phenocryst was about 5%, and the composition included opaque mineral aggregates and albite. The matrix included biotite, chlorite, epidote, quartz and albite. Sample G1631-4, a biotite-albite schist ( $49^{\circ}18'25''$  N,  $125^{\circ}06'31''$  E), was located near Sample G1631-1 (Figures 2 and 3d–e). Petrographically, the biotite-albite schist had porphyroblastic, lepidoblastic texture and schistose structure, consisting of biotite (~15%), chlorite (~8%), epidote (~12%), albite (~40%) and quartz (~25%) (Figure 3f). The crystalloblasts were composed of oligoclase and albite, and the oligoclase was semi-euhedral wide plate with matrix components interspersed, and content of less than 1%. The albite was granular and contained matrix minerals biotite, chlorite and epidote inclusions, accounting for about 5%. The matrix included biotite, chlorite, epidote, quartz and albite (Figure 3f).



**Figure 3.** Field occurrence and microscope views of the Hadayang schists. (a–c) Epidote-biotite-albite schist. (d–f) Biotite-albite schist.

### 3. Analytical Methods

#### 3.1. Major and Trace Element Analysis

The major and trace element analyses were carried out at the Shenyang Mineral Resources Supervision and Inspection Center, Shenyang, China. Whole-rock major element concentrations were determined by X-ray fluorescence spectrometry, yielding an analytical

precision better than 2%. Trace element and rare earth element (REE) concentrations were determined by ICP-MS, yielding an analytical precision better than 5% for elements with concentrations of >10 ppm, <8% for elements with concentrations of <10 ppm and <10% for the transition metals.

### 3.2. Zircon U-Pb Dating

U-Pb dating analyses were conducted by LA-ICP-MS at Beijing Createch Testing Technology Co., Ltd. (Beijing, China). The detailed operating conditions for the laser ablation system and the ICP-MS instrument and data reduction were the same as described by Hou et al. [63]. Laser sampling was performed using an ESI NWR 193 nm laser ablation system. An AnalytikJena PQMS Elite ICP-MS (Analytik Jena AG, Jena, Germany) instrument was used to acquire ion-signal intensities. Helium was applied as a carrier gas. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP. Each analysis incorporated a background acquisition of approximately 15–20 s (gas blank) followed by 45 s of data acquisition from the sample. Off-line raw data selection and integration of background and analyte signals, and time-drift correction and quantitative calibration for U-Pb dating, were performed by ICPMSDataCal [64]. Zircon GJ-1 was used as the external standard for U-Pb dating, and was analyzed twice every 5–10 analyses. Time-dependent drifts of U-Th-Pb isotopic ratios were corrected using a linear interpolation (with time) for every 5–10 analyses according to the variations of GJ-1 (i.e., 2 zircon GJ-1 + 5–10 samples + 2 zircon GJ-1) [64]. Uncertainty of preferred values for the external standard GJ-1 was propagated to the ultimate results of the samples. In all analyzed zircon grains, the common Pb correction was not necessary due to the low signal of common  $^{204}\text{Pb}$  and high  $^{206}\text{Pb}/^{204}\text{Pb}$ . U, Th and Pb concentration was calibrated by NIST 610. Concordia diagrams and weighted mean calculations were made using IsoPlot/Ex\_ver3. The zircon Plesovice was dated as unknown samples and yielded a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $337.5 \pm 2.4$  Ma (2SD,  $n = 5$ ), which was in good agreement with the recommended  $^{206}\text{Pb}/^{238}\text{U}$  age of  $337.13 \pm 0.37$  Ma (2SD) [65].

### 3.3. Lu-Hf Isotope Analysis

Zircon in situ Hf isotope analysis was carried out using a RESOLUTION SE 193 laser-ablation system attached to a Thermo Fisher Scientific Neptune Plus MC-ICP-MS at Beijing Createch Testing Technology Co., Ltd (Beijing, China). Instrumental conditions and data acquisition protocols were as described by Hou et al. [66]. A stationary spot used a beam diameter of  $\sim 55$   $\mu\text{m}$ . Helium was used as the carrier gas to transport ablated material from the laser-ablation cell after which it was mixed with Ar prior to entering the ICP-MS torch.  $^{176}\text{Lu}/^{175}\text{Lu} = 0.02658$  and  $^{176}\text{Yb}/^{173}\text{Yb} = 0.796218$  ratios were determined to correct for the isobaric interferences of  $^{176}\text{Lu}$  and  $^{176}\text{Yb}$  on  $^{176}\text{Hf}$ . For instrumental mass bias correction, Yb isotope ratios were normalized to  $^{172}\text{Yb}/^{173}\text{Yb} = 1.35274$  and Hf isotope ratios to  $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$  using an exponential law. The mass bias behavior of Lu was assumed to follow that of Yb; the mass bias correction protocol was as described by Hou et al. [66].

## 4. Analytical Results

### 4.1. Whole-Rock Geochemistry

Results of the major element, trace element and REE analyses of the samples from the Hadayang schists are listed in Table 1.

Table 1. Analytical results for the major (w%) and trace elements ( $\times 10^{-6}$ ) of Hadayang schists.

| Lithology                          |           | Epidote-Biotite-Albite Schist |           |           |           |           | Biotite-Albite Schist |           |           |           |           |           |
|------------------------------------|-----------|-------------------------------|-----------|-----------|-----------|-----------|-----------------------|-----------|-----------|-----------|-----------|-----------|
| Sample No.                         | G1631-1.1 | G1631-1.2                     | G1631-1.3 | G1631-1.4 | G1631-1.5 | G1631-1.6 | G1631-4.1             | G1631-4.2 | G1631-4.3 | G1631-4.4 | G1631-4.5 | G1631-4.6 |
| SiO <sub>2</sub> (%)               | 49.28     | 50.55                         | 50.47     | 50.16     | 49.46     | 51.15     | 58.07                 | 58.36     | 58.82     | 55.44     | 57.72     | 56.23     |
| Al <sub>2</sub> O <sub>3</sub> (%) | 16.75     | 16.56                         | 16.76     | 16.51     | 16.99     | 16.73     | 15.98                 | 15.84     | 16.17     | 16.46     | 16.27     | 16.30     |
| Fe <sub>2</sub> O <sub>3</sub> (%) | 8.08      | 7.80                          | 7.18      | 7.97      | 7.95      | 7.61      | 2.97                  | 2.73      | 2.65      | 2.89      | 5.57      | 5.18      |
| FeO (%)                            | 3.05      | 3.28                          | 3.32      | 3.14      | 3.41      | 3.32      | 3.73                  | 4.00      | 4.09      | 4.40      | 2.43      | 2.97      |
| CaO (%)                            | 12.68     | 11.54                         | 9.51      | 11.27     | 12.09     | 11.42     | 4.43                  | 4.93      | 4.24      | 5.30      | 5.93      | 6.97      |
| MgO (%)                            | 3.31      | 3.59                          | 3.99      | 3.45      | 3.19      | 3.28      | 3.96                  | 3.83      | 4.01      | 4.40      | 3.04      | 3.17      |
| K <sub>2</sub> O (%)               | 0.17      | 0.18                          | 0.73      | 0.26      | 0.09      | 0.02      | 0.76                  | 0.86      | 1.40      | 0.90      | 1.38      | 1.97      |
| Na <sub>2</sub> O (%)              | 0.32      | 0.42                          | 1.28      | 0.47      | 0.26      | 0.03      | 4.82                  | 3.86      | 4.33      | 3.97      | 2.77      | 2.68      |
| TiO <sub>2</sub> (%)               | 1.80      | 1.70                          | 1.79      | 1.68      | 1.77      | 1.66      | 1.08                  | 1.02      | 1.02      | 1.06      | 1.58      | 1.34      |
| P <sub>2</sub> O <sub>5</sub> (%)  | 1.07      | 1.02                          | 1.12      | 1.02      | 1.05      | 1.03      | 0.61                  | 0.57      | 0.58      | 0.61      | 0.75      | 0.69      |
| MnO (%)                            | 0.14      | 0.15                          | 0.13      | 0.15      | 0.16      | 0.15      | 0.18                  | 0.17      | 0.13      | 0.19      | 0.13      | 0.15      |
| LOI (%)                            | 3.48      | 3.45                          | 3.45      | 3.45      | 3.36      | 3.47      | 3.24                  | 3.59      | 2.67      | 4.05      | 2.23      | 2.26      |
| SUM                                | 100.14    | 100.26                        | 99.75     | 99.53     | 99.78     | 99.86     | 99.83                 | 99.75     | 100.11    | 99.67     | 99.81     | 99.90     |
| FeO <sup>T</sup>                   | 10.33     | 10.29                         | 9.79      | 10.32     | 10.57     | 10.18     | 6.40                  | 6.45      | 6.47      | 7.01      | 7.44      | 7.63      |
| Mg#                                | 36.51     | 38.50                         | 42.25     | 37.53     | 35.14     | 36.62     | 52.61                 | 51.58     | 52.63     | 52.97     | 42.30     | 42.74     |
| Na <sub>2</sub> O/K <sub>2</sub> O | 1.96      | 2.31                          | 1.76      | 1.84      | 2.98      | 1.56      | 6.35                  | 4.47      | 3.08      | 4.43      | 2.01      | 1.36      |
| Na <sub>2</sub> O+K <sub>2</sub> O | 0.51      | 0.62                          | 2.09      | 0.76      | 0.36      | 0.04      | 5.77                  | 4.91      | 5.88      | 5.09      | 4.26      | 4.76      |
| σ                                  | 0.03      | 0.04                          | 0.46      | 0.06      | 0.02      | 0.00      | 1.95                  | 1.37      | 1.99      | 1.73      | 1.12      | 1.55      |
| Y                                  | 27.63     | 27.19                         | 28.93     | 27.84     | 26.50     | 27.18     | 28.98                 | 26.43     | 26.03     | 27.01     | 43.88     | 36.10     |
| La                                 | 34.09     | 33.83                         | 30.10     | 31.19     | 32.41     | 32.91     | 44.17                 | 36.95     | 38.22     | 43.62     | 54.62     | 49.92     |
| Ce                                 | 75.52     | 75.02                         | 68.90     | 71.33     | 72.55     | 72.89     | 93.02                 | 80.91     | 82.54     | 93.07     | 119.90    | 109.83    |
| Pr                                 | 9.97      | 9.50                          | 9.39      | 9.51      | 9.56      | 9.69      | 10.92                 | 10.07     | 10.20     | 11.56     | 14.78     | 12.36     |
| Nd                                 | 47.38     | 48.12                         | 46.47     | 46.41     | 45.61     | 46.99     | 55.88                 | 47.35     | 47.19     | 53.38     | 66.40     | 58.93     |
| Sm                                 | 11.51     | 11.46                         | 11.63     | 11.25     | 11.13     | 11.25     | 12.39                 | 11.05     | 11.07     | 11.84     | 15.27     | 12.42     |
| Eu                                 | 2.54      | 2.39                          | 2.76      | 2.58      | 2.41      | 2.51      | 3.17                  | 2.90      | 2.97      | 3.22      | 2.93      | 2.78      |
| Gd                                 | 7.49      | 7.54                          | 7.80      | 7.65      | 7.48      | 7.68      | 7.91                  | 7.21      | 7.41      | 7.88      | 10.35     | 8.31      |
| Tb                                 | 1.18      | 1.20                          | 1.25      | 1.20      | 1.15      | 1.21      | 1.25                  | 1.15      | 1.14      | 1.21      | 1.68      | 1.41      |
| Dy                                 | 6.10      | 6.05                          | 6.47      | 6.21      | 5.91      | 6.05      | 6.47                  | 5.93      | 5.95      | 6.31      | 9.14      | 7.19      |
| Ho                                 | 1.13      | 1.07                          | 1.20      | 1.19      | 1.11      | 1.11      | 1.20                  | 1.15      | 1.11      | 1.16      | 1.71      | 1.34      |
| Er                                 | 3.05      | 2.86                          | 3.18      | 2.98      | 2.95      | 3.07      | 3.59                  | 3.15      | 3.05      | 3.17      | 4.92      | 4.09      |
| Tm                                 | 0.46      | 0.42                          | 0.46      | 0.46      | 0.42      | 0.46      | 0.52                  | 0.48      | 0.47      | 0.50      | 0.76      | 0.66      |
| Yb                                 | 2.28      | 2.25                          | 2.41      | 2.26      | 2.15      | 2.25      | 2.93                  | 2.63      | 2.59      | 2.58      | 3.91      | 3.36      |

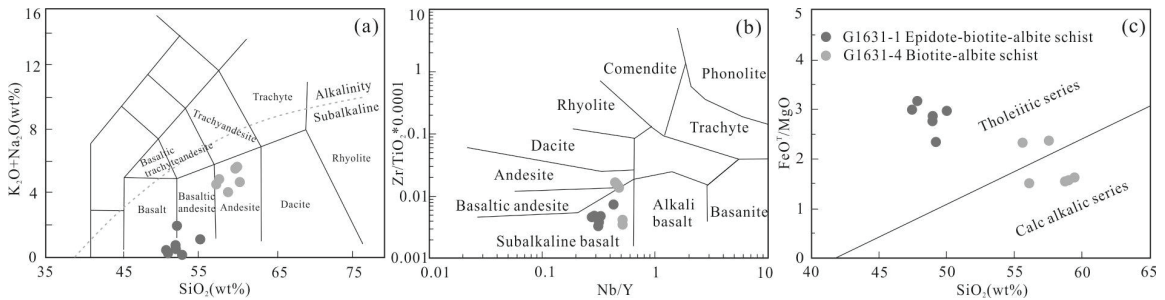


Table 1. Cont.

| Lithology                        | Epidote-Biotite-Albite Schist |           |           |           |           |           |           |           |           |           | Biotite-Albite Schist |           |  |  |
|----------------------------------|-------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------------------|-----------|--|--|
|                                  | G1631-1.1                     | G1631-1.2 | G1631-1.3 | G1631-1.4 | G1631-1.5 | G1631-1.6 | G1631-4.1 | G1631-4.2 | G1631-4.3 | G1631-4.4 | G1631-4.5             | G1631-4.6 |  |  |
| Sample No.                       |                               |           |           |           |           |           |           |           |           |           |                       |           |  |  |
| Lu                               | 0.31                          | 0.31      | 0.34      | 0.33      | 0.31      | 0.30      | 0.38      | 0.37      | 0.36      | 0.37      | 0.55                  | 0.47      |  |  |
| ΣREE                             | 202.99                        | 202.01    | 192.34    | 194.53    | 195.14    | 198.36    | 243.82    | 211.29    | 214.24    | 239.68    | 306.92                | 273.07    |  |  |
| LREE                             | 181.00                        | 180.32    | 169.25    | 172.27    | 173.66    | 176.24    | 219.56    | 189.22    | 192.18    | 216.50    | 273.90                | 246.24    |  |  |
| HREE                             | 21.98                         | 21.69     | 23.10     | 22.27     | 21.48     | 22.12     | 24.25     | 22.07     | 22.06     | 23.18     | 33.02                 | 26.83     |  |  |
| L/H                              | 8.23                          | 8.31      | 7.33      | 7.74      | 8.09      | 7.97      | 9.05      | 8.57      | 8.71      | 9.34      | 8.29                  | 9.18      |  |  |
| La <sub>N</sub> /Yb <sub>N</sub> | 10.73                         | 10.78     | 8.97      | 9.89      | 10.80     | 10.49     | 10.82     | 10.09     | 10.58     | 12.06     | 10.02                 | 10.65     |  |  |
| δCe                              | 0.99                          | 1.01      | 1.00      | 1.01      | 1.00      | 0.99      | 1.01      | 1.01      | 1.00      | 1.00      | 1.01                  | 1.05      |  |  |
| δEu                              | 0.78                          | 0.74      | 0.83      | 0.80      | 0.76      | 0.78      | 0.92      | 0.93      | 0.94      | 0.96      | 0.67                  | 0.79      |  |  |
| Li                               | 18.58                         | 20.34     | 27.07     | 22.73     | 20.42     | 21.77     | 25.75     | 25.34     | 26.55     | 29.34     | 36.92                 | 40.63     |  |  |
| Sc                               | 14.27                         | 14.17     | 15.34     | 15.52     | 15.04     | 15.69     | 11.35     | 12.81     | 12.47     | 12.44     | 13.23                 | 12.99     |  |  |
| V                                | 401.29                        | 379.56    | 347.99    | 361.07    | 417.77    | 400.93    | 107.69    | 126.32    | 111.54    | 131.04    | 202.25                | 166.49    |  |  |
| Cr                               | 39.74                         | 43.51     | 29.62     | 42.25     | 41.89     | 39.04     | 86.51     | 82.63     | 75.99     | 82.93     | 23.71                 | 36.53     |  |  |
| Co                               | 24.30                         | 24.63     | 30.59     | 27.44     | 25.92     | 27.25     | 12.06     | 12.83     | 13.02     | 13.17     | 16.46                 | 15.25     |  |  |
| Ni                               | 21.15                         | 22.40     | 21.70     | 21.98     | 22.28     | 23.29     | 34.82     | 39.55     | 36.45     | 40.00     | 23.84                 | 24.71     |  |  |
| Ga                               | 23.20                         | 23.44     | 21.69     | 22.00     | 24.98     | 23.42     | 18.47     | 19.86     | 18.39     | 19.02     | 20.92                 | 20.71     |  |  |
| Rb                               | 8.83                          | 8.46      | 31.45     | 13.85     | 5.57      | 3.97      | 26.70     | 30.04     | 48.56     | 30.16     | 45.00                 | 59.66     |  |  |
| Sr                               | 1100                          | 1200      | 893       | 995       | 1400      | 1300      | 566       | 586       | 554       | 5408      | 944                   | 942       |  |  |
| Zr                               | 87.75                         | 61.90     | 71.92     | 73.22     | 88.55     | 80.19     | 185.02    | 176.05    | 166.34    | 168.27    | 27.95                 | 51.58     |  |  |
| Nb                               | 10.84                         | 10.27     | 11.11     | 10.74     | 9.10      | 8.95      | 15.52     | 14.40     | 14.34     | 15.77     | 30.61                 | 23.04     |  |  |
| Ba                               | 78.40                         | 106.57    | 146.80    | 113.68    | 82.57     | 71.06     | 308.28    | 357.57    | 419.52    | 400.07    | 474.22                | 591.36    |  |  |
| Hf                               | 0.84                          | 0.75      | 0.80      | 0.81      | 0.76      | 0.83      | 0.78      | 0.66      | 0.80      | 0.74      | 0.83                  | 0.64      |  |  |
| Ta                               | 0.85                          | 0.80      | 0.85      | 0.76      | 0.87      | 0.77      | 0.67      | 0.64      | 0.68      | 0.63      | 1.60                  | 1.07      |  |  |
| Th                               | 17.66                         | 7.07      | 6.77      | 5.97      | 5.97      | 5.51      | 7.27      | 6.82      | 7.21      | 7.56      | 7.74                  | 6.39      |  |  |
| U                                | 2.11                          | 2.20      | 2.24      | 2.13      | 2.14      | 2.08      | 2.44      | 2.33      | 2.16      | 2.40      | 3.19                  | 2.29      |  |  |

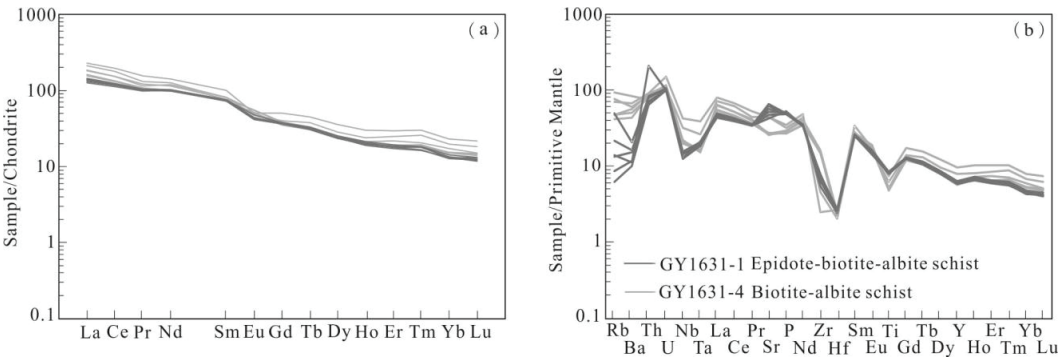
4.1.1. The Epidote-Biotite-Albite Schists

The epidote-biotite-albite schists had 49.28–51.15 wt% SiO<sub>2</sub>, 3.19–3.99 wt% MgO, 15.84–16.99 wt% Al<sub>2</sub>O<sub>3</sub>, 1.66–1.80 wt% TiO<sub>2</sub>, 0.03–1.28 wt% Na<sub>2</sub>O, 0.02–0.73 wt% K<sub>2</sub>O, 9.51–12.68 wt% CaO and 9.79–10.57 wt% total FeO. They had Mg# of  $[Mg\# = 100 \times MgO_{molar} / (MgO_{molar} + FeO_{molar})]$  35.14–42.25. The Na<sub>2</sub>O/K<sub>2</sub>O ratios ranged from 1.56–2.98, indicating that the samples belonged to the sodium series. As can be seen from the plot of SiO<sub>2</sub> vs. K<sub>2</sub>O + Na<sub>2</sub>O and Nb/Y vs. Zr/TiO<sub>2</sub>\*0.0001 diagrams (Figure 4a–b), all of these metavolcanic rocks plot in the basalt and basaltic andesite field. On a plot of SiO<sub>2</sub> vs. <sup>T</sup>FeO/MgO (Figure 4c), the samples plot in the tholeiitic field.



**Figure 4.** Classification and series diagrams of the Hadayang schists. (a) Plot of SiO<sub>2</sub> vs. K<sub>2</sub>O + Na<sub>2</sub>O (after [67]), with the alkalic/subalkalic boundary of [68] shown; (b) plot of Zr/TiO<sub>2</sub>\*0.0001 vs. Nb/Y (after [69]); (c) plot of <sup>T</sup>FeO/MgO vs. SiO<sub>2</sub> (after [70]).

The epidote-biotite-albite schists had total rare earth element (REE) concentrations from 194.53 to 202.99 ppm, with an average value of 197.56 ppm. On the chondrite-normalized REE diagram (Figure 5a), the light rare earth elements (LREEs) are moderately enriched relative to the heavy rare earth elements (HREEs) with (La/Yb)<sub>N</sub> ratios ranging from 8.97 to 10.78, while the HREEs are relatively flat. These metavolcanic rocks had slightly negative Eu anomalies ( $\delta Eu = 0.74–0.83$ ). The primitive-mantle-normalized incompatible element diagrams (Figure 5b) show that the epidote-biotite-albite schists were relatively enriched in large ion lithophile elements (LILEs) (such as Rb, Ba, Th and U) relative to high-field-strength elements (HFSEs) (such as Nb, P and Ti).



**Figure 5.** Chondrite-normalized REE patterns (a) and primitive-mantle-normalized trace element spidergrams (b) for the Hadayang schists. Normalization values are taken from [71,72].

4.1.2. The Biotite-Albite Schists

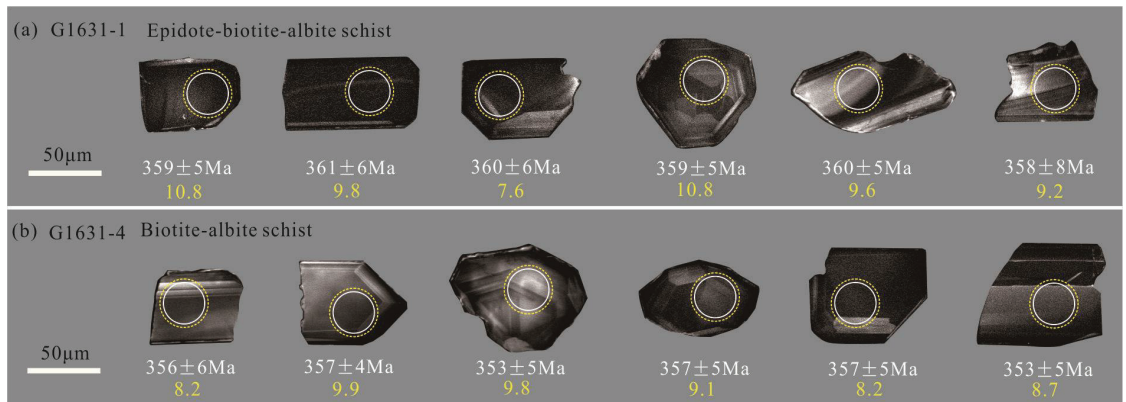
The biotite-albite schists had SiO<sub>2</sub> of 57.59–60.69 wt% and high TiO<sub>2</sub> (1.05–1.62 wt%),  $\Sigma FeO$  (6.63–7.81 wt%) and Al<sub>2</sub>O<sub>3</sub> (16.47–17.21 wt%). Their alkalis (K<sub>2</sub>O + Na<sub>2</sub>O) ranged

from 4.26 to 5.77 wt%, and the low  $K_2O/Na_2O$  ratio (0.16 to 0.74) indicated that the samples belonged to the sodium series. All of the samples plot in the andesite field on a  $SiO_2$  vs.  $Na_2O + K_2O$  diagram (Figure 4a). As can be seen from the plot of  $Zr/TiO_2 \times 0.0001$  vs.  $Nb/Y$  (Figure 4b), most of the samples plot in the subalkaline basalt and andesite fields. On the other hand, on the plot of  $FeO^T/MgO$  vs.  $SiO_2$ , except for two samples that fall into the tholeiitic field, the biotite-albite schist samples plot in the calc-alkaline field.

The biotite-albite schists had variable total rare earth element (REE) concentrations from 211.29 to 306.92 ppm, with an average value of 248.17 ppm. These metavolcanic rocks exhibited LREEs enrichment ( $(La/Yb)_N = 10.02$ – $12.06$ ) and slight negative Eu anomalies ( $\delta Eu = 0.67$ – $0.96$ ) (Figure 5a). On a primitive-mantle-normalized trace element plot (Figure 5b), the biotite-albite schist samples also appear as enriched in large ion lithophile elements (LILEs) relative to the high-field-strength elements (HFSEs), which were similar to those in the epidote-biotite-albite schists.

#### 4.2. Zircon U-Pb Dating

Cathodoluminescence (CL) images and concordia plots for the analyzed zircons are shown in Figure 6. Zircons from the epidote-biotite-albite schist sample (G1631-1) and biotite-albite schist sample (G1631-4) were mainly euhedral and elongate, with aspect ratios of 1:1–2:1. They showed straight rhythmic stripes, typical oscillatory zoning or sector zoning in CL images (Figure 6), with high Th/U ratios (0.49–1.38, Table 2), which is characteristic of magmatic zircons [73]. In total, 60 concordant  $^{206}Pb/^{238}U$  ages, obtained from 70 zircon grains, ranged from 338 to 370 Ma. Two samples yielded similar zircon U-Pb ages around 360 Ma (Figure 7), with weighted mean  $^{206}Pb/^{238}U$  ages of  $360 \pm 2$  Ma (G1631-1,  $n = 35$ , MSWD = 1.4) and  $355 \pm 3$  Ma (G1631-4,  $n = 35$ , MSWD = 2.1). The two ages were interpreted as the crystallization ages of the magmatic protolith of the two schists.



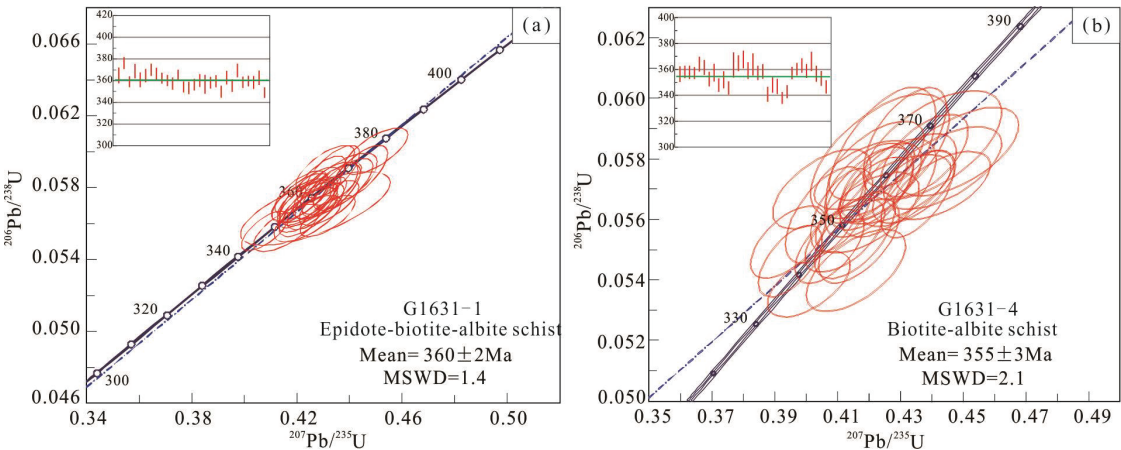
**Figure 6.** Cathodoluminescence images of zircon grains selected for analysis from the epidote-biotite-albite schist (a) and biotite-albite schist (b). The smaller white circles represent locations of LA-ICP-MS U-Pb dating, whereas the bigger yellow circles (dotted line) indicate locations of Hf isotopic analyses.

Table 2. LA-ICP-MS zircon U-Pb dating results for the Hadayang schists.

| Analytical No.                        | Th<br>(10 <sup>−6</sup> ) | U<br>(10 <sup>−6</sup> ) | Th/U | Isotopic Ratio                      |        |        |                                     |        |        | Age (Ma)                             |     |     |                                     | Concordance |                                     |     |                                      |     |    |
|---------------------------------------|---------------------------|--------------------------|------|-------------------------------------|--------|--------|-------------------------------------|--------|--------|--------------------------------------|-----|-----|-------------------------------------|-------------|-------------------------------------|-----|--------------------------------------|-----|----|
|                                       |                           |                          |      | <sup>206</sup> Pb/ <sup>238</sup> U |        |        | <sup>207</sup> Pb/ <sup>235</sup> U |        |        | <sup>207</sup> Pb/ <sup>206</sup> Pb |     |     | <sup>206</sup> Pb/ <sup>238</sup> U |             | <sup>207</sup> Pb/ <sup>235</sup> U |     | <sup>207</sup> Pb/ <sup>206</sup> Pb |     |    |
|                                       |                           |                          |      | Ratio                               | 1σ     | Ratio  | Ratio                               | 1σ     | Ratio  | 1σ                                   | Age | 1σ  | Age                                 |             | 1σ                                  | Age | 1σ                                   | Age | 1σ |
| G1631-1 Epidote biotite albite schist |                           |                          |      |                                     |        |        |                                     |        |        |                                      |     |     |                                     |             |                                     |     |                                      |     |    |
| 1                                     | 334.7                     | 354.2                    | 0.94 | 0.0582                              | 0.0011 | 0.4358 | 0.0097                              | 0.0543 | 0.0008 | 365                                  | 7   | 367 | 387                                 | 32          |                                     |     | 99.5%                                |     |    |
| 2                                     | 551.7                     | 501.4                    | 1.10 | 0.0601                              | 0.0009 | 0.4499 | 0.0080                              | 0.0543 | 0.0006 | 376                                  | 5   | 377 | 6                                   | 389         | 19                                  |     | 99.7%                                |     |    |
| 3                                     | 484.3                     | 436.0                    | 1.11 | 0.0573                              | 0.0008 | 0.4235 | 0.0067                              | 0.0537 | 0.0007 | 359                                  | 5   | 359 | 5                                   | 367         | 28                                  |     | 100.0%                               |     |    |
| 4                                     | 1201.1                    | 1055.1                   | 1.14 | 0.0589                              | 0.0010 | 0.4434 | 0.0073                              | 0.0547 | 0.0005 | 369                                  | 6   | 373 | 5                                   | 398         | 16                                  |     | 98.9%                                |     |    |
| 5                                     | 640.3                     | 554.4                    | 1.15 | 0.0576                              | 0.0011 | 0.4249 | 0.0077                              | 0.0536 | 0.0007 | 361                                  | 7   | 360 | 6                                   | 354         | 30                                  |     | 99.7%                                |     |    |
| 6                                     | 1369.8                    | 927.8                    | 1.48 | 0.0582                              | 0.0010 | 0.4373 | 0.0075                              | 0.0545 | 0.0006 | 365                                  | 6   | 368 | 5                                   | 391         | 24                                  |     | 99.2%                                |     |    |
| 7                                     | 610.1                     | 586.2                    | 1.04 | 0.0591                              | 0.0009 | 0.4304 | 0.0073                              | 0.0529 | 0.0007 | 370                                  | 5   | 364 | 5                                   | 324         | 30                                  |     | 98.4%                                |     |    |
| 8                                     | 550.6                     | 744.5                    | 0.74 | 0.0585                              | 0.0009 | 0.4291 | 0.0062                              | 0.0533 | 0.0006 | 366                                  | 5   | 363 | 4                                   | 339         | 24                                  |     | 99.2%                                |     |    |
| 9                                     | 691.4                     | 608.9                    | 1.14 | 0.0578                              | 0.0008 | 0.4215 | 0.0066                              | 0.0528 | 0.0006 | 362                                  | 5   | 357 | 5                                   | 320         | 24                                  |     | 98.6%                                |     |    |
| 10                                    | 1105.5                    | 1001.7                   | 1.10 | 0.0575                              | 0.0008 | 0.4288 | 0.0065                              | 0.0541 | 0.0005 | 360                                  | 5   | 362 | 5                                   | 372         | 20                                  |     | 98.4%                                |     |    |
| 11                                    | 475.6                     | 522.9                    | 0.91 | 0.0570                              | 0.0009 | 0.4269 | 0.0072                              | 0.0543 | 0.0006 | 357                                  | 5   | 361 | 5                                   | 383         | 21                                  |     | 99.9%                                |     |    |
| 12                                    | 1172.7                    | 909.3                    | 1.29 | 0.0583                              | 0.0008 | 0.4349 | 0.0063                              | 0.0541 | 0.0005 | 365                                  | 5   | 367 | 5                                   | 376         | 20                                  |     | 99.5%                                |     |    |
| 13                                    | 168.8                     | 288.6                    | 0.59 | 0.0565                              | 0.0008 | 0.4316 | 0.0069                              | 0.0554 | 0.0007 | 354                                  | 5   | 364 | 5                                   | 432         | 5                                   |     | 97.2%                                |     |    |
| 14                                    | 230.1                     | 272.5                    | 0.84 | 0.0563                              | 0.0009 | 0.4239 | 0.0084                              | 0.0546 | 0.0008 | 353                                  | 5   | 359 | 6                                   | 395         | 36                                  |     | 98.3%                                |     |    |
| 15                                    | 473.3                     | 483.8                    | 0.98 | 0.0568                              | 0.0008 | 0.4233 | 0.0070                              | 0.0540 | 0.0006 | 356                                  | 5   | 358 | 5                                   | 372         | 24                                  |     | 99.4%                                |     |    |
| 16                                    | 1575.6                    | 1139.1                   | 1.38 | 0.0574                              | 0.0009 | 0.4213 | 0.0071                              | 0.0532 | 0.0005 | 360                                  | 6   | 357 | 5                                   | 345         | 22                                  |     | 99.2%                                |     |    |
| 17                                    | 480.5                     | 534.4                    | 0.90 | 0.0569                              | 0.0014 | 0.4268 | 0.0189                              | 0.0539 | 0.0013 | 357                                  | 8   | 361 | 14                                  | 365         | 49                                  |     | 98.9%                                |     |    |
| 18                                    | 656.6                     | 584.9                    | 1.12 | 0.0571                              | 0.0008 | 0.4252 | 0.0068                              | 0.0544 | 0.0007 | 358                                  | 5   | 360 | 5                                   | 387         | 25                                  |     | 99.4%                                |     |    |
| 19                                    | 1081.4                    | 877.1                    | 1.23 | 0.0574                              | 0.0008 | 0.4238 | 0.0076                              | 0.0535 | 0.0006 | 360                                  | 5   | 359 | 5                                   | 350         | 32                                  |     | 99.7%                                |     |    |
| 20                                    | 740.6                     | 669.2                    | 1.11 | 0.0558                              | 0.0009 | 0.4160 | 0.0083                              | 0.0539 | 0.0006 | 350                                  | 5   | 353 | 6                                   | 365         | 24                                  |     | 99.1%                                |     |    |
| 21                                    | 538.6                     | 513.2                    | 1.05 | 0.0579                              | 0.0010 | 0.4330 | 0.0073                              | 0.0543 | 0.0007 | 363                                  | 6   | 365 | 5                                   | 383         | 21                                  |     | 99.5%                                |     |    |
| 22                                    | 254.0                     | 298.4                    | 0.85 | 0.0567                              | 0.0009 | 0.4244 | 0.0073                              | 0.0544 | 0.0008 | 355                                  | 6   | 359 | 5                                   | 387         | 33                                  |     | 98.9%                                |     |    |
| 23                                    | 1794.4                    | 1046.2                   | 1.72 | 0.0590                              | 0.0010 | 0.4334 | 0.0067                              | 0.0533 | 0.0005 | 369                                  | 6   | 366 | 5                                   | 343         | 22                                  |     | 99.2%                                |     |    |
| 24                                    | 683.2                     | 584.2                    | 1.17 | 0.0572                              | 0.0008 | 0.4321 | 0.0075                              | 0.0547 | 0.0006 | 359                                  | 5   | 365 | 5                                   | 398         | 22                                  |     | 98.3%                                |     |    |
| 25                                    | 292.0                     | 374.7                    | 0.78 | 0.0574                              | 0.0008 | 0.4210 | 0.0072                              | 0.0532 | 0.0007 | 360                                  | 5   | 357 | 5                                   | 345         | 28                                  |     | 99.2%                                |     |    |
| 26                                    | 410.1                     | 476.3                    | 0.86 | 0.0572                              | 0.0009 | 0.4236 | 0.0074                              | 0.0538 | 0.0007 | 358                                  | 6   | 359 | 5                                   | 365         | 23                                  |     | 99.7%                                |     |    |
| 27                                    | 188.0                     | 248.3                    | 0.76 | 0.0579                              | 0.0011 | 0.4308 | 0.0082                              | 0.0541 | 0.0007 | 363                                  | 6   | 364 | 7                                   | 376         | 30                                  |     | 99.7%                                |     |    |
| 28                                    | 1332.8                    | 971.5                    | 1.37 | 0.0556                              | 0.0007 | 0.4076 | 0.0059                              | 0.0532 | 0.0006 | 349                                  | 5   | 347 | 4                                   | 345         | 19                                  |     | 99.4%                                |     |    |
| 29                                    | 334.7                     | 354.2                    | 0.94 | 0.0582                              | 0.0011 | 0.4358 | 0.0097                              | 0.0543 | 0.0008 | 365                                  | 7   | 367 | 7                                   | 387         | 32                                  |     | 99.5%                                |     |    |
| 30                                    | 551.7                     | 501.4                    | 1.10 | 0.0601                              | 0.0009 | 0.4499 | 0.0080                              | 0.0543 | 0.0006 | 376                                  | 5   | 377 | 6                                   | 389         | 19                                  |     | 99.7%                                |     |    |
| 31                                    | 484.3                     | 436.0                    | 1.11 | 0.0573                              | 0.0008 | 0.4235 | 0.0067                              | 0.0537 | 0.0007 | 359                                  | 5   | 359 | 5                                   | 367         | 28                                  |     | 100.0%                               |     |    |
| 32                                    | 1201.1                    | 1055.1                   | 1.14 | 0.0589                              | 0.0010 | 0.4434 | 0.0073                              | 0.0547 | 0.0005 | 369                                  | 6   | 373 | 5                                   | 398         | 16                                  |     | 98.9%                                |     |    |
| 33                                    | 640.3                     | 554.4                    | 1.15 | 0.0576                              | 0.0011 | 0.4249 | 0.0077                              | 0.0536 | 0.0007 | 361                                  | 7   | 360 | 6                                   | 354         | 30                                  |     | 99.7%                                |     |    |
| 34                                    | 1369.8                    | 927.8                    | 1.48 | 0.0582                              | 0.0010 | 0.4373 | 0.0075                              | 0.0545 | 0.0006 | 365                                  | 6   | 368 | 5                                   | 391         | 24                                  |     | 99.2%                                |     |    |
| 35                                    | 610.1                     | 586.2                    | 1.04 | 0.0591                              | 0.0009 | 0.4304 | 0.0073                              | 0.0529 | 0.0007 | 370                                  | 5   | 364 | 5                                   | 324         | 30                                  |     | 98.4%                                |     |    |

Table 2. Cont.

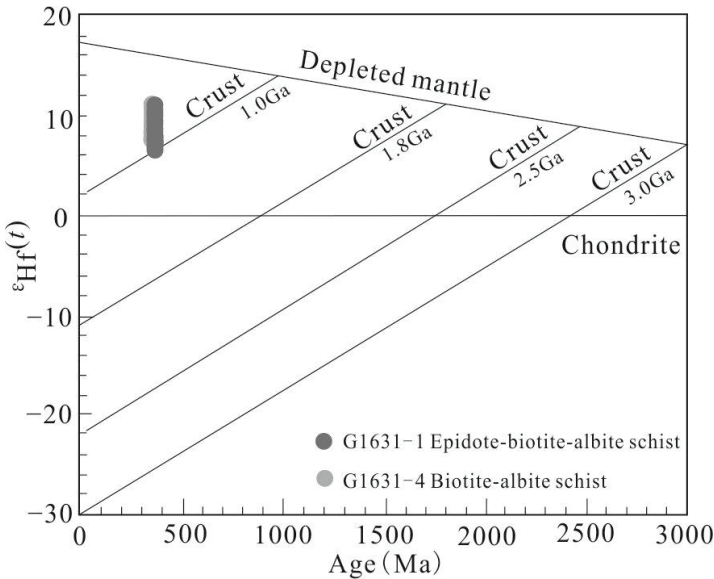
| Analytical No.                                 | Th<br>(10 <sup>−6</sup> ) | U<br>(10 <sup>−6</sup> ) | Th/U | Isotopic Ratio                      |        |                                     |        | Age (Ma)                            |        |                                     |    | Concordance |     |     |    |        |
|------------------------------------------------|---------------------------|--------------------------|------|-------------------------------------|--------|-------------------------------------|--------|-------------------------------------|--------|-------------------------------------|----|-------------|-----|-----|----|--------|
|                                                |                           |                          |      | <sup>206</sup> Pb/ <sup>238</sup> U |        | <sup>207</sup> Pb/ <sup>235</sup> U |        | <sup>206</sup> Pb/ <sup>238</sup> U |        | <sup>207</sup> Pb/ <sup>235</sup> U |    |             |     |     |    |        |
|                                                |                           |                          |      | Ratio                               | 1σ     | Ratio                               | 1σ     | Age                                 | 1σ     | Age                                 | 1σ |             |     |     |    |        |
| G1631-4 Chlorite epidote biotite albite schist |                           |                          |      |                                     |        |                                     |        |                                     |        |                                     |    |             |     |     |    |        |
| 1                                              | 414.8                     | 339.8                    | 1.22 | 0.0568                              | 0.0010 | 0.4355                              | 0.0077 | 0.0557                              | 0.0008 | 356                                 | 6  | 367         | 5   | 443 | 32 | 97.0%  |
| 2                                              | 268.7                     | 273.3                    | 0.98 | 0.0571                              | 0.0007 | 0.4433                              | 0.0102 | 0.0561                              | 0.0010 | 358                                 | 5  | 373         | 7   | 458 | 41 | 95.9%  |
| 3                                              | 211.8                     | 198.9                    | 1.06 | 0.0571                              | 0.0008 | 0.4344                              | 0.0087 | 0.0552                              | 0.0009 | 358                                 | 5  | 366         | 6   | 420 | 35 | 97.8%  |
| 4                                              | 285.3                     | 300.2                    | 0.95 | 0.0570                              | 0.0007 | 0.4223                              | 0.0078 | 0.0537                              | 0.0008 | 357                                 | 4  | 358         | 6   | 367 | 33 | 99.7%  |
| 5                                              | 161.0                     | 296.5                    | 0.54 | 0.0581                              | 0.0009 | 0.4377                              | 0.0092 | 0.0546                              | 0.0008 | 364                                 | 6  | 369         | 7   | 395 | 33 | 98.6%  |
| 6                                              | 52.5                      | 100.1                    | 0.52 | 0.0577                              | 0.0009 | 0.4436                              | 0.0124 | 0.0558                              | 0.0014 | 362                                 | 6  | 373         | 9   | 456 | 54 | 97.0%  |
| 7                                              | 91.9                      | 110.7                    | 0.83 | 0.0562                              | 0.0009 | 0.4195                              | 0.0109 | 0.0541                              | 0.0012 | 353                                 | 5  | 356         | 8   | 376 | 53 | 99.2%  |
| 8                                              | 321.8                     | 326.1                    | 0.99 | 0.0570                              | 0.0011 | 0.4262                              | 0.0100 | 0.0542                              | 0.0008 | 358                                 | 7  | 361         | 7   | 389 | 33 | 99.2%  |
| 9                                              | 133.0                     | 179.9                    | 0.74 | 0.0555                              | 0.0008 | 0.4124                              | 0.0084 | 0.0540                              | 0.0010 | 348                                 | 5  | 351         | 6   | 372 | 39 | 99.1%  |
| 10                                             | 138.7                     | 284.9                    | 0.49 | 0.0561                              | 0.0010 | 0.4062                              | 0.0084 | 0.0526                              | 0.0009 | 352                                 | 6  | 346         | 6   | 322 | 37 | 98.3%  |
| 11                                             | 209.1                     | 210.6                    | 0.99 | 0.0551                              | 0.0008 | 0.4075                              | 0.0072 | 0.0537                              | 0.0008 | 346                                 | 5  | 347         | 5   | 367 | 35 | 99.7%  |
| 12                                             | 459.3                     | 411.0                    | 1.12 | 0.0580                              | 0.0016 | 0.4238                              | 0.0116 | 0.0531                              | 0.0008 | 363                                 | 10 | 359         | 8   | 345 | 32 | 98.9%  |
| 13                                             | 189.4                     | 209.4                    | 0.90 | 0.0582                              | 0.0010 | 0.4482                              | 0.0129 | 0.0557                              | 0.0013 | 365                                 | 6  | 376         | 9   | 439 | 50 | 97.0%  |
| 14                                             | 348.6                     | 343.1                    | 1.02 | 0.0587                              | 0.0011 | 0.4316                              | 0.0087 | 0.0534                              | 0.0008 | 368                                 | 7  | 364         | 6   | 346 | 27 | 98.9%  |
| 15                                             | 159.3                     | 192.3                    | 0.83 | 0.0573                              | 0.0010 | 0.4323                              | 0.0103 | 0.0547                              | 0.0010 | 359                                 | 6  | 365         | 7   | 398 | 36 | 98.3%  |
| 16                                             | 102.2                     | 129.5                    | 0.79 | 0.0581                              | 0.0014 | 0.4235                              | 0.0146 | 0.0532                              | 0.0016 | 364                                 | 8  | 359         | 10  | 345 | 67 | 96.6%  |
| 17                                             | 151.1                     | 170.2                    | 0.89 | 0.0570                              | 0.0009 | 0.4050                              | 0.0103 | 0.0515                              | 0.0011 | 357                                 | 5  | 345         | 8   | 261 | 50 | 96.6%  |
| 18                                             | 128.2                     | 179.6                    | 0.71 | 0.0572                              | 0.0009 | 0.4192                              | 0.0087 | 0.0532                              | 0.0010 | 359                                 | 5  | 356         | 6   | 339 | 47 | 99.2%  |
| 19                                             | 212.1                     | 226.9                    | 0.93 | 0.0543                              | 0.0009 | 0.4159                              | 0.0104 | 0.0553                              | 0.0010 | 341                                 | 6  | 353         | 7.5 | 433 | 39 | 96.5%  |
| 20                                             | 163.6                     | 203.1                    | 0.81 | 0.0555                              | 0.0009 | 0.4156                              | 0.0084 | 0.0544                              | 0.0009 | 348                                 | 6  | 353         | 6   | 391 | 39 | 98.6%  |
| 21                                             | 380.3                     | 405.1                    | 0.94 | 0.0553                              | 0.0009 | 0.4168                              | 0.0085 | 0.0546                              | 0.0007 | 347                                 | 6  | 354         | 6   | 395 | 34 | 98.0%  |
| 22                                             | 145.1                     | 179.4                    | 0.81 | 0.0538                              | 0.0007 | 0.4009                              | 0.0087 | 0.0539                              | 0.0010 | 338                                 | 4  | 342         | 6   | 367 | 43 | 98.8%  |
| 23                                             | 420.8                     | 585.3                    | 0.72 | 0.0546                              | 0.0008 | 0.3950                              | 0.0067 | 0.0523                              | 0.0006 | 343                                 | 5  | 338         | 5   | 302 | 24 | 98.5%  |
| 24                                             | 110.9                     | 133.7                    | 0.83 | 0.0570                              | 0.0008 | 0.4283                              | 0.0118 | 0.0546                              | 0.0015 | 357                                 | 5  | 362         | 8   | 395 | 61 | 98.6%  |
| 25                                             | 70.2                      | 127.1                    | 0.55 | 0.0575                              | 0.0007 | 0.4186                              | 0.0105 | 0.0526                              | 0.0011 | 360                                 | 5  | 355         | 8   | 322 | 51 | 98.6%  |
| 26                                             | 141.9                     | 153.0                    | 0.93 | 0.0579                              | 0.0009 | 0.4224                              | 0.0100 | 0.0529                              | 0.0011 | 363                                 | 5  | 358         | 7   | 324 | 48 | 98.6%  |
| 27                                             | 122.8                     | 179.0                    | 0.69 | 0.0572                              | 0.0008 | 0.4239                              | 0.0085 | 0.0537                              | 0.0010 | 359                                 | 5  | 359         | 6   | 361 | 39 | 100.0% |
| 28                                             | 245.0                     | 234.4                    | 1.05 | 0.0584                              | 0.0012 | 0.4403                              | 0.0145 | 0.0547                              | 0.0015 | 366                                 | 7  | 371         | 10  | 467 | 58 | 98.6%  |
| 29                                             | 249.3                     | 250.8                    | 0.99 | 0.0569                              | 0.0010 | 0.4200                              | 0.0093 | 0.0536                              | 0.0010 | 357                                 | 6  | 356         | 7   | 354 | 47 | 99.7%  |
| 30                                             | 369.7                     | 389.9                    | 0.95 | 0.0563                              | 0.0009 | 0.4113                              | 0.0065 | 0.0530                              | 0.0006 | 343                                 | 6  | 350         | 5   | 328 | 32 | 99.1%  |
| 31                                             | 337.6                     | 274.2                    | 1.23 | 0.0552                              | 0.0008 | 0.3943                              | 0.0079 | 0.0516                              | 0.0007 | 346                                 | 5  | 338         | 6   | 265 | 32 | 97.7%  |
| 32                                             | 414.8                     | 339.8                    | 1.22 | 0.0568                              | 0.0010 | 0.4355                              | 0.0077 | 0.0557                              | 0.0008 | 356                                 | 6  | 367         | 5   | 443 | 32 | 97.0%  |
| 33                                             | 268.7                     | 273.3                    | 0.98 | 0.0571                              | 0.0007 | 0.4433                              | 0.0102 | 0.0561                              | 0.0010 | 358                                 | 5  | 373         | 7   | 458 | 41 | 95.9%  |
| 34                                             | 211.8                     | 198.9                    | 1.06 | 0.0571                              | 0.0008 | 0.4344                              | 0.0087 | 0.0552                              | 0.0009 | 358                                 | 5  | 366         | 6   | 420 | 35 | 97.8%  |
| 35                                             | 285.3                     | 300.2                    | 0.95 | 0.0570                              | 0.0007 | 0.4223                              | 0.0078 | 0.0537                              | 0.0008 | 357                                 | 4  | 358         | 7   | 367 | 33 | 99.7%  |



**Figure 7.** U-Pb concordia and weighted mean ages for the epidote-biotite-albite schist (a) and biotite-albite schist (b).

4.3. Zircon Hf Isotopies

The zircons from the epidote-biotite-albite schist (sample G1631-1) had homogeneous  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios of 0.282749 to 0.282872, with  $\epsilon\text{Hf}(t)$  values of +6.5 to +11.0 (Figure 8), one-stage Hf model ( $T_{\text{DM1}}$ ) ages from 552 to 746 Ma and two-stage Hf model ( $T_{\text{DM2}}$ ) ages from 661 to 902 Ma. Similarly, the zircons from the biotite-albite schist sample (sample G1631-4) also possessed relatively homogeneous Hf isotopic compositions of 0.282783 to 0.282870,  $\epsilon\text{Hf}(t)$  values of +7.9 to +10.9 (Figure 8),  $T_{\text{DM1}}$  ages from 547 to 649 Ma and  $T_{\text{DM2}}$  ages from 660 to 859 Ma (Table 3). All of these characteristics indicate that the parent magmas of the Hadayang schists were produced from a relatively depleted mantle source.



**Figure 8.** Diagrams of zircon Hf isotopic of the Hadayang schists.



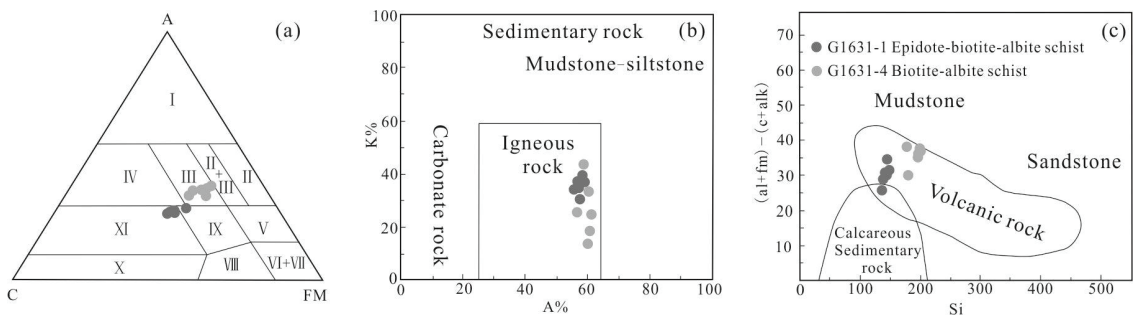
Table 3. In situ zircon Lu-Hf isotopic results for the Hadayang schists.

| Analytical Spot                       | t (Ma) | <sup>176</sup> Yb/<br><sup>177</sup> Hf | <sup>176</sup> Lu/<br><sup>177</sup> Hf | <sup>176</sup> Hf/<br><sup>177</sup> Hf | I <sub>Hf</sub> | ε <sub>Hf</sub> (0) | ε <sub>Hf</sub> (t) | T <sub>DM1</sub> (Hf)<br>(Ma) | T <sub>DM2</sub> (Hf)<br>(Ma) | f <sub>Lu/Hf</sub> |
|---------------------------------------|--------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------|---------------------|---------------------|-------------------------------|-------------------------------|--------------------|
| G1631-1 Epidote-biotite-albite schist |        |                                         |                                         |                                         |                 |                     |                     |                               |                               |                    |
| 1                                     | 365    | 0.065324                                | 0.001772                                | 0.282827                                | 0.282815        | 2.0                 | 9.6                 | 615                           | 756                           | −0.95              |
| 2                                     | 359    | 0.069656                                | 0.001920                                | 0.282866                                | 0.282853        | 3.3                 | 10.8                | 560                           | 672                           | −0.94              |
| 3                                     | 361    | 0.082890                                | 0.002175                                | 0.282798                                | 0.282783        | 0.9                 | 8.3                 | 665                           | 832                           | −0.93              |
| 4                                     | 362    | 0.053714                                | 0.001471                                | 0.282834                                | 0.282824        | 2.2                 | 9.8                 | 600                           | 737                           | −0.96              |
| 5                                     | 360    | 0.112169                                | 0.002980                                | 0.282772                                | 0.282752        | 0.0                 | 7.2                 | 718                           | 902                           | −0.91              |
| 6                                     | 357    | 0.056043                                | 0.001614                                | 0.282853                                | 0.282842        | 2.9                 | 10.3                | 576                           | 701                           | −0.95              |
| 7                                     | 360    | 0.059902                                | 0.001785                                | 0.282776                                | 0.282764        | 0.1                 | 7.6                 | 690                           | 876                           | −0.95              |
| 8                                     | 357    | 0.092929                                | 0.002522                                | 0.282821                                | 0.282804        | 1.7                 | 9.0                 | 637                           | 787                           | −0.92              |
| 9                                     | 358    | 0.056231                                | 0.001558                                | 0.282795                                | 0.282785        | 0.8                 | 8.3                 | 657                           | 829                           | −0.95              |
| 10                                    | 360    | 0.088918                                | 0.002387                                | 0.282836                                | 0.28282         | 2.3                 | 9.6                 | 612                           | 748                           | −0.93              |
| 11                                    | 363    | 0.093148                                | 0.002687                                | 0.282749                                | 0.282731        | −0.8                | 6.5                 | 746                           | 948                           | −0.92              |
| 12                                    | 359    | 0.069427                                | 0.001865                                | 0.282872                                | 0.282859        | 3.5                 | 11.0                | 552                           | 661                           | −0.94              |
| 13                                    | 360    | 0.023950                                | 0.000701                                | 0.282780                                | 0.282775        | 0.3                 | 8.0                 | 664                           | 850                           | −0.98              |
| 14                                    | 358    | 0.064122                                | 0.002020                                | 0.282823                                | 0.282809        | 1.8                 | 9.2                 | 625                           | 773                           | −0.94              |
| 15                                    | 363    | 0.047436                                | 0.001443                                | 0.282801                                | 0.282791        | 1.0                 | 8.7                 | 647                           | 812                           | −0.96              |
| G1631-4 Biotite-albite schist         |        |                                         |                                         |                                         |                 |                     |                     |                               |                               |                    |
| 1                                     | 356    | 0.050095                                | 0.001393                                | 0.282794                                | 0.282785        | 0.8                 | 8.3                 | 655                           | 829                           | −0.96              |
| 2                                     | 358    | 0.034306                                | 0.000991                                | 0.282851                                | 0.282844        | 2.8                 | 10.4                | 569                           | 695                           | −0.97              |
| 3                                     | 358    | 0.033785                                | 0.000965                                | 0.282789                                | 0.282782        | 0.6                 | 8.2                 | 656                           | 835                           | −0.97              |
| 4                                     | 357    | 0.071549                                | 0.002065                                | 0.282846                                | 0.282832        | 2.6                 | 10.0                | 593                           | 723                           | −0.94              |
| 5                                     | 364    | 0.031583                                | 0.000947                                | 0.282801                                | 0.282794        | 1.0                 | 8.8                 | 639                           | 804                           | −0.97              |
| 6                                     | 353    | 0.050729                                | 0.001448                                | 0.282840                                | 0.28283         | 2.4                 | 9.8                 | 592                           | 731                           | −0.96              |
| 7                                     | 358    | 0.105460                                | 0.003007                                | 0.282851                                | 0.282831        | 2.8                 | 10.0                | 600                           | 724                           | −0.91              |
| 8                                     | 352    | 0.050404                                | 0.001402                                | 0.282870                                | 0.282861        | 3.5                 | 10.9                | 547                           | 660                           | −0.96              |
| 9                                     | 359    | 0.030825                                | 0.000972                                | 0.282847                                | 0.28284         | 2.7                 | 10.3                | 574                           | 703                           | −0.97              |
| 10                                    | 357    | 0.059140                                | 0.001785                                | 0.282820                                | 0.282808        | 1.7                 | 9.1                 | 625                           | 776                           | −0.95              |
| 11                                    | 359    | 0.059194                                | 0.001850                                | 0.282783                                | 0.282771        | 0.4                 | 7.9                 | 679                           | 859                           | −0.94              |
| 12                                    | 357    | 0.074471                                | 0.002239                                | 0.282795                                | 0.28278         | 0.8                 | 8.2                 | 669                           | 839                           | −0.93              |
| 13                                    | 359    | 0.062644                                | 0.001924                                | 0.282823                                | 0.28281         | 1.8                 | 9.2                 | 624                           | 772                           | −0.94              |
| 14                                    | 357    | 0.056902                                | 0.001824                                | 0.282832                                | 0.28282         | 2.1                 | 9.6                 | 609                           | 751                           | −0.95              |
| 15                                    | 353    | 0.081466                                | 0.002392                                | 0.282814                                | 0.282798        | 1.5                 | 8.7                 | 645                           | 802                           | −0.93              |

5. Discussion

5.1. Protolith Restoration

The trace elements of the Hadayang schists were generally enriched in LILEs and depleted of HFSEs, Sr/Ba > 1, Cr/Ni > 1. Furthermore, the samples retained the crystalloblasts, which indicates that Hadayang schists should be a metagneous rock. On a plot of A-C-FM diagram (Figure 9a), the epidote-biotite-albite schist samples plot in the calc-silicate rock and quartzite and basic volcanic rocks and ferrous-dolomitic tuff fields, while the biotite-albite schist samples plot in the intermediate-acid volcanic rock field. As can be seen from the plot of K vs. A (Figure 9b), all of the samples were igneous rock. On the other hand, on the (al + fm) – (c + alk) vs. Si diagram (Figure 9c), all the samples were volcanic rocks.



**Figure 9.** Classification diagrams of the Hadayang schists. (a) A-C-FM diagram (after [74]) (I—claystone and acidic volcanic rock; II—claystone and subgrauwacke; II+III—intermediate-felsic volcanic rock and subgrauwacke; III—intermediate volcanic rock; IV—arkose; V—tuffaceous siltstone; IX—basic volcanic rock and ferric dolomitic marlite; XI—calcium silicate rock and quartzite; X—calcium silicate rock; VIII—ultrabasic rock; VI+VII—silico-ferric sedimentary rock and ultrabasic rock); (b) A-K diagram (after [75]); (c) (al + fm) – (c + alk)-Si diagram (after [75]).

According to the comprehensive analysis of geochemical and petrographic characteristics, the protolith of Hadayang schist was a set of intermediate-basic volcanic rocks, among which the protolith of the epidotite-biotite-albite schist was a basalt, and the protolith of the biotite-albite schist was andesite.

### 5.2. Geochronological Framework

The Hadayang schists were previously considered to be Precambrian in age [76], but our chronological data indicate that they formed in the Late Devonian to Early Carboniferous period. Although the magmatic activity in this period was relatively weak in the region [77], in recent years, Late Devonian–Early Carboniferous magmatic rocks have been successively identified in the XB, such as in the Yakeshi-Huolongmen, Handagai, Nenjiang and Zhalantun-Zhalaite areas. The Late Devonian–Early Carboniferous magmatic rocks in the Yakeshi-Huolongmen area include rhyolite (ca. 364–379 Ma) [78], basalt ( $373 \pm 5$  Ma) [79], diorite ( $381 \pm 2$  Ma) [77] and gabbro (ca. 341–344 Ma) [78]. Biotite granite ( $364 \pm 4$  Ma) [80] and monzonitic granite ( $379 \pm 4$  Ma) [81] are found in the Handagai area. Silicic volcanic rocks (ca. 352–354 Ma) [16,58,59], monzonitic granite ( $352 \pm 1$  Ma) [16], syenite granite ( $381 \pm 2$  Ma) [60], hornblende gabbro ( $363 \pm 1$  Ma) [61] and hornblende rock ( $362 \pm 1$  Ma) [61] have been identified in the Nenjiang area. A large number of Late Devonian–Early Carboniferous granites, including alkali feldspar granite, syenite granite, monzonitic granite and granodiorite, with ages ranging from ca. 343 to 379 Ma [13,16,77,78,80–85], were exposed in the Zhalantun-Zhalaite Banner area. In addition, there are some basic–intermediate magmatic rocks scattered in this area, including andesite (ca. 346–362 Ma) [14,86,87], basaltic andesite ( $373 \pm 3$  Ma) [88], quartz diorite (ca. 357–359 Ma) [16,78], gabbro diorite ( $350 \pm 1$  Ma) [78] and gabbro ( $353 \pm 2$  Ma) [59]. In summary, a magmatic activity occurred in the XB during the Late Devonian–Early Carboniferous period, but the tectonic significance of this magmatic event is still controversial.

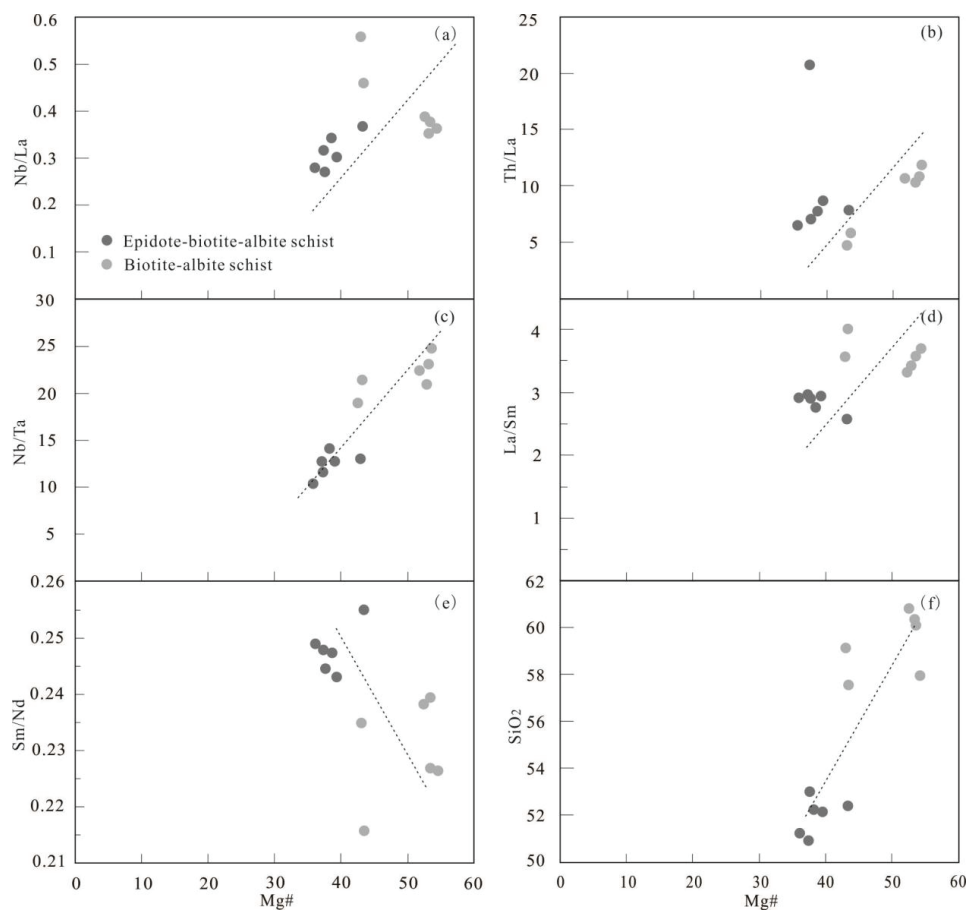
### 5.3. Petrogenesis

#### 5.3.1. Crustal Contamination

Before using the elemental and isotopic compositions of the samples to discuss the petrogenesis of the schists, we first assess the effects of post-magmatic alteration. The protolith of the Hadayang schists was an intermediate-basic volcanic rock, which had undergone greenschist facies metamorphism under the influence of regional metamorphism in a later period, which is supported by their LOI content of 2.23–4.05 wt% and the fact that some of the minerals had been partially replaced by chlorite and epidote. After rock metamorphism, high-field-strength elements (HFSEs), such as REEs, Y, Th, U, Zr,

Hf, Ti, Nb, Ta, etc., tend to exhibit inert migration characteristics without significant migration [89], so the characteristics of HFSEs can better reflect the protolith characteristics of metamorphic rocks.

Mantle-derived magma will inevitably be subjected to crustal contamination during the ascent process [90]. The crustal material is characterized by low Nb/La, Sm/Nd, Nb/Ta and Mg#, and high Th/La, La/Sm and SiO<sub>2</sub>. Therefore, Mg# is positively correlated with the ratios of Nb/La, Nb/Ta and Sm/Nd, and negatively correlated with Th/La, La/Sm and SiO<sub>2</sub>, which can indicate crustal contamination [91]. As can be seen from Figure 10, Mg# was positively correlated with Nb/La, Nb/Ta, Th/La, La/Sm and SiO<sub>2</sub>, and negatively correlated with Sm/Nd, which is significantly different from the characteristics of crustal contamination. In addition, the Hadayang schists had significantly depleted Zr and Hf elements (Figure 5b), excluding inherited zircons, and had positive  $\epsilon_{\text{Hf}}(t)$  values of +5.8 to +9.3, suggesting that crustal contamination was not a significant factor during the magmatic evolution of the Hadayang schists.

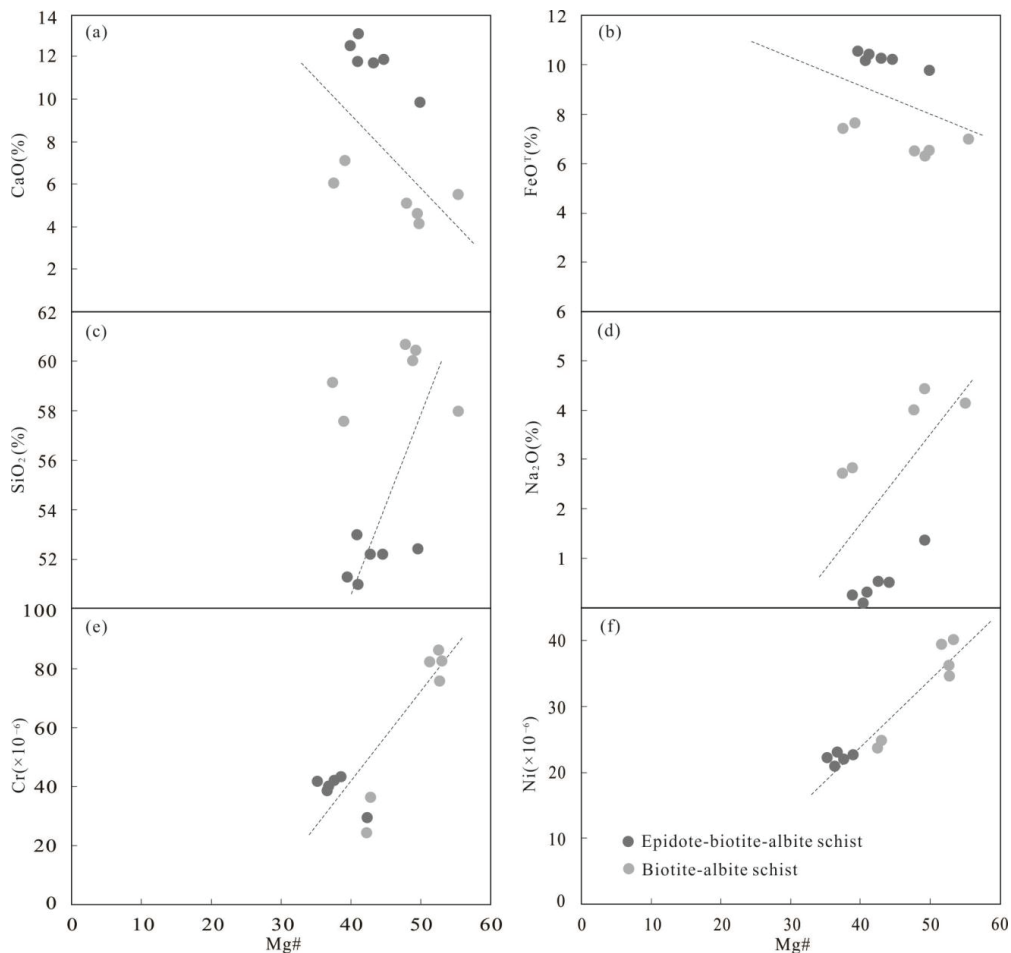


**Figure 10.** Plots of Nb/La vs. Mg# (a), Th/La vs. Mg# (b), Nb/Ta vs. Mg# (c), La/Sm vs. Mg# (d), Sm/Nd vs. Mg# (e) and SiO<sub>2</sub> vs. Mg# (f) for the Hadayang schists.

5.3.2. Fractional Crystallization

The Hadayang schists had low Mg# (35.2–53.0), Cr (23.7–86.5 ppm), Ni (21.1–40.0 ppm) and Co (12.1–30.6 ppm) contents relative to primitive-mantle-derived magmas, suggesting that our samples were evolved magmas rather than primitive magmas. The negative

correlation between Mg# and CaO and  $\text{FeO}^T$ , and the fact that Mg# was positively correlated with Cr, Ni,  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$ , indicated olivine and clinopyroxene fractionation (Figure 11). Based on the negative Eu anomalies, plagioclase fractionation also must have played an important role in the evolution of these magmas.



**Figure 11.** Plots of CaO vs. Mg# (a),  $\text{FeO}^T$  vs. Mg# (b),  $\text{SiO}_2$  vs. Mg# (c),  $\text{Na}_2\text{O}$  vs. Mg# (d), Cr vs. Mg# (e) and Ni vs. Mg# (f) for the Hadayang schists.

5.3.3. Magma Source

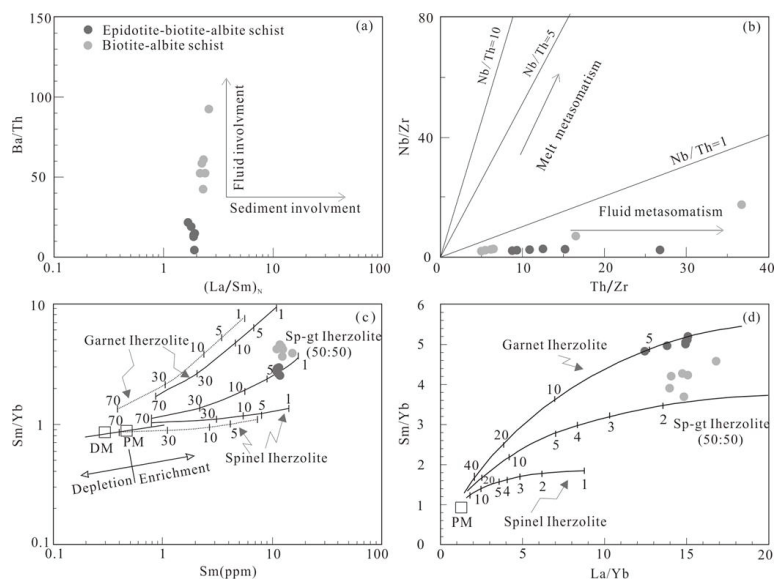
The source region of basic volcanic rocks is generally asthenosphere or lithospheric mantle [92]. The low silica and alkali contents of the Hadayang schists, and their high MgO, Ti, Co and Cr contents, all favor a mantle magmatic source. This conclusion is also supported by the positive  $\epsilon_{\text{Hf}}(t)$  values (the average values were +8.93 and +9.29, respectively) (Figure 8). The  $T_{\text{DMI}}$  ages (552 to 781 Ma and 547 to 679 Ma, respectively) indicated that their parental magma fractionated from mantle in the Neoproterozoic period. As mentioned above, the Hadayang schists have LILE enrichment and significant HFSE depletion with moderately fractionated REE patterns and relatively low HREE abundances, suggesting that the components of the magma source may have included aqueous fluids released by dehydration of the subducted oceanic plate and/or partial melts derived from the subducted oceanic crust/sediments. The Ba/Th ratio of the Hadayang schist

samples varied significantly, while the  $(\text{La}/\text{Sm})_N$  ratio was relatively constant (Figure 12b), indicating that fluids played a key role in the enrichment process, and the influence of sediment was small or absent. The wide range of the  $\text{Sr}/\text{Nd}$  (10.1–30.7) ratio values further indicated that fluid action played a major role in the process of mantle-derived magma enrichment. The above characteristics are supported by the  $\text{Nb}/\text{Zr}$  vs.  $\text{Th}/\text{Zr}$  plot (Figure 12a). The abundances and ratios of REEs are widely used to distinguish the source regions of magma and the degree of partial melting [93]. As can be seen in  $\text{Sm}/\text{Yb}$  vs.  $\text{Sm}$  and  $\text{Sm}/\text{Yb}$  vs.  $\text{La}/\text{Yb}$  plots (Figure 12c, d), the Hadayang schist samples plot mainly near or slightly deviating from the garnet + spinel lherzolite melting curves, and they fall between these two melting curves with starting compositions of primitive mantle, implying a mantle source consisting of spinel and garnet lherzolite, and that it took 1%–5% partial melting of this mantle source to produce the parent magma of the Hadayang schists (Figure 12c,d).

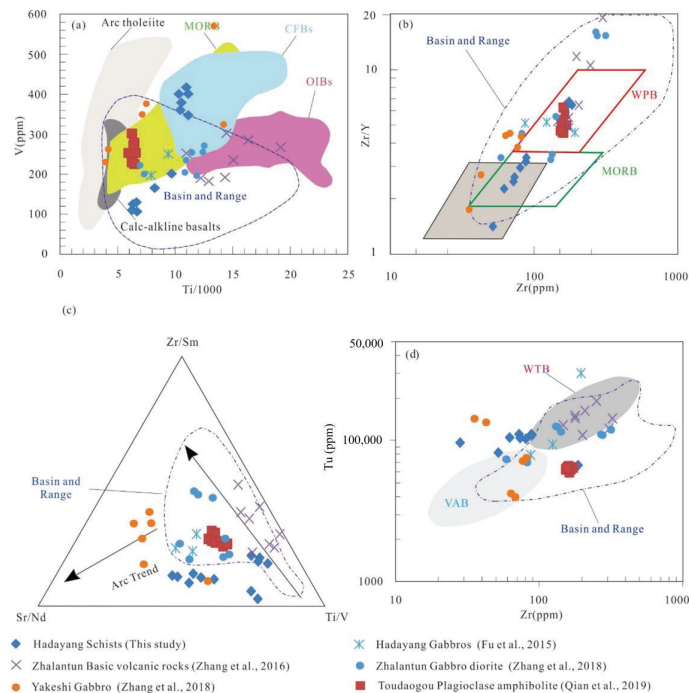
#### 5.4. Tectonic Evolution and Geological Significance

Although a lot of progress has been made in the study of Late Devonian–Early Carboniferous magmatic rocks in the XB, there are still major disputes about their tectonic setting, including the active continental margin or island arc [16,58,59,79,82,83,86,87], back-arc basin [61,88], post-collision extensional [60] and subduction-related extension environment [78,81]. Some authors also believe that there was a transition from passive continental margin to island arc environment during this period [84,94]. In the following discussion, we suggest that the Late Devonian–Early Carboniferous magmatic rocks were formed in an intracontinental extension setting.

As mentioned in an earlier section, the Hadayang schists were characterized by LILE enrichment and significant HFSE depletion, and also exhibited moderately fractionated REE patterns and relatively low HREE abundances, which is also seen in the Late Devonian to Early Carboniferous basic magmatic rocks of the XB [61,78,86,88]. These geochemical characteristics are similar to those arc-type magmatic rocks [98], but there is some uncertainty in judging whether basic igneous rocks are arc magmatic rocks [99–101]. Previous studies have shown that the participation of fluids can change the geochemical characteristics of trace elements, and the precipitation of water-bearing fluid from subducting plates, or the release of water-bearing fluid from deep fluid circulation under the background of subducting plates, may lead to water-rich fluid metasomatism in the mantle source region, forming arc-like trace element characteristics [101–103]. Due to the differences in the contents of Zr, Ti and Sr elements between arc-like basalts and arc basalts, it is very effective to distinguish the two types of basalts by using a discriminant diagram of the above three elements [101]. On the plots of  $\text{Ti}/1000$  vs.  $\text{V}$ ,  $\text{Zr}$  vs.  $\text{Zr}/\text{Y}$  and  $\text{Zr}$  vs.  $\text{Ti}$  (Figure 13a,b,d), all of the Late Devonian to Early Carboniferous intermediate-basic magmatic rocks in the XB plot in the intraplate basalt field or deviating from the arc basalt area, similar to the geochemical characteristics of the North American Basin and Range basalt. As can be seen from the plot of  $\text{Zr}/\text{Sm}-\text{Sr}/\text{Nd}-\text{Ti}/\text{V}$  (Figure 13c), most of the samples plot in or near the intraplate magma and Basin and Range regions, which is significantly different from the nearly vertical characteristics of arc basalt. Based on the above analysis, we propose that the Late Devonian–Early Carboniferous intermediate-basic magmatic rocks in the eastern XB may have been formed in an intracontinental extension tectonic setting similar to the North American Basin and Range basalt. Coincidentally, the same tectonic background also appears in the western part of the XB. Previous studies have shown that the Erenhot–Hegenshan ophiolite in the XB was formed during the Late Devonian–Early Carboniferous [104–110] and was the product of the upwelling process of the asthenosphere caused by the extension of the lithosphere [111,112]. Based on the identification of basement rocks and other evidence around the ophiolite [113], it was indicated that the ophiolite would have been formed in the continental crust extension zone [6,114]. In summary, we believe that the XB would have been in the stage of intracontinental extension during the Late Devonian–Early Carboniferous.



**Figure 12.** Plots of Nb/Zr vs. Th/Zr ((a), after [95]), La/Sm vs. Sm/Yb ((b), after [96]), Sm vs. Sm/Yb ((c), after [97]) and La/Yb vs. Sm/Yb ((d), after [97]) for the Hadayang schists.



**Figure 13.** Structural discrimination diagrams of V vs. Ti/1000 ((a), after [115]), Zr/Y vs. Zr ((b), after [89]), Zr/Sm-Sr/Nd-Ti/V (c) and Ti vs. Zr ((d), after [116]) for Late Devonian to Early Carboniferous intermediate-basic rocks in the eastern XB. CFB = continental flood basalts; OIBs = ocean-island basalts; MORB = mid-ocean ridge basalt; WPB = within-plate basalts; IAB = island arc basalts; VAB = volcanic arc basalt; WTB = within-plate tholeiitic basalt.



## 6. Conclusions

1. The protolith of the Hadayang schists was intermediate-basic volcanic rock. LA-ICP-MS U-Pb dating of zircons from the epidote-biotite-albite schist and biotite-albite schist yielded crystallization ages of  $360 \pm 2$  Ma (MSWD = 1.4) and  $355 \pm 3$  Ma (MSWD = 2.1). This, combined with the presence of contemporaneous magmatic rocks in the region, indicates an important magmatic event in the eastern XB during the Late Devonian–Early Carboniferous.
2. The magma source of the Hadayang schists was a mantle that consisted of both spinel and garnet lherzolite, with a partial melting degree of 1%–5%, and which underwent fractional crystallization of olivine, orthopyroxene and plagioclase.
3. The Late Devonian–Early Carboniferous intermediate-basic magmatic rocks in the eastern XB were formed in an intracontinental extension setting, which is consistent with the tectonic setting of contemporaneous ophiolites in the western section. The Xing'an block would have been in the stage of intracontinental extension during the Late Devonian–Early Carboniferous.

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## Article

# Ore Genesis of the Lower Urgen Porphyry Molybdenum Deposit in the Northern Great Xing'an Range, Northeast China: Constraints from Molybdenite Re-Os Dating, Fluid Inclusions, and H-O-S-Pb Isotopes

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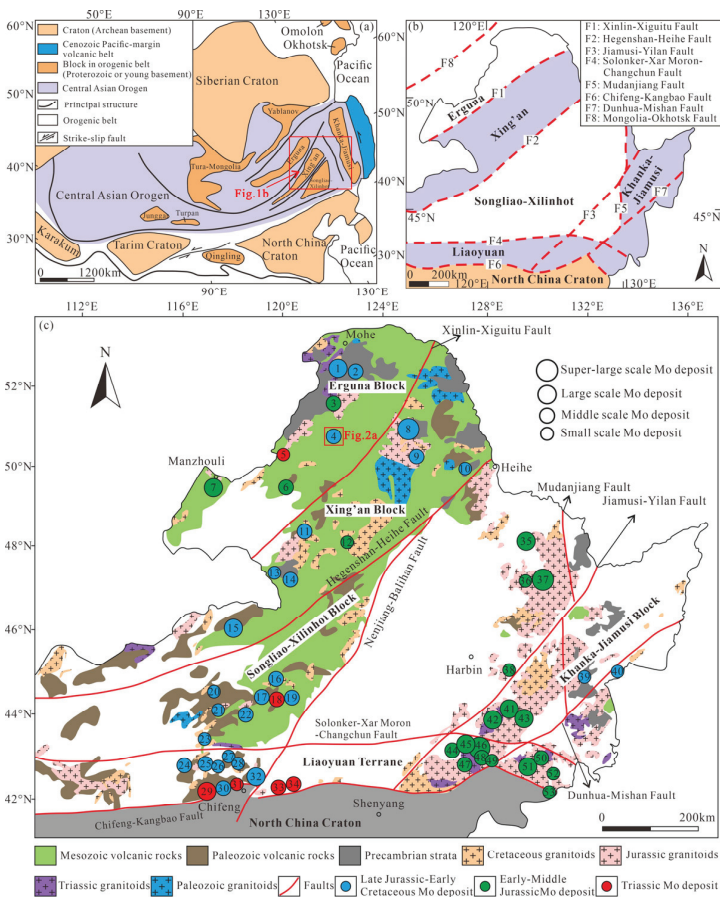
**Abstract:** The Lower Urgen molybdenum deposit (44,856 t Mo @ 0.141%), situated in the northern Great Xing'an Range, is a newly discovered porphyry molybdenum deposit. Mineralization is characterized by veinlet-disseminated- and vein-type quartz–sulfide orebodies primarily occurring in the cupola of the Early Cretaceous granite porphyry stock. In this study, we present a detailed description of the ore geology, molybdenite Re-Os dating, H-O-S-Pb isotopic compositions, and fluid inclusion (FI) analyses including petrography, laser Raman, and microthermometry to precisely constrain the timing of ore formation, the origin of ore-forming fluids and materials, as well as the metal precipitation mechanism. Molybdenite Re-Os dating yielded two model ages of  $141.2 \pm 1.5$  and  $147.7 \pm 1.7$  Ma, coeval with the regional Late Jurassic–Early Cretaceous molybdenum metallogenesis. The hydrothermal process can be divided into three stages: the quartz–molybdenite(–pyrite) stage, quartz–polymetallic sulfide stage, and quartz–carbonate stage. Four types of FIs were distinguished for quartz, including two-phase liquid-rich (L-type), saline (S-type), CO<sub>2</sub>-rich (C1-type), and CO<sub>2</sub>-bearing (C2-type) FIs. Microthermometric data showed that the homogenization temperatures and salinities from the early to late stages were 240–430 °C, 5.0–11.9, and 30.1–50.8 wt% NaCl equiv.; 180–280 °C and 3.0–9.1 wt% NaCl equiv.; and 120–220 °C and 0.2–7.9 wt% NaCl equiv., respectively, suggesting a decreasing trend. H-O isotopic compositions indicate that the ore-forming fluids were initially of magmatic origin with the increasing incorporation of meteoric water. S-Pb isotopic compositions indicate that the ore-forming materials originated from granitic magmas, and the mineralization is genetically related to the ore-bearing granite porphyry stock in the deposit. Fluid immiscibility and fluid–rock interaction are collectively responsible for the massive deposition of molybdenite in stage 1, whereas fluid mixing and immiscibility played a critical role in the deposition of polymetallic sulfide in stage 2.

**Keywords:** molybdenite Re-Os dating; fluid inclusions; H-O-S-Pb isotopes; lower urgen molybdenum deposit; NE China

1. Introduction

Porphyry deposits are commonly spatially, temporally, and genetically related to intermediate–acid hypabyssal porphyry intrusions [1], and provide more than 75%, 50%, and 20% of the world’s molybdenum, copper, and gold resources, respectively [2–5]. Mineralization mainly occurs as veinlets and disseminations concentrated in or near the cupolas of porphyry intrusions, and is related to the hydraulic fracturing resulting from fluid exsolution from magmas [3,6,7]. Taking the economic importance of porphyry molybdenum deposits into account, the study of the genesis and metallogenic models of these deposits has always been an essential subject in ore deposit research [8–16].

China has the largest molybdenum resources worldwide, accounting for about 54% of the world’s known economic molybdenum resources [17], which appear in six predominant molybdenum metallogenic provinces, i.e., NE China, Qinling-Dabie, Yanliao, Sanjiang, the middle-lower Yangtze River Valley, and South China [18]. NE China is situated in the eastern Central Asian Orogenic Belt (CAOB) tectonically. A long-term tectonomagmatic evolutionary history has made it a significant polymetallic metallogenic province around the world [19–25] (Figure 1). More than 11.4 Mt of molybdenum has now been discovered in NE China, including 4 super-large (>0.5 Mt Mo), 11 large (0.1–0.5 Mt Mo), 22 medium (0.01–0.1 Mt Mo), and 18 small (<0.01 Mt Mo) molybdenum deposits, marking NE China as the largest molybdenum metallogenic province in China [26] (Figure 1c).



**Figure 1.** (a) Simplified tectonic map of the Central Asian Orogenic Belt (modified from [27,28]). (b) Schematic tectonic map of NE China (modified from [29]). (c) Distribution of major molybdenum

deposits in NE China (modified from [20]). Deposit locations: 1—Jiliuhe; 2—Fukeshan; 3—Taipingchuan; 4—Lower Urgen; 5—Badaguan; 6—Zishi; 7—Wunugetushan; 8—Chalukou; 9—Daheishan; 10—Yezhugou; 11—Taipinggou; 12—Baojiagou; 13—Nanxingan; 14—Jiazishan; 15—Diyanqinamu; 16—Aolunhua; 17—Banlashan; 18—Laojiagou; 19—Haolibao; 20—Hashitu; 21—Erbadi; 22—Yangchang; 23—Longtoushan; 24—Hongshanzi; 25—Xiaodonggou; 26—Liutiaogou; 27—Gangzi; 28—Tuohe; 29—Chehugou; 30—Nianzigou; 31—Yuanbaoshan; 32—Jiguanshan; 33—Baimashi; 34—Kulitu; 35—Huojihe; 36—Cuiling; 37—Luming; 38—Wudaoling; 39—Kanchuangou; 40—Jinchanggou; 41—Fuanpu; 42—Jidetun; 43—Dashihе; 44—Houdaomu; 45—Xingshan; 46—Daheishan; 47—Sangedingzi; 48—Sifangdianzi; 49—Xinhualong; 50—Liushengdian; 51—Sanchazi; 52—Dongfeng; 53—Shirengou.

The Lower Urgen deposit in Inner Mongolia, NE China, is a newly discovered porphyry molybdenum deposit, with estimated reserves of 44,856 t of molybdenum at an average grade of 0.141% [30]. The geochronology, petrogenesis, and tectonic context of the barren granites in the mining area have been the primary subjects of earlier investigations of the deposit [31]. Nonetheless, the direct timing of molybdenum mineralization, ore-forming fluids and the metal source, and metallogenic processes remains enigmatic. In accordance with a thorough field investigation and petrographic observations of thin sections, we present comprehensive descriptions of the geology, mineralization stages, and hydrothermal alteration in the Lower Urgen molybdenum deposit. The new molybdenite Re-Os geochronology, fluid inclusion (FI) study (petrography, laser Raman, and microthermometry analyses), and isotope geochemistry (H-O-S-Pb) for the deposit are investigated. By combining our results with available geochronology and geodynamic research in the region, we aim to (1) restrict the timing of molybdenum mineralization in the Lower Urgen molybdenum deposit; (2) determine ore-forming fluids and the metal source; and (3) decipher fluid evolution processes and ore precipitation mechanisms. This study not only contributes to the establishment of a plausible metallogenetic model for the Lower Urgen molybdenum deposit, but also has important implications for the comprehension of regional molybdenum metallogenesis and the future molybdenum prospecting and exploration.

## 2. Regional Geology

The tectonic components of NE China include the Erguna Block in the northwest, the Xing'an and Songliao-Xilinhот blocks in the central part, the Khanka-Jiamusi Block in the southeast, and the Liaoyuan Terrane in the south [28] (Figure 1). Major faults separating these tectonic units include the Hegenshan-Heihe, Solonker-Xar Moron-Changchun, Xinlin-Xiguitu, and Mudanjiang faults [28,29] (Figure 1b). NE China has experienced a multi-stage Phanerozoic tectonic evolutionary history, including the subduction and final closure of the Palaeo-Asian Ocean (PAO) during the Paleozoic to Early Mesozoic [28,32–35], the south-directed subduction and closure of the Mongol-Okhotsk Ocean (MOO), and the west-directed subduction and subsequent rollback of the Palaeo-Pacific Ocean (PPO) plate during the Mesozoic [29,36,37]. Due to the overprinting of multiple tectonic domains, NE China experienced extensive tectonomagmatic events, accompanied by intense metallogenesis [19–25]. Three episodes of Mesozoic molybdenum mineralization are recognized in the region, including the Triassic, Early–Middle Jurassic, and Late Jurassic–Early Cretaceous [18,24]. The major location of the Triassic molybdenum deposits is along the Solonker-Xar Moron-Changchun Fault (SXCF), with minor occurrences in the northern and central Great Xing'an Range (NCGXR). The Triassic molybdenum deposits near the SXCF were formed in a syn-collision compressional to post-collision extensional environment induced through the tectonic evolution of the PAO [18,38–43], whereas the Triassic molybdenum deposits in the NCGXR were formed in a subduction-dominated compressional environment induced through the SE-directed subduction of the MOO plate [44–48]. The Early–Middle Jurassic molybdenum deposits are concentrated in the Lesser Xing'an

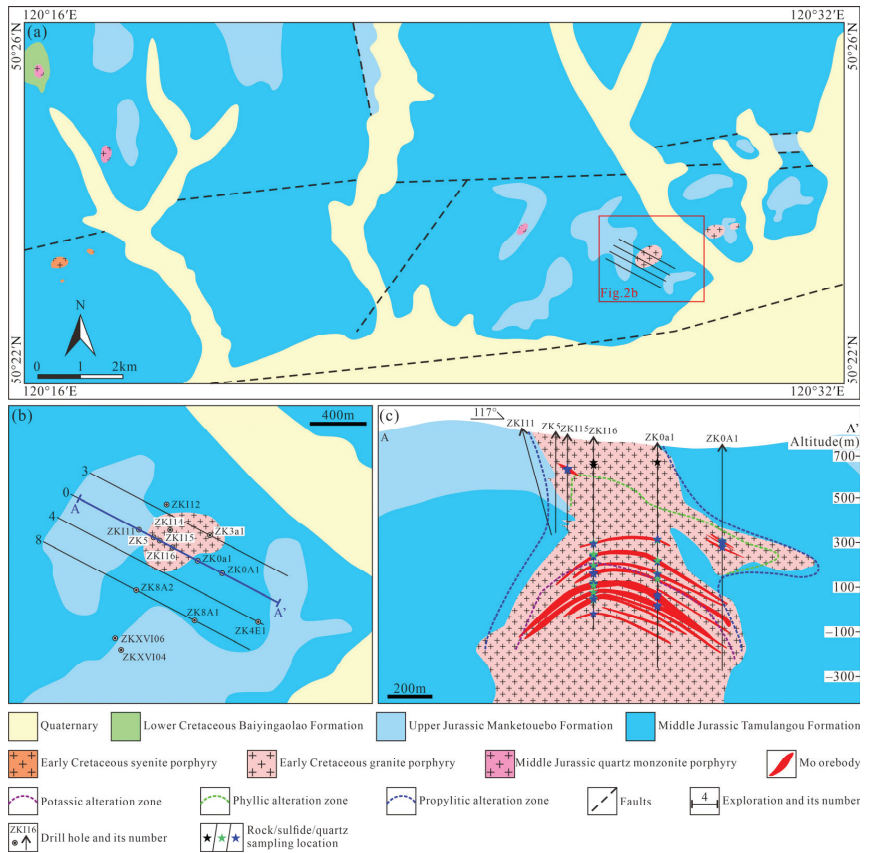
Zhangguangcai Range (LXZR) and sparsely distributed in the NCGXR, which were formed in a compressional environment controlled by the overprinting influence of the SE-directed subduction of the MOO plate in the west and the NW-directed subduction of the PPO plate in the east [49–64]. Molybdenum deposits from the Late Jurassic to Early Cretaceous are mostly concentrated in the GXR, with sporadic occurrences in the LXZR, which were formed in a post-orogenic extensional environment triggered by the PPO and MOO tectonic domains [56,63,65–88].

The NCGXR comprises two main units, i.e., the Erguna and Xing'an blocks (Figure 1c). The amalgamation of the Erguna and Xing'an blocks occurred along the Xinlin-Xiguitu Fault in the Early Palaeozoic induced by the closure of the PAO [28,89–92]. Volcanic-sedimentary rocks of the Xinghuadukou, Ergunahe, Jiageda, and Luomahu groups; Neoproterozoic magmatic rocks; and minor Palaeoproterozoic gneisses compose the basement of the Erguna Block [29,93,94]. Multiple Late Palaeozoic–Late Mesozoic episodes of accretion and collision occurred on the Erguna Block, resulting in the formation of tremendous intrusions, volcanics, and volcanoclastic rocks [95,96]. Widespread Mesozoic igneous rocks; Early Palaeozoic basement rocks composed of the Wolegen, Xinkailing, Zalantun, and Fengshuigouhe groups; together with the Xinghuadukou Complex and dispersed Palaeozoic plutons and sediments constitute the Xing'an Block, the primary component of the GXR [29]. Neoproterozoic granite is locally distributed in the western region [97]. Mesozoic volcanics are categorized by the Tamulangou, Manketouebo, Manitu, Baiyingaolao, and Meiletu Formations (Fms), from oldest to youngest [93]. The Palaeozoic strata were extensively emplaced through substantial Palaeozoic to Mesozoic granitic intrusions. The latest geochronological evidence indicates that the magmatism within the NCGXR took place in two periods: the Palaeozoic granites consisting of granite, monzogranite, granodiorite, quartz diorite, and syenogranite mainly distributed in the northeastern part with zircon U-Pb ages of 517–420 and 359–250 Ma; and the Mesozoic granites, comprising monzogranite, syenogranite, granodiorite, granite porphyry, quartz porphyry, and quartz monzogranite, which are more widespread than the Palaeozoic intrusions and yielded a zircon U-Pb age of 250–118 Ma [29,98–104] (Figure 1c).

### 3. Ore Deposit Geology

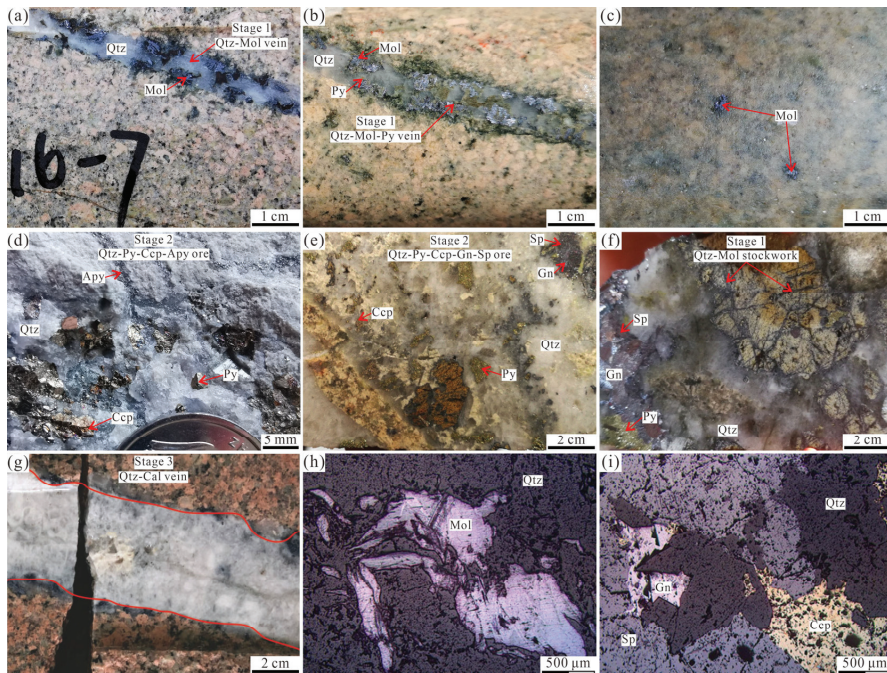
The Lower Urgen molybdenum deposit (120°27'30" E, 50°22'42" N), situated in the central NCGXR, discovered in 2017, is still in exploration and not in production (Figure 1c). The strata exposed in the mining area comprise the Tamulangou Fm of the Middle Jurassic, Manketouebo Fm of the Upper Jurassic, Baiyingaolao Fm of the Lower Cretaceous, and Quaternary [30] (Figure 2). The Tamulangou Fm comprises intermediate–basic volcanics including trachyandesite, andesite, and basaltic-trachyandesite. The Manketouebo Fm comprises felsic volcanics including volcanic breccia, rhyolite, and volcanic agglomerate. The Baiyingaolao Fm is locally dispersed in the northwestern part, which is composed of rhyolite, rhyolitic breccia lava, and tuff [30]. Mesozoic granitoids include quartz monzonite porphyry, syenite porphyry, and granite porphyry. The Middle Jurassic quartz monzonite porphyry outcrops are scattered in the western and central regions. The Early Cretaceous syenite porphyry locally occurs in the western region, while the Early Cretaceous granite porphyry outcrops are mostly distributed in the eastern region [30] (Figure 2). Zhang et al. [31] obtained precise zircon U-Pb ages of the barren quartz monzonite porphyry and syenite porphyry of  $165.0 \pm 2.5$  Ma and  $125.5 \pm 1.9$  Ma, respectively. Mineralization is characterized by concealed veinlet-disseminated- and vein-type quartz–sulfide orebodies mostly hosted in the cupola of the Early Cretaceous granite porphyry (Figures 2c and 3). Ore minerals are mainly molybdenite and pyrite, as well as subordinate chalcopyrite, sphalerite, arsenopyrite, and galena (Figure 3). K-feldspar, quartz, and sericite are the predominant gangue minerals, accompanied by epidote, biotite, and calcite (Figures 3g and 4). Molybdenite occurs as medium-coarse grained (1.2–7 mm) crystals with platy and leaf-like forms in ore-bearing quartz veins and granite porphyry (Figure 3a–c). Pyrite is present as euhedral to subhedral octahedral–dodecahedral crystals, and usually coexists with

molybdenite, chalcopyrite, sphalerite, and galena in granular aggregate forms (Figure 3). Sphalerite occurs as medium-coarse grained (1.5–7 mm) anhedral crystals, and is often intergrown with galena, chalcopyrite, and pyrite (Figure 3e,f,i). Chalcopyrite appears as fine-medium grained (0.4–1.3 mm) irregular crystals. It often coexists with pyrite and occurs in small amounts with galena and sphalerite (Figure 3d,e,i). Arsenopyrite is observed as rhomboid euhedral crystals (Figure 3d). Galena is observed as fine-medium-grained (0.6–4.5 mm) irregular crystals, and is often coeval with sphalerite, pyrite, and chalcopyrite in quartz veins (Figure 3e,f,i). Superposition mineralization in the cupola of the granite porphyry is ubiquitous, and no obvious metallogenic zonation is observed.





phyry with intense potassic alteration (Figure 4a). The phyllic alteration is distinguished by the replacement of primary K-feldspar and plagioclase in the granite porphyry with quartz and sericite (Figure 4e). Quartz–pyrite–chalcopyrite, quartz–galena–sphalerite, and quartz–molybdenite(–pyrite) veins are usually developed in the phyllic alteration zone (Figure 4b,c). The propylitic alteration generally represents low-temperature hydrothermal alteration, which is featured by plagioclase replaced by epidote [1,3] (Figure 4d,f).



**Figure 3.** Representative photographs (a–g) and photomicrographs (h,i) of the mineralization in the Lower Urgen molybdenum deposit. (a) Quartz–molybdenite vein of stage 1 in the granite porphyry. (b) Quartz–molybdenite–pyrite vein of stage 1 in the granite porphyry. (c) Molybdenite occurs as disseminations. (d) Quartz–pyrite–chalcopyrite–arsenopyrite ore of stage 2. (e) Quartz–pyrite–chalcopyrite–galena–sphalerite ore of stage 2. (f) The brecciated fragments of granite porphyry containing quartz–molybdenite stockworks of stage 1 hosted by a quartz–pyrite–galena–sphalerite vein of stage 2. (g) Quartz–calcite vein of stage 3. (h) Molybdenite. (i) Galena intergrown with sphalerite. Sphalerite replacing chalcopyrite along crystal margins. Abbreviations: Mol, molybdenite; Py, pyrite; Ccp, chalcopyrite; Gn, galena; Sp, sphalerite; Apy, arsenopyrite; Qtz, quartz; Cal, calcite.

There are three main stages of hydrothermal processes in the Lower Urgen molybdenum deposit according to crosscutting relationships and mineral paragenetic sequences, including the quartz–molybdenite(–pyrite) stage (stage 1), quartz–polymetallic sulfide stage (stage 2), and quartz–carbonate stage (stage 3).

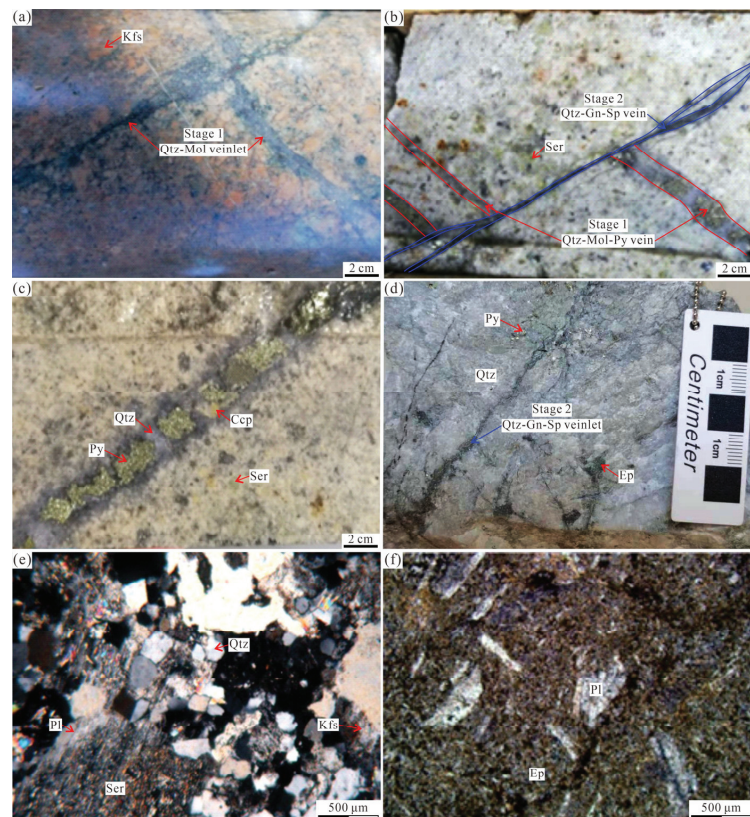
Stage 1 is the main molybdenum mineralization stage. Molybdenite, pyrite, quartz, and sericite are developed in this stage. Various types of veins were formed, including quartz–molybdenite veins and veinlets (Figures 3a and 4a), quartz–molybdenite stockworks (Figure 3f), and quartz–molybdenite–pyrite veins (Figures 3b and 4b). Disseminated molybdenite ores can also be found (Figure 3c).

Stage 2 is featured by an assemblage of chalcopyrite, sphalerite, arsenopyrite, pyrite, galena, quartz, sericite, and epidote. The most common sulfide is pyrite, which appears as fine-medium-grained euhedral to subhedral crystals and aggregates, which often form quartz–sulfide veins with chalcopyrite, galena, sphalerite, and quartz, i.e.,



quartz–pyrite–chalcopyrite–arsenopyrite veins (Figure 3d), quartz–chalcopyrite–pyrite veins (Figure 4c), quartz–pyrite–chalcopyrite–sphalerite–galena veins (Figure 3e), and quartz–pyrite–sphalerite–galena veins (Figure 3f). Galena and sphalerite are often intergrown, and they form quartz–galena–sphalerite veins and veinlets (Figure 4b,d). The brecciated fragments of granite porphyry containing stage 1 quartz–molybdenite stockworks can be found in stage 2 quartz–pyrite–sphalerite–galena veins (Figure 3f). Additionally, stage 2 quartz–galena–sphalerite veins cut stage 1 quartz–molybdenite–pyrite veins (Figure 4b).

Stage 3 represents the termination of the hydrothermal activity in the Lower Urgen molybdenum deposit. During this stage, quartz and calcite make up the majority of the veins, and sulfides are no longer found in this veins' stage (Figure 3g).



**Figure 4.** Representative hand specimen (a–d) and photomicrographs (crossed-polarized light) (e,f) of gangue minerals from the Lower Urgen molybdenum deposit. (a) Quartz–molybdenite veinlets of stage 1 occur in the granite porphyry with potassic alteration. (b) Quartz–molybdenite–pyrite veins of stage 1 cut by quartz–galena–sphalerite of stage 2. These ore veins occur in the granite porphyry with phyllic alteration. (c) Quartz–pyrite–chalcopyrite vein of stage 2 occurs in the granite porphyry with phyllic alteration. (d) Quartz–galena–sphalerite veinlets of stage 2 are spatially related to silicification and propylitic alteration. (e) Phyllic-altered granite porphyry is characterized by quartz and sericite replacing plagioclase along fractures and crystal margins. (f) Propylitic-altered andesite is featured with epidote replacing plagioclase. Abbreviations: Qtz, quartz; Kfs, K-feldspar; Pl, plagioclase; Ser, sericite; Ep, epidote; Mol, molybdenite; Py, pyrite; Gn, galena; Sp, sphalerite; Ccp, chalcopyrite.

## 4. Sampling and Analytical Methods

### 4.1. Samples

Samples for this study were all collected from drillholes, containing three granite porphyry samples, twenty-nine sulfide samples, and twenty-eight quartz samples. The sample locations are indicated in Figure 2c. All granite porphyry samples (T0a1-1, T0a1-2, and T16-1) were fresh and used for whole-rock Pb isotope analyses. Twenty-nine sulfide samples comprised sixteen molybdenite samples, seven pyrite samples, four chalcopyrite samples, and two galena samples. Sixteen molybdenite samples were obtained from stage 1 molybdenite(–pyrite)-bearing quartz veins, while the other sulfide samples were all collected from stage 2 sulfide-bearing quartz veins. Two molybdenite samples (G5 and LE-1) were used for Re–Os isotope analyses. Six molybdenite samples (LU16-1, LU16-2, LU16-3, LU16-4, LU16-5, and LU16-6), two pyrite samples (LU16-7 and LU16-8), two chalcopyrite samples (LU16-9 and LU16-10), and one galena sample (LU16-11) were used for S isotope analyses. Eight molybdenite samples (D17-2, D17-3, D17-4, D17-5, D17-7, D0A1-1, D0A1-2, and D0a1-1), five pyrite samples (G10-2, G11-2, G13, G14, and D17-1), two chalcopyrite samples (D17-2 and G8-2), and one galena sample (G8-3) were used for Pb isotope analyses. The quartz samples were obtained from veins of all stages, including seven samples from stage 1 molybdenite(–pyrite)-bearing quartz veins, nine samples from stage 2 sulfide-bearing quartz veins, and five samples from stage 3 quartz–carbonate veins. Seven quartz samples of stage 1 veins (B16-1, B16-2, B16-3, B16-4, B16-5, B16-6, B16-7), seven quartz samples of stage 2 veins (D14-1, D16-1, D16-4, D16-6, D16-7, D16-8, and D16-9), and three quartz samples of stage 3 veins (G8-1, G10-1, and G11-1) were used for H–O isotope analyses. Seven quartz samples of stage 1 veins (BG16-1, BG16-2, BG16-3, BG16-4, BG16-5, BG16-6, and BG16-7), two quartz samples of stage 2 veins (BG8-1 and BG14-1), and two quartz samples of stage 3 veins (BG8-2 and BG8-3) were used for the FI study. For investigations of FIs in quartz cores, thirty-six double-polished thin sections (200 µm thick) were prepared.

### 4.2. Molybdenite Re–Os Isotope Dating

Re–Os isotope analyses were carried out at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences in Guiyang, China. A TJA PQ ExCell ICP–MS was applied to measure the contents of Re,  $^{187}\text{Re}$ , and  $^{187}\text{Os}$ . We followed the analytical procedures reported in [105,106]. The Re–Os model ages were calculated using the formula  $t = 1/\lambda [\ln(1 + ^{187}\text{Os}/^{187}\text{Re})]$ , where  $\lambda$  is the decay constant for  $^{187}\text{Re}$  ( $1.666 \times 10^{-11} \text{ year}^{-1}$ ) [107].

### 4.3. FIs Laser Raman Spectroscopy

A Renishaw inVia laser Raman probe at the Beijing Createch Testing Technology Co., Ltd. in Beijing, China, was applied to examine the vapor and liquid components of quartz-hosted FIs at room temperature. For detection, a laser power of 20 mW and an argon ion laser with a wavelength of 514.5 nm were used. The spectrum was measured from 1000 to  $4000 \text{ cm}^{-1}$  with a counting time of 20 s for each scan. Detailed analytical procedures are consistent with those in [108].

### 4.4. FIs Microthermometry

FI microthermometry was conducted using a Linkam THMS 600 heating-freezing stage with a stage of  $-195$  to  $600^\circ\text{C}$  mounted on a Zeiss microscope at the Beijing Createch Testing Technology Co., Ltd., Beijing, China. The accuracy of temperature observations is  $0.2^\circ\text{C}$  through cooling,  $\pm 0.2^\circ\text{C}$  for  $0$ – $100^\circ\text{C}$ , and  $\pm 2^\circ\text{C}$  for  $100$ – $450^\circ\text{C}$ . To properly record the phase transformation process, the heating rate was decreased to  $0.1^\circ\text{C}/\text{min}$  close to the freezing point and  $0.2^\circ\text{C}/\text{min}$  close to the homogenization temperature. To prevent unintentional deviations, FI results were only collected on FI assemblages (FIAs) [109]. During heating, seven different temperature types were recorded, including  $\text{CO}_2$ –ice melting temperatures ( $T_{\text{mCO}_2}$ ), first ice melting temperatures ( $T_{\text{fmice}}$ ), final ice melting temperatures

( $T_{m_{ice}}$ ), final clathrate melting temperatures ( $T_{m_{clath}}$ ),  $CO_2$  homogenization temperatures ( $T_{h_{CO_2}}$ ), halite dissolution temperatures ( $T_{m_H}$ ), and final homogenization temperatures ( $T_h$ ).  $T_{m_{clath}}$  was used to determine the salinities of the fluid system composed of NaCl,  $CO_2$ , and  $H_2O$  [110].  $T_{m_{ice}}$  and  $T_{m_H}$  were used to obtain the salinities of the fluid system composed of NaCl and  $H_2O$  [111,112]. Using the Flincor program, the bulk molar volume of FIs, the density of the bulk fluids and carbonic liquid, and mole fractions of compositions were acquired [113–115].

4.5. Quartz H-O Isotopes

H-O isotope analyses were carried out using a MAT253 mass spectrometer at the Beijing Research Institute of Uranium Geology in Beijing, China. The accuracies of the H and O isotopic measurements are better than  $\pm 2\text{‰}$  and  $\pm 0.2\text{‰}$ , respectively. The fractionation formula  $1000 \ln \alpha_{\text{quartz water}} = 3.38 \times 10^6 T^{-1} - 3.40$  was applied to calculate the  $\delta^{18}O_{H_2O}$  of fluids, where T is the Kelvin temperature [116]. The average FI homogenization temperature for each stage was used to determine the  $\delta^{18}O_{H_2O}$  values.

4.6. S-Pb Isotopes

The sulfide S-Pb isotope measurements were performed at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. A Delta V Plus mass spectrometer was used to analyze the S isotopic compositions of sulfides with an analytical accuracy of  $\pm 2\text{‰}$ . Sulfide  $\delta^{34}S$  values were calculated on sulfur dioxide produced via the traditional extraction method described in [117]. The  $\delta^{34}S$  results were recorded using the Canyon Diablo Troilite (CDT).

Thermal ionization mass spectrometry using an ISOPROBE-T mass spectrometer was used to analyze the Pb isotopic compositions of sulfides and granite porphyry. The accuracy for 1  $\mu\text{g}$  of  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  was greater than 0.005% ( $2\sigma$ ). The Pb isotopic analyses are reported with respect to Pb standard reference NBS-981 values, as follows:  $^{206}\text{Pb}/^{204}\text{Pb} = 16.934 \pm 0.007$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.486 \pm 0.012$ , and  $^{208}\text{Pb}/^{204}\text{Pb} = 36.673 \pm 0.033$  [118].

5. Results

5.1. Molybdenite Re-Os Ages

Table 1 lists the results of Re and Os isotope compositions of two molybdenite samples from the Lower Urgen deposit. The  $^{187}\text{Re}$  and  $^{187}\text{Os}$  contents of the samples vary from 19,468 to 27,503 ppb and 47.958 to 64.540 ppb, respectively. The Re contents of the samples are 31,202–43,934 ppb. The two Re-Os model ages are  $141.2 \pm 1.5$  and  $147.7 \pm 1.7$  Ma.

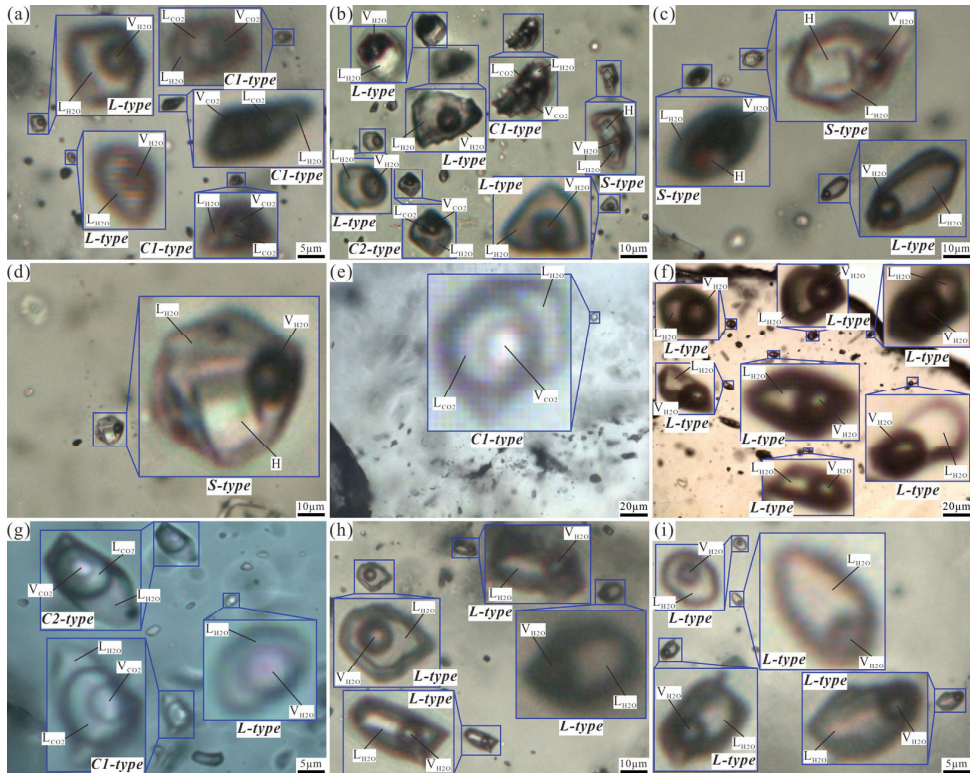
Table 1. Re–Os isotopic data for molybdenite from the Lower Urgen molybdenum deposit.

| Sample No. | Re (ppb) |           | Os (ppb) |           | $^{187}\text{Re}$ (ppb) |           | $^{187}\text{Os}$ (ppb) |           | Model Age (Ma) |           |
|------------|----------|-----------|----------|-----------|-------------------------|-----------|-------------------------|-----------|----------------|-----------|
|            | Re       | $1\sigma$ | Os       | $1\sigma$ | $^{187}\text{Re}$       | $1\sigma$ | $^{187}\text{Os}$       | $1\sigma$ | Age            | $1\sigma$ |
| G5         | 43,934   | 1558      | 0.083    | 0.008     | 27,503                  | 975       | 64.540                  | 0.698     | 141.2          | 1.5       |
| LE-1       | 31,202   | 528       | 0.128    | 0.015     | 19,468                  | 231       | 47.958                  | 0.523     | 147.7          | 1.7       |

5.2. FI Petrography

Primary and secondary FIs were identified based on the criteria suggested by [109,119]. All descriptions strictly follow the concept of FIAs [109]. An FIA only applies to FI vacuoles that developed along the identical growth bands in an individual crystal, as well as within the same T-P circumstances. Nonetheless, extremely few FIs are dispersed within or along the growth bands, and the bulk is too small to be quantified ( $<5 \mu\text{m}$ ). Most FIs that are suitable for measurement appear as isolated, clustered, or randomly distributed (Figure 5). As suggested by [109,119–121], FIs that are away from apparent cracks and appear as isolated, clustered, or randomly distributed forms are considered as primary FIs, and these FIs are selected for further investigation. In contrast, FIs along healed fractures that have apparent secondary causes are not considered. Four different types of FIs are recognized

based on phase components at room temperature and phase changes due to variations in temperature, including the two-phase (L + V) liquid-rich (L-type), saline (S-type), CO<sub>2</sub>-rich (C1-type), and CO<sub>2</sub>-bearing (C2-type) FIs. The descriptions of the petrographic features of each FI type are as follows.



**Figure 5.** Representative photomicrographs of FIs in quartz veins of different stages at Lower Urgen. (a) Phase separation recorded by L- and C1-type FIs at stage 1. (b) An immiscibility FIA consisting of L-, S-, C1-, and C2-type FIs at stage 1. (c) Coexistence of L- and S-type FIs at stage 1. (d) Isolate S-type FI at stage 1. (e) Isolate C1-type FI at stage 1. (f) An FIA containing many primary L-type FIs at stage 1. (g) Phase separation recorded by L-, C1-, and C2-type FIs at stage 2. (h) An FIA containing many primary L-type FIs at stage 2. (i) An FIA containing four L-type FIs at stage 3. Abbreviations: H, halite; L<sub>CO<sub>2</sub></sub>, liquid CO<sub>2</sub>; V<sub>CO<sub>2</sub></sub>, vapor CO<sub>2</sub>; L<sub>H<sub>2</sub>O</sub>, liquid H<sub>2</sub>O; V<sub>H<sub>2</sub>O</sub>, vapor H<sub>2</sub>O.

L-type FIs are ubiquitous in all stages of quartz. At room temperature, they have a vapor phase and a liquid phase with L<sub>H<sub>2</sub>O</sub>/(L<sub>H<sub>2</sub>O</sub> + V<sub>H<sub>2</sub>O</sub>) ratios of 65–90 vol% (Figure 5). With diameters ranging from 5 to 15 µm, these FIs can be ellipsoidal, rectangular, negative-crystal, or irregular in shape. L-type FIs occur alongside S-, C1-, and C2-type FIs in stage 1 as immiscibility FIAs (Figure 5a–c). They are also intergrown with C1- and C2-type FIs and form immiscibility FIAs in stage 2 quartz crystals (Figure 5g). In quartz veins of stages 1 and 2, L-type FIs are abundant and make up around 50% of all FIs; however, stage 3 veins solely contain L-type FIs.

Only stage 1 quartz veins have S-type FIs, which exhibit high salinities and densities. S-type FIs are composed of a cubic halite daughter mineral, a liquid phase, and a vapor bubble (3–10 vol%). They are elliptical, negative-crystal, or irregular in shape, with diameters of 7 to 15 µm. S-type FIs can exist alone or with L-, C1-, and C2-type FIs to form immiscibility



FIAs in stage 1 (Figure 5b–d). In abundance, S-type FIAs account for about 10% of all FIAs in stage 1 veins.

C1-type FIAs occur as ellipsoidal, circular, or negative-crystal shapes, and have a diameter of 5 to 13  $\mu\text{m}$ . The  $\text{CO}_2$  phase content ranges from 60 to 85 vol%. Usually, 60 to 80 vol% of the entire  $\text{CO}_2$  phase is made up of vapor  $\text{CO}_2$ . C1-type FIAs commonly appear in the three-phase form ( $\text{V}_{\text{CO}_2} + \text{L}_{\text{CO}_2} + \text{L}_{\text{H}_2\text{O}}$ ), with a small amount of the two-phase form ( $\text{V}_{\text{CO}_2} + \text{L}_{\text{H}_2\text{O}}$ ) (Figure 5a,b,e,g). The two-phase FIAs are regarded as  $\text{CO}_2$ -rich FIAs as clathrates were observed during freezing runs. In abundance, C1-type FIAs frequently coexist as immiscibility FIAs with L-, S-, and C2-type FIAs (Figure 5a–c,g), and account for about 25 vol% and 30 vol% of all FIAs in veins of stages 1 and 2, respectively.

At room temperature, C2-type FIAs exist in the three-phase ( $\text{V}_{\text{CO}_2} + \text{L}_{\text{CO}_2} + \text{L}_{\text{H}_2\text{O}}$ ) state, and minor FIAs display a two-phase ( $\text{V}_{\text{CO}_2} + \text{L}_{\text{H}_2\text{O}}$ ) form (Figure 5b,g). During freezing, clathrates are also observed in these two-phase C2-type FIAs and can therefore be distinguished from L-type FIAs. Typically, vapor  $\text{CO}_2$  makes about 60–80 vol% of the total  $\text{CO}_2$  phase, and the amount of  $\text{CO}_2$  phase varies from 15 to 45 vol%. These FIAs are irregular or nearly ellipsoidal in shape with a diameter of 5–15  $\mu\text{m}$ . C2-type FIAs are intergrown with L- and C1-type FIAs (Figure 5g), together with small quantities of S-type FIAs (Figure 5b), and account for approximately 15 vol% and 20 vol% of all FIAs in veins of stages 1 and 2, respectively.

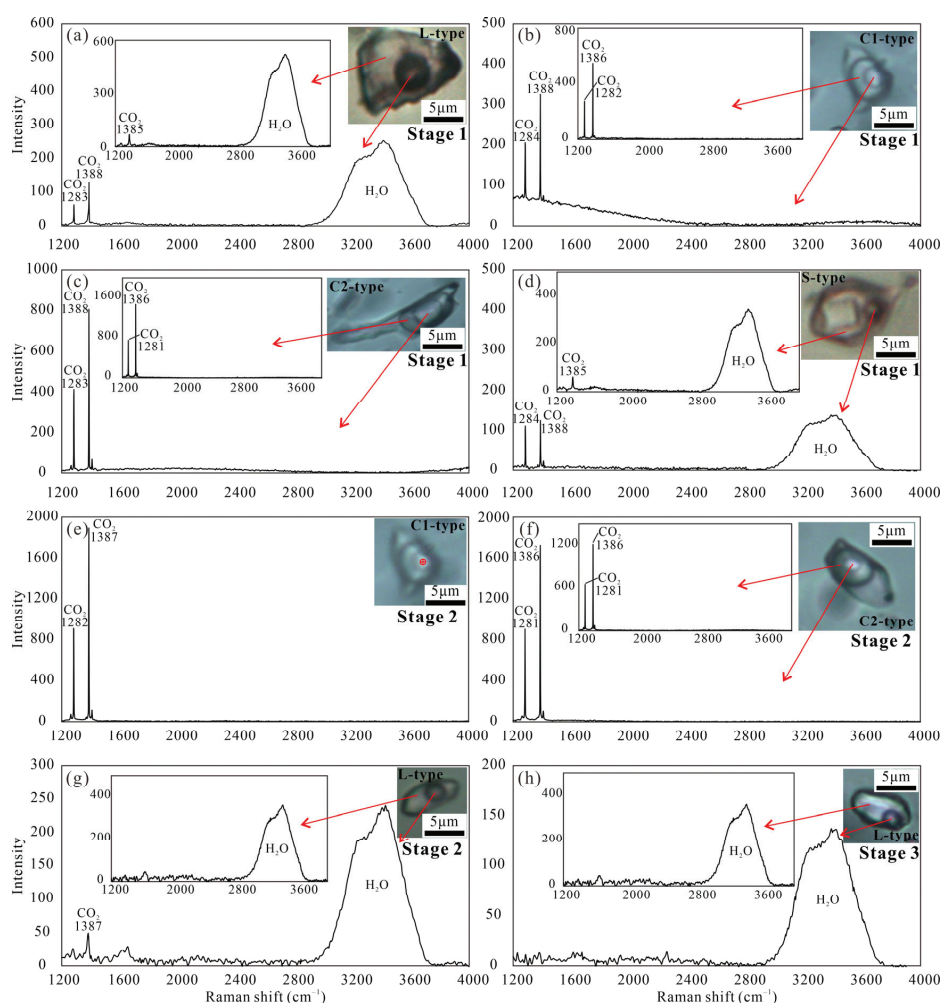
### 5.3. FI Laser Raman Spectroscopy

Figure 6 illustrates the components of typical FIAs from quartz veins of all stages. A substantial volume of  $\text{H}_2\text{O}$  and a negligible amount of  $\text{CO}_2$  (1385  $\text{cm}^{-1}$ , 1283 and 1388  $\text{cm}^{-1}$ , respectively) were detected in both the liquid and vapor phase in L-type FIAs of stage 1 (Figure 6a). C1-type FIAs of stage 1 contain  $\text{CO}_2$  as the only species in both the vapor and liquid  $\text{CO}_2$  phases (1284 and 1388  $\text{cm}^{-1}$ , 1282 and 1386  $\text{cm}^{-1}$ , respectively) (Figure 6b). C2-type FIAs of stage 1 have a similar vapor and liquid phase composition to stage 1 C1-type FIAs, with  $\text{CO}_2$  as the only component of the  $\text{CO}_2$  phase (1283 and 1388  $\text{cm}^{-1}$ , 1281 and 1386  $\text{cm}^{-1}$ , respectively) (Figure 6c). Analogous liquid and vapor phase components, which are predominately made of  $\text{H}_2\text{O}$  and include a little amount of  $\text{CO}_2$  (1385  $\text{cm}^{-1}$ , 1284 and 1388  $\text{cm}^{-1}$ , respectively), are present in S-type FIAs of stage 1 (Figure 6d). Consequently, a  $\text{NaCl-H}_2\text{O-CO}_2$  system is represented by the fluids in the quartz–molybdenite(–pyrite) stage. C1-type FIAs of stage 2 show typical  $\text{CO}_2$  spectra (1282 and 1387  $\text{cm}^{-1}$ ) in the vapor  $\text{CO}_2$  phase (Figure 6e). The compositions of the vapor and liquid  $\text{CO}_2$  phase of C2-type FIAs in stage 2 only contain  $\text{CO}_2$  (1281 and 1386  $\text{cm}^{-1}$ ) (Figure 6f).  $\text{H}_2\text{O}$  is the predominant gas species in the vapor phase of L-type FIAs in stage 2 quartz, with only trace amounts of  $\text{CO}_2$  (1387  $\text{cm}^{-1}$ ). In contrast, only  $\text{H}_2\text{O}$  was detected in the liquid phase of L-type FIAs in stage 2 quartz (Figure 6g). Thus, a  $\text{NaCl-H}_2\text{O-CO}_2$  system is represented by the fluids in the quartz–polymetallic sulfide stage. L-type FIAs of stage 3 lack  $\text{CO}_2$  detection and only have  $\text{H}_2\text{O}$  for the compositions of the liquid and vapor phases, demonstrating the characteristic of a  $\text{NaCl-H}_2\text{O}$  system (Figure 6h).

### 5.4. FI Microthermometry

Only primary FIAs were chosen for microthermometry to prevent interpretation errors brought by the post-ore modification. Using the FIA concept, the reliability of microthermometric results has been assessed [109]. Large disparities in homogenization temperatures in spatially close FIAs prevent them from being unequivocally classified as an FIA; instead, they are thought to be the result of necking, stretching, or heterogeneous entrapment [120]. The microthermometry data for isolated FIAs are considered, barring a significant discrepancy with surrounding FIAs [121]. If the homogenization temperature variation within a cluster of a single FI type is below 15  $^\circ\text{C}$ , the possibility of post-entrapment modification, generational overlap, or heterogeneous trapping of FIAs is ruled out, and it is argued that these FIAs represent a uniform fluid entrapment. We thus suggest that those results are trustworthy and that the overall average of a cluster is adequate for additional research [120]. An immiscibility FIA is a group of FIAs of various types that possess comparable ranges of ho-

mogenization temperature (variation below 15 °C) but distinct homogenization processes. In this case, the complete FIA was represented for statistical analysis by the average of several types of FIs.

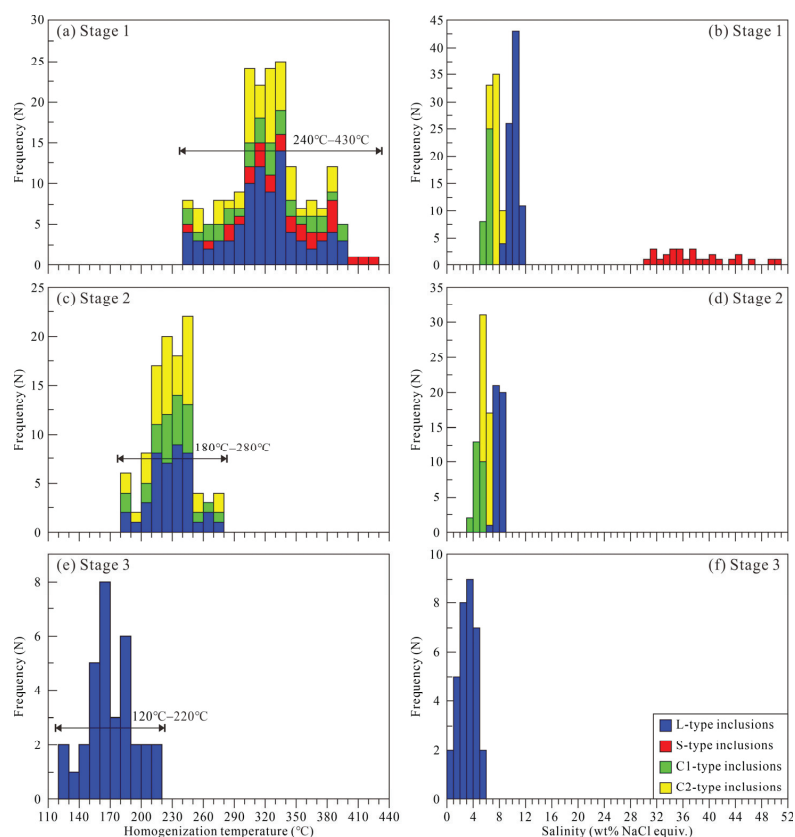


**Figure 6.** Representative laser Raman spectra for FIs from the Lower Urgen molybdenum deposit. (a) Raman spectra of stage 1 L-type FI reflect the presence of H<sub>2</sub>O and minor amounts of CO<sub>2</sub>. (b) Raman spectra of stage 1 C1-type FI indicate the presence of CO<sub>2</sub> in the CO<sub>2</sub> phase (V<sub>CO<sub>2</sub></sub> + L<sub>CO<sub>2</sub></sub>). (c) Raman spectra of stage 1 C2-type FI reflect the existence of CO<sub>2</sub> in the CO<sub>2</sub> phase (V<sub>CO<sub>2</sub></sub> + L<sub>CO<sub>2</sub></sub>). (d) Raman spectra of stage 1 S-type FI indicate the presence of H<sub>2</sub>O and minor amounts of CO<sub>2</sub>. (e) Raman spectra of stage 2 C1-type FI reflect the occurrence of CO<sub>2</sub> in vapor CO<sub>2</sub>. (f) Raman spectra of stage 2 C2-type FI indicate the existence of CO<sub>2</sub> in the CO<sub>2</sub> phase (V<sub>CO<sub>2</sub></sub> + L<sub>CO<sub>2</sub></sub>). (g) Raman spectra of stage 2 L-type FI reflect the presence of H<sub>2</sub>O and minor amounts of CO<sub>2</sub>. (h) Raman spectra of stage 3 L-type FI indicate the existence of H<sub>2</sub>O.

In this investigation, microthermometric results for 320 FIAs of three stages are listed in Table S1 (see the Supplementary Materials) and illustrated in Figure 7. The T<sub>fmi</sub> for L-type FIs of all stages ranges from −21.6 to −20.8 °C, consistent with the eutectic temperature of the H<sub>2</sub>O–NaCl system, indicating that most of the dissolved salts are



NaCl [111,122]. As mentioned in Section 5.3, the L- and S-type FIs sometimes display weak CO<sub>2</sub> signals, but the CO<sub>2</sub> characteristics cannot be observed during the petrography observation and microthermometry of these FIs. The detection limit of CO<sub>2</sub> through laser Raman spectroscopy can be as low as 1 bar, while the phase transition of CO<sub>2</sub> can be observed in microthermometry with a CO<sub>2</sub> pressure of at least 10.4 bar (the melting of CO<sub>2</sub> clathrate can be observed) or 45 bar (solid phase of CO<sub>2</sub> melting can be observed) [123]. In summary, the amount of CO<sub>2</sub> in the S-type FIs of stage 1 and L-type FIs of stages 1 and 2 is extremely low and almost negligible, and thus the salinities of these FIs were obtained using the  $T_{mH}$  and  $T_{mice}$ , respectively.



**Figure 7.** Histograms of homogenization temperatures (a,c,e) and salinities (b,d,f) for FIs in quartz from the Lower Urgan molybdenum deposit according to the concept of FIAs.

The entrapped fluid characteristics are often dramatically changed through post-entrapment modification (dismemberment and/or migration) in quartz-hosted FIs [124,125]. Euhedral quartz crystals that are naturally formed frequently exhibit these modifications in addition to quartz phenocrysts and veins. Although not verified, a satisfactory FI preservation state is recommended if the FIs display constant phase ratios, develop in clear trails or growth bands, and provide densely concentrated microthermometric values [125]. On the contrary, regular negative-crystal forms are neither necessary nor indicative of the preservation of syn-entrapment characteristics of FIs. Unless they adhere to specified growth bands, clusters of randomly scattered FIs often reflect secondary or pseudosecondary FI trails that have dissolved. Audétat [124] demonstrated that the decline in FI volume caused by post-entrapment modification results in a decrease in the homogenization temperature,

a steepening of the isochore, and an increase in fluid density. By contrast, in magmatic–hydrothermal systems, water loss from FIs seldom surpasses twenty percent; consequently, the fluid salinities that are determined should, in most instances, be almost accurate. In the current research, FIs inside or along the growth zones of euhedral quartz occur incredibly seldom, and the bulk of them are too small to investigate ( $<5\ \mu\text{m}$ ). Post-entrapment modification may have occurred to varied degrees in clustered, isolated, and randomly dispersed FIs, but it seems inescapable. However, to guarantee that the chosen FIAs only had slight effects of post-entrapment modification, FIAs that displayed obvious post-entrapment modification features, e.g., deformation, movement tracks, stretching, shrinkage, or deteriorating halos, have been excluded [119,124–126]. Nonetheless, the genuine densities and homogenization temperatures of the examined FIs are slightly lower and higher than the calculated data, respectively. Comparatively, FI salinities are frequently less influenced, and most of them tend to have maintained their original salinities. As a result, we primarily concentrate on the salinities of the examined FIs, while the homogenization temperatures are used as a reference.

Stage 1 veins contain L-, S-, C1-, and C2-type FIs. The Th of L-type FIs ranges from 240 to 400 °C, and the  $T_{\text{mice}}$  varies between  $-8.2$  and  $-5.1$  °C (corresponding to 8.0–11.9 wt% NaCl equiv.). The disappearance of the vapor bubbles indicates complete homogenization. The  $T_{\text{mH}}$  of S-type FIs is between 160 and 428 °C (corresponding to 30.1–50.8 wt% NaCl equiv.). Halite dissolution or the disappearance of vapor bubbles is an indicator that S-type FIs homogenize between 245 and 428 °C. The  $T_{\text{mCO}_2}$  of C1-type FIs ranges from  $-59.8$  to  $-57.0$  °C. C1-type FIs have a  $T_{\text{mclath}}$  of  $5.9$ – $7.4$  °C and calculated salinities of 5.0–7.5 wt% NaCl equiv. At  $14.5$ – $21.5$  °C, the  $\text{CO}_2$  phase homogenizes to the vapor  $\text{CO}_2$  phase. At  $240$ – $397$  °C, the liquid  $\text{H}_2\text{O}$  phase disappears, signifying the completion of the homogenization. C2-type FIs have a  $T_{\text{mCO}_2}$  of  $-59.8$  to  $-57.0$  °C and  $T_{\text{mclath}}$  of  $5.1$ – $6.8$  °C, corresponding to salinities of 6.0–8.8 wt% NaCl equiv. At  $20.3$ – $25.9$  °C,  $\text{CO}_2$  homogenizes to the vapor  $\text{CO}_2$  phase, and at  $241$ – $395$  °C, C2-type FIs finally homogenize to the liquid phase (Figure 7a,b).

L-, C1-, and C2-type FIs can be found in stage 2 quartz veins. Compared to stage 1 FIs, these FIs have a lower Th and lower salinities (Figure 7c,d). L-type FIs have a  $T_{\text{mice}}$  of  $-5.9$  to  $-3.7$  °C, corresponding to 6.0–9.1 wt% NaCl equiv. At  $182$ – $278$  °C, L-type FIs homogenize and are characterized by the vapor bubbles' disappearance. C1-type FIs yield a  $T_{\text{mCO}_2}$  of  $-59.8$  to  $-57.0$  °C,  $T_{\text{mclath}}$  of  $6.8$ – $8.5$  °C, and calculated salinities of 3.0–6.0 wt% NaCl equiv. At  $14.6$ – $22.5$  °C, the  $\text{CO}_2$  phase homogenizes to the vapor  $\text{CO}_2$  phase, and at  $181$ – $277$  °C, the liquid  $\text{H}_2\text{O}$  phase is eliminated, indicating complete homogenization. C2-type FIs contain a  $T_{\text{mCO}_2}$  that varies between  $-59.8$  and  $-56.8$  °C and a  $T_{\text{mclath}}$  of  $6.2$ – $7.9$  °C (corresponding to 4.1–7.1 wt% NaCl equiv.). The homogeneity of the  $\text{CO}_2$  phase is featured by the elimination of the liquid  $\text{CO}_2$  phase, and the  $T_{\text{HCO}_2}$  has a range of  $21.9$ – $25.9$  °C. Total homogenization occurs when the vapor  $\text{CO}_2$  phase is eliminated, and the Th of C2-type FIs has a range of  $180$ – $277$  °C (Figure 7c,d).

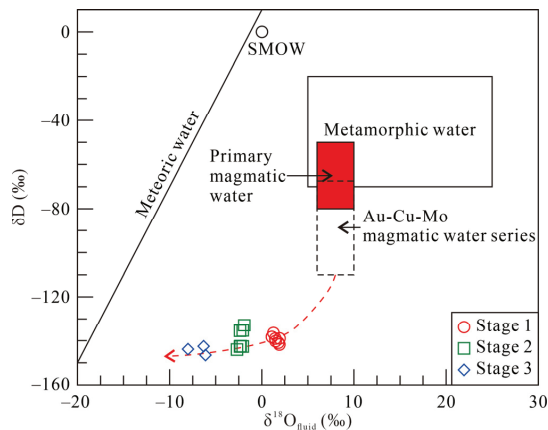
L-type FIs are the only FIs found in quartz–carbonate veins of stage 3, which have  $T_{\text{mice}}$  values between  $-5.0$  and  $-0.1$  °C and NaCl equivalent salinities between 0.2 and 7.9 wt%. At  $120$ – $218$  °C, these FIs ultimately homogenize to the liquid phase (Figure 7e,f).

### 5.5. Quartz H-O Isotopic Compositions

The hydrogen and oxygen isotopic compositions of analyzed quartz samples are presented in Table 2 and shown in Figure 8. Seven quartz samples of stage 1 veins have  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values ranging from  $-141.8$  to  $-136.5$ ‰ and  $7.2$ – $8.0$ ‰, respectively. The  $\delta^{18}\text{O}_{\text{fluid}}$  values are determined to be between 1.1 and 1.9‰. The  $\delta\text{D}$  values of seven quartz samples collected from stage 2 veins are  $-144.1$  to  $-129.9$ ‰, the  $\delta^{18}\text{O}$  values range between 7.3 and 8.1‰, and the calculated  $\delta^{18}\text{O}_{\text{fluid}}$  values are  $-2.7$  to  $-1.9$ ‰. The  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values in three quartz samples from stage 3 veins are  $-146.6$  to  $-142.6$ ‰ and  $5.8$ – $7.7$ ‰, respectively, and the calculated  $\delta^{18}\text{O}_{\text{fluid}}$  values are between  $-8.0$  and  $-6.1$ ‰.

**Table 2.** Hydrogen and oxygen isotopic compositions of quartz from the Lower Urgen molybdenum deposit.

| Sample No. | Stage   | Mineral | $\delta D$ (‰) | $\delta^{18}O_{\text{quartz}}$ (‰) | T (°C) | $\delta^{18}O_{\text{fluid}}$ (‰) |
|------------|---------|---------|----------------|------------------------------------|--------|-----------------------------------|
| B16-1      | Stage 1 | Quartz  | −140.2         | 7.6                                | 323    | 1.5                               |
| B16-2      | Stage 1 | Quartz  | −138.3         | 7.2                                | 323    | 1.1                               |
| B16-3      | Stage 1 | Quartz  | −136.5         | 7.4                                | 323    | 1.3                               |
| B16-4      | Stage 1 | Quartz  | −140.9         | 7.9                                | 323    | 1.8                               |
| B16-5      | Stage 1 | Quartz  | −139.0         | 8.0                                | 323    | 1.9                               |
| B16-6      | Stage 1 | Quartz  | −141.8         | 8.0                                | 323    | 1.9                               |
| B16-7      | Stage 1 | Quartz  | −139.1         | 7.6                                | 323    | 1.5                               |
| D14-1      | Stage 2 | Quartz  | −142.7         | 7.9                                | 229    | −2.1                              |
| D16-1      | Stage 2 | Quartz  | −135.5         | 7.6                                | 229    | −2.4                              |
| D16-4      | Stage 2 | Quartz  | −142.5         | 7.7                                | 229    | −2.3                              |
| D16-6      | Stage 2 | Quartz  | −135.4         | 7.9                                | 229    | −2.1                              |
| D16-7      | Stage 2 | Quartz  | −129.9         | 8.1                                | 229    | −1.9                              |
| D16-8      | Stage 2 | Quartz  | −142.7         | 7.6                                | 229    | −2.4                              |
| D16-9      | Stage 2 | Quartz  | −144.1         | 7.3                                | 229    | −2.7                              |
| G8-1       | Stage 3 | Quartz  | −146.6         | 7.7                                | 170    | −6.1                              |
| G10-1      | Stage 3 | Quartz  | −143.9         | 5.8                                | 170    | −8.0                              |
| G11-1      | Stage 3 | Quartz  | −142.6         | 7.5                                | 170    | −6.3                              |



**Figure 8.**  $\delta D$  versus  $\delta^{18}O_{\text{fluid}}$  diagram for the Lower Urgen molybdenum deposit (base map after [127]). The magmatic water field of the Au-Cu-Mo series is from [128].

5.6. Sulfide S Isotopic Compositions

In Table 3 and Figure 9, the S isotopic compositions of molybdenite, pyrite, chalcopyrite, and galena collected from the Lower Urgen molybdenum deposit are displayed. Sulfide  $\delta^{34}S$  values range from 3.9 to 5.5‰, with an average value of 5.2‰. Six molybdenite samples contain  $\delta^{34}S$  values of 5.4–5.5‰. Two pyrite samples and two chalcopyrite samples have  $\delta^{34}S$  values of 5.4‰ and 4.8–5.4‰, respectively. One galena sample has a  $\delta^{34}S$  value of 3.9‰.

**Table 3.** Sulfur isotopic compositions of sulfides from the Lower Urgen molybdenum deposit.

| Sample No. | Stage   | Mineral     | $\delta^{34}S$ (‰) |
|------------|---------|-------------|--------------------|
| LU16-1     | Stage 1 | Molybdenite | 5.5                |
| LU16-2     | Stage 1 | Molybdenite | 5.4                |
| LU16-3     | Stage 1 | Molybdenite | 5.5                |

Table 3. Cont.

| Sample No. | Stage   | Mineral      | $\delta^{34}\text{S}$ (‰) |
|------------|---------|--------------|---------------------------|
| LU16-4     | Stage 1 | Molybdenite  | 5.5                       |
| LU16-5     | Stage 1 | Molybdenite  | 5.5                       |
| LU16-6     | Stage 1 | Molybdenite  | 5.5                       |
| LU16-7     | Stage 2 | Pyrite       | 5.4                       |
| LU16-8     | Stage 2 | Pyrite       | 5.4                       |
| LU16-9     | Stage 2 | Chalcopyrite | 5.4                       |
| LU16-10    | Stage 2 | Chalcopyrite | 4.8                       |
| LU16-11    | Stage 2 | Galena       | 3.9                       |

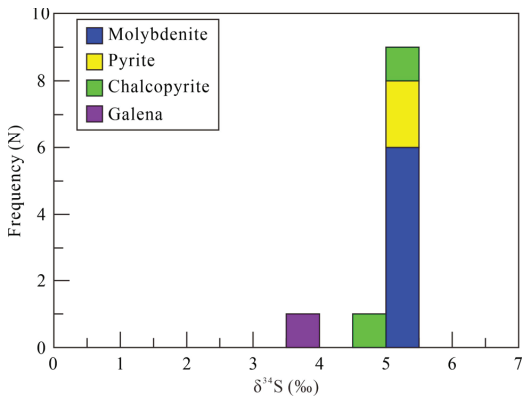


Figure 9. Histogram of sulfur isotopic compositions of metal sulfides from the Lower Urgen molybdenum deposit.

5.7. Sulfides and Whole-Rock Pb Isotopic Compositions

The Pb isotopic compositions of molybdenite, pyrite, chalcopyrite, galena, and granite porphyry are given in Table 4 and Figure 10. The  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios for eight molybdenite samples are 18.340–18.412, 15.540–15.546, and 38.130–38.212, respectively. Five pyrite samples contain  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios of 18.336–18.510, 15.542–15.569, and 38.131–38.312, respectively. The  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios of two chalcopyrite samples are 18.336–18.340, 15.541–15.547, and 38.131–38.143, respectively. One galena sample has  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios of 18.343, 15.550, and 38.149, respectively. The  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios of three molybdenum-bearing granite porphyry samples range from 18.535 to 18.599, 15.571 to 15.574, and 38.419 to 38.583, respectively.

Table 4. Pb isotopic composition of sulfide and granite porphyry samples from the Lower Urgen molybdenum deposit.

| Sample No. | Stage | Mineral     | $^{206}\text{Pb}/^{204}\text{Pb}$ | 2 $\sigma$ | $^{207}\text{Pb}/^{204}\text{Pb}$ | 2 $\sigma$ | $^{208}\text{Pb}/^{204}\text{Pb}$ | 2 $\sigma$ | $\mu$ |
|------------|-------|-------------|-----------------------------------|------------|-----------------------------------|------------|-----------------------------------|------------|-------|
| D17-2      | 1     | Molybdenite | 18.340                            | 0.0004     | 15.542                            | 0.0003     | 38.137                            | 0.0008     | 9.36  |
| D17-3      | 1     | Molybdenite | 18.340                            | 0.0005     | 15.543                            | 0.0005     | 38.153                            | 0.0011     | 9.36  |
| D17-4      | 1     | Molybdenite | 18.355                            | 0.0004     | 15.544                            | 0.0004     | 38.164                            | 0.0009     | 9.36  |
| D17-5      | 1     | Molybdenite | 18.343                            | 0.0004     | 15.540                            | 0.0004     | 38.135                            | 0.0009     | 9.35  |
| D17-7      | 1     | Molybdenite | 18.340                            | 0.0004     | 15.540                            | 0.0004     | 38.130                            | 0.0009     | 9.35  |
| D0A1-1     | 1     | Molybdenite | 18.412                            | 0.0004     | 15.546                            | 0.0004     | 38.212                            | 0.0009     | 9.36  |
| D0A1-2     | 1     | Molybdenite | 18.387                            | 0.0004     | 15.544                            | 0.0004     | 38.183                            | 0.0010     | 9.36  |
| D0a1-1     | 1     | Molybdenite | 18.363                            | 0.0004     | 15.543                            | 0.0003     | 38.170                            | 0.0009     | 9.36  |

Table 4. Cont.

| Sample No. | Stage | Mineral          | <sup>206</sup> Pb/ <sup>204</sup> Pb | 2σ     | <sup>207</sup> Pb/ <sup>204</sup> Pb | 2σ     | <sup>208</sup> Pb/ <sup>204</sup> Pb | 2σ     | μ    |
|------------|-------|------------------|--------------------------------------|--------|--------------------------------------|--------|--------------------------------------|--------|------|
| G10-2      | 2     | Pyrite           | 18.373                               | 0.0005 | 15.549                               | 0.0004 | 38.174                               | 0.0010 | 9.37 |
| G11-2      | 2     | Pyrite           | 18.510                               | 0.0004 | 15.557                               | 0.0004 | 38.249                               | 0.0010 | 9.37 |
| G13        | 2     | Pyrite           | 18.471                               | 0.0004 | 15.569                               | 0.0003 | 38.312                               | 0.0008 | 9.40 |
| G14        | 2     | Pyrite           | 18.341                               | 0.0003 | 15.549                               | 0.0003 | 38.148                               | 0.0008 | 9.37 |
| D17-1      | 2     | Pyrite           | 18.336                               | 0.0003 | 15.542                               | 0.0002 | 38.131                               | 0.0006 | 9.36 |
| D17-2      | 2     | Chalcopyrite     | 18.336                               | 0.0005 | 15.541                               | 0.0004 | 38.131                               | 0.0011 | 9.36 |
| G8-2       | 2     | Chalcopyrite     | 18.340                               | 0.0004 | 15.547                               | 0.0003 | 38.143                               | 0.0008 | 9.37 |
| G8-3       | 2     | Galena           | 18.343                               | 0.0004 | 15.550                               | 0.0004 | 38.149                               | 0.0009 | 9.37 |
| T0a1-1     | –     | Granite porphyry | 18.599                               | 0.0005 | 15.574                               | 0.0005 | 38.583                               | 0.0013 | 9.40 |
| T0a1-2     | –     | Granite porphyry | 18.565                               | 0.0005 | 15.573                               | 0.0004 | 38.515                               | 0.0012 | 9.40 |
| T16-1      | –     | Granite porphyry | 18.535                               | 0.0004 | 15.571                               | 0.0004 | 38.419                               | 0.0010 | 9.39 |

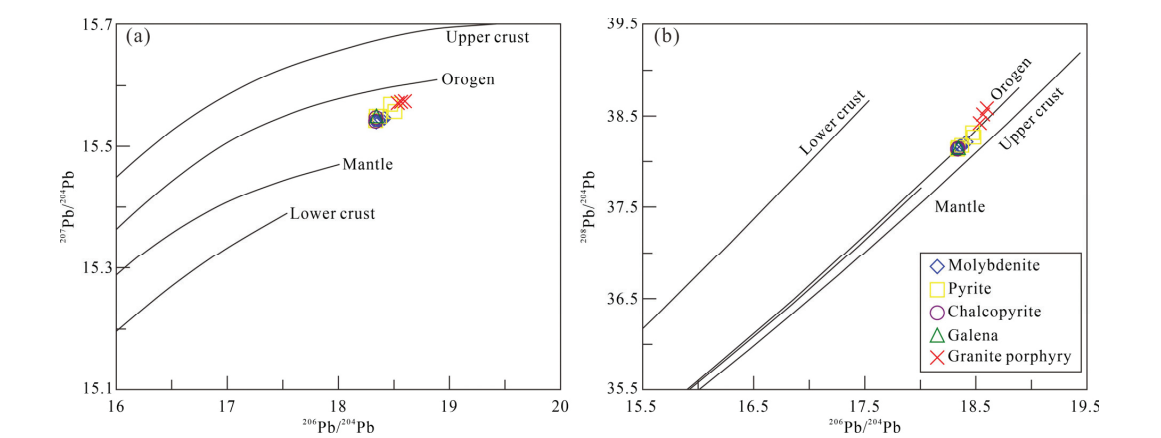


Figure 10. (a) <sup>207</sup>Pb/<sup>204</sup>Pb versus <sup>206</sup>Pb/<sup>204</sup>Pb diagram. (b) <sup>208</sup>Pb/<sup>204</sup>Pb versus <sup>206</sup>Pb/<sup>204</sup>Pb diagram (modified from [129]).

6. Discussion

6.1. Timing of Molybdenum Metallogenesis

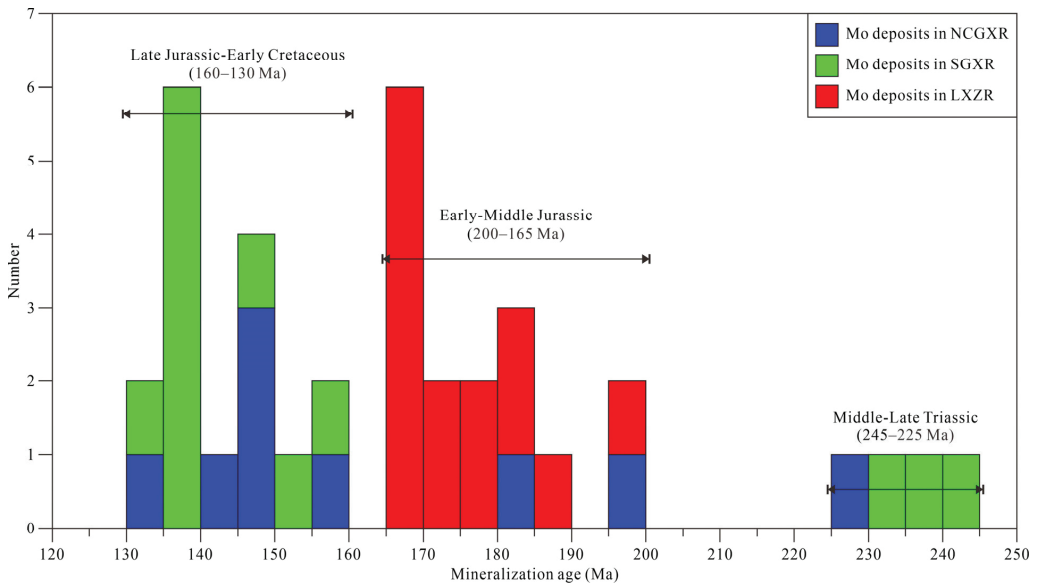
From both scientific and economic perspectives, it is crucial to constrain the length and time of magmatic–hydrothermal systems [130]. Precise isotopic dating of hydrothermal minerals is an essential technique for determining the geochronology of hydrothermal processes in relation to intrusive magmatism and for constructing genetic models of hydrothermal deposits. As the primary product of hydrothermal mineralization, molybdenite obtained from ore-bearing quartz veins in molybdenum deposits is suggested as a Re–Os geochronometer for directly dating molybdenum mineralization events. In this contribution, two Re–Os model ages of  $141.2 \pm 1.5$  and  $147.7 \pm 1.7$  Ma were obtained. The wide range of Re–Os model ages could be attributed to Re and Os isotope decoupling, the considerable spatial Re heterogeneity, the post-ore deformation, and the analytical procedure [130–136]. For instance, many explanations based on post-crystallization diffusion of <sup>187</sup>Os are proposed to answer the Re and Os decoupling mechanism. ReS<sub>2</sub> inclusions or 3R polytype molybdenite formed during the crystallization of molybdenite would, over time, result in a chemical gradient for <sup>187</sup>Os that may homogenize during a thermal event. Decoupling could also result from the exsolution of Os-rich sulfides or diffusion of Os to crystal dislocations within the molybdenite during metamorphism [133,134]. The heterogeneous distribution of Re in



molybdenite samples could also lead to the discrepancy of Re-Os model ages, which may be related to the overall abundance of Re in the hydrothermal fluids [136], compositional changes in the hydrothermal fluid with time [132], or partitioning of Re between liquid and vapor [130]. Additionally, a relatively wide range of molybdenite Re-Os model ages has been reported in numerous magmatic–hydrothermal deposits, such as the Haigou Au deposit (311.3–306.7 Ma; [131]), Lala Fe–Cu deposit (1097–1081 Ma; [137]), Kenge Mo deposit (1957–1950 Ma; [138]), Porcupine Mo deposit (1896–1882 Ma; [138]), Kedengjian Cu deposit (99.1–95.7 Ma; [139]), Mada Mo deposit (150.9–136.9 Ma; [140]), Meiziwo W deposit (165.6–156.2 Ma; [141]), Yaoling W deposit (165.9–156.2 Ma; [141]), Banlashan Mo deposit (142.7–131.8 Ma; [26]), Huashandong W deposit (827.8–795.3 Ma; [142]), Jiguanshan Mo deposit (156.2–151.7 Ma; [143]), and Dongbeigou Mo deposit (132.6–127.1 Ma; [144]). Zhang et al. [31] reported that the barren quartz monzonite porphyry and syenite porphyry stocks were emplaced at  $165.0 \pm 2.5$  and  $125.5 \pm 1.9$  Ma, respectively. Our recent geochronology study yielded a zircon U–Pb age of  $142.3 \pm 0.5$  Ma for molybdenum-bearing granite porphyry stock (unpublished data). In recent decades, advances in high-precision dating, numerical simulation, and diffusion modeling mostly argue for short-lived (<1 Ma) timescales for the lifetime of magmatic–hydrothermal systems [7,145–152]. The Re–Os model age of molybdenite sample G5 ( $141.2 \pm 1.5$  Ma) is highly consistent with the emplacement time of the molybdenum-bearing granite porphyry stock within the analytical uncertainty. Spatially, the molybdenum mineralization in the deposit is characterized by veinlet-disseminated- and vein-type quartz–sulfide orebodies hosted in the cupola of the ore-bearing granite porphyry stock (Figure 2c). Geochemically, the metal sulfides obtained in this study have similar lead isotopic compositions to those of the ore-bearing granite porphyry stock (discussed in Section 6.3). This evidence collectively demonstrates that the molybdenum mineralization at Lower Urgen was temporally, spatially, and genetically associated with the molybdenum-bearing granite porphyry stock, supporting an intrusion-related origin during the Early Cretaceous. In contrast, the barren quartz monzonite porphyry and syenite porphyry stocks record pre-ore and post-ore magmatic events, respectively. Our findings also indicate that accurate and precise molybdenite Re–Os ages representing the true timing of ore formation need an integrated combination of careful geology, geochemistry, and multiple dating methods.

Considering the Mesozoic intense and widespread molybdenum mineralization in NE China, molybdenum mineralization at Lower Urgen is not a singular instance. By collecting published molybdenite Re–Os ages for Mesozoic molybdenum deposits within NE China, we determine three periods of molybdenum metallogenesis events in the region: Middle–Late Triassic (245–225 Ma), Early–Middle Jurassic (200–165 Ma), and Late Jurassic–Early Cretaceous (160–130 Ma) (Table S2 and Figure 11). The Middle–Late Triassic molybdenum deposits are primarily located in the southern GXR (SGXR) and along the SXCF, with minor occurrences in the NCGXR, including the Laojiagou (234.9 Ma; [41]), Chehugou (245 Ma; [85]), Kulitu (236 Ma; [153]), and Badaguan deposits (228.8–225.1 Ma; [46,48,154]). Molybdenum deposits formed in the Early to Middle Jurassic are abundant within the LXZR, and scattered in the NCGXR, including the Daheishan (169.2–168.0 Ma; [52,155,156]), Xingshan (167.3 Ma; [53]), Jidetun (168.9–168.0 Ma; [54,58,157]), Fu’anpu (168.2–166.9 Ma; [57,158]), Houdaomu (167.5 Ma; [159]), Shuangshan (171.6 Ma; [160]), Jiapigou (196 Ma; [160]), Sancha (183.1 Ma; [160]), Dashihe (186.7 Ma; [161]), Liushengdian (169.3–168.7 Ma; [159,162]), Sifangdianzi (176.6 Ma; [59]), Luming (177.9–176.7 Ma; [61,62]), Huojihe (181.3 Ma; [64]), Xinhualong (171.3 Ma; [159]), Wunugetushan (180.5–177.6 Ma; [49,163]), and Taipingchuan deposits (200.1 Ma; [164]). Most of the molybdenum deposits dated between the Late Jurassic and Early Cretaceous are located in the GXR, including the Chalukou (150–148 Ma; [65,67]), Taipinggou (130.1–129.4 Ma; [72,165]), Jiazishan (147.4 Ma; [166]), Diyanqinamu (156.2 Ma; [167]), Hashitu (150 Ma; [75]), Aolunhua (132–129.4 Ma; [79,168,169]), Shabutai (135.3 Ma; [26]), Haisugou (136.4 Ma; [26]), Banlashan (143–136.1 Ma; [26,169]), Yangchang (138.5 Ma; [169]), Hongshanzi (138.2–137.2 Ma; [83]), Xiaodonggou (138.1–135.5 Ma; [84,170]), Nianzigou (154.3–153 Ma; [85,86,153]), and Jiguanshan deposits (155.4–151.1 Ma; [143,171]). The zircon

U-Pb ages of ore-bearing granodiorites record the granitic magmatism in the Kanchuangou and Jinchanggou deposits at 111.1 [56] and 114 Ma [63], respectively. Unfortunately, no accurate molybdenite Re-Os ages of these two deposits have been reported, and the genetic relationship between molybdenum mineralization and host granodiorites remains to be further investigated. Hence, the molybdenum mineralization in these two deposits is not involved in the present study. The Early Cretaceous molybdenum mineralization in Lower Urgen is in accordance with the Late Jurassic–Early Cretaceous molybdenum metallogenesis in the NCGXR.



**Figure 11.** Histogram of molybdenite Re-Os isochron ages for Mesozoic molybdenum deposits in NE China. Abbreviations: NCGXR, northern and central Great Xing’an Range; SGXR, southern Great Xing’an Range; LXZR, lesser Xing’an-Zhangguangcai Range. Data sources are listed in Table S2.

## 6.2. Source of Mineralizing Fluids

Stage 1 quartz has calculated  $\delta^{18}\text{O}_{\text{fluid}}$  values (1.1 to 1.9‰) that are lower than normal magmatic fluids (7–9‰; [172]) and substantially higher than normal Mesozoic meteoric water (−18‰; [173]). The  $\delta^{18}\text{O}_{\text{fluid}}$  values of the quartz samples from the late quartz–carbonate stage are more depleted (−8.0 to −6.1‰) and comparable to the values of Mesozoic meteoric water [127,173] (Figure 8). This  $\delta^{18}\text{O}_{\text{fluid}}$  variation trend implies the mixing of magmatic fluids with later meteoric water during the mineralization at Lower Urgen. Furthermore, in agreement with the documented  $\delta\text{D}$  values of Mesozoic meteoric water in the GXR (−140 to −90‰; [173]), the  $\delta\text{D}$  values of all stages (−146.6 to −129.9‰) are much lower than those of magmatic water (−50 to −85‰; [174]). The depletion of  $\delta\text{D}$  in the mineralizing fluids could be controlled through (1) fluid boiling or immiscibility [175], (2) magma degassing led by major meteoric water incursion [176], and (3) hydrogen isotope fractionation between the mineralizing fluids and some reduced species (e.g.,  $\text{CH}_4$ ). As shown in Figure 5, the coexistence of multiple FI types in stages 1 and 2 indicates intense fluid immiscibility during ore precipitation. The decreasing trend of Th and salinity in the FIs from stage 1 to 3 indicates increasing meteoric water input toward the late fluid system (Figure 7). However, no reduced species such as  $\text{CH}_4$  have been detected in the  $\text{H}_2\text{O}$ -dominated ore-forming fluids, which indicates that hydrogen isotope fractionation is likely negligible [127]. Hence, we preliminarily speculate that fluid immiscibility and meteoric water input could explain the  $\delta\text{D}$  depletion of ore-forming fluids at Lower Urgen. In the  $\delta\text{D}$  versus  $\delta^{18}\text{O}_{\text{fluid}}$  diagram, the calculated  $\delta^{18}\text{O}_{\text{fluid}}$  and  $\delta\text{D}$  values also show a clear

evolution trend from stage 1 to 3, and the data are plotted between the magmatic and meteoric water fields (Figure 8). Therefore, we conclude that the mineralizing fluids of the Lower Urgen deposit were primarily of magmatic origin with progressive meteoric water input.

### 6.3. Source of Sulfur and Lead

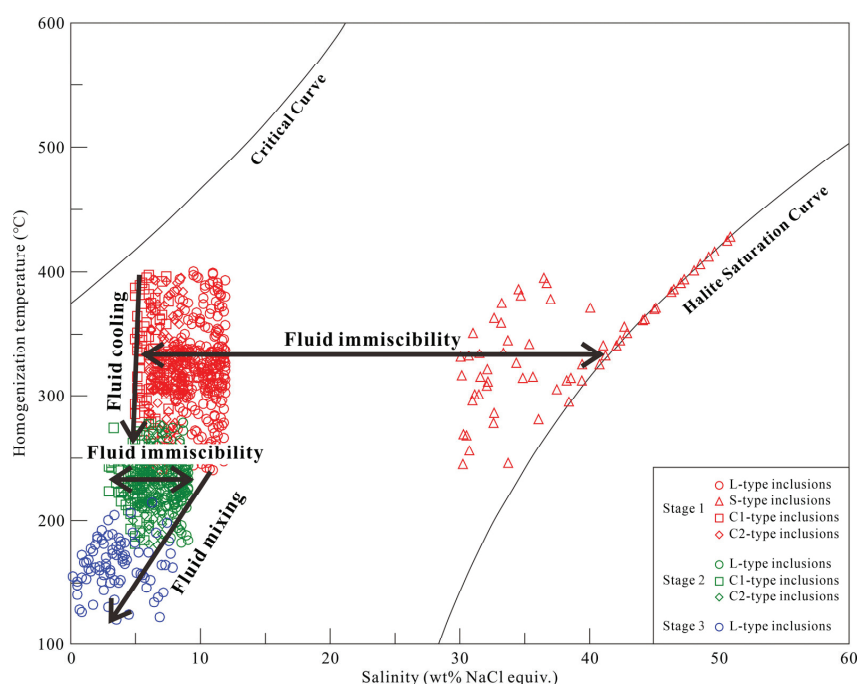
S isotopes can be used to trace the source of sulfur in sulfide minerals, despite the fact that the entire S isotopic components could be influenced by pH, temperature, ion activity, and  $f_{O_2}$  [177–179]. The  $\delta^{34}\text{S}$  data of sulfides can be utilized to determine their origin because no sulfate minerals have been found in the Lower Urgen district. The molybdenite, pyrite, chalcopyrite, and galena have  $\delta^{34}\text{S}$  values of 5.4–5.5‰, 5.4‰, 4.8–5.4‰, and 3.9‰, respectively, implying that these sulfides have reached sulfide equilibrium fractionation [179]. The sulfides  $\delta^{34}\text{S}$  values of the Lower Urgen deposit display a restricted range (3.9–5.5‰), which is commonly interpreted as a magma-derived sulfur [180] (Figure 9).

The source of the lead in the mineralizing fluids has been constrained using the lead isotope ratios of sulfides. The Pb isotopic ratios of sulfides can provide information about the source of Pb since sulfide minerals often have minimal radiogenic Pb isotopes and extremely low quantities of Th and U [129,181]. By contrasting the Pb isotope ratios of molybdenite, pyrite, chalcopyrite, galena, and molybdenum-bearing granite porphyry, the Pb source of the Lower Urgen molybdenum deposit can be determined. The sulfide samples have narrow ranges of  $^{206}\text{Pb}/^{204}\text{Pb}$  (18.336–18.510),  $^{207}\text{Pb}/^{204}\text{Pb}$  (15.540–15.569), and  $^{208}\text{Pb}/^{204}\text{Pb}$  (38.130–38.312), implying an individual or successfully mixed lead origin. The Pb isotopic ratios of sulfides in the Lower Urgen deposit are distinct from those of the surrounding Mesozoic strata (e.g., Tamulagou and Manketouebo Fms) ( $^{206}\text{Pb}/^{204}\text{Pb}$  = 18.08–18.32,  $^{207}\text{Pb}/^{204}\text{Pb}$  = 15.46–15.55, and  $^{208}\text{Pb}/^{204}\text{Pb}$  = 37.62–38.10) [93,182], but similar to those of the ore-bearing granite porphyry stock in the deposit ( $^{206}\text{Pb}/^{204}\text{Pb}$  = 18.535–18.599,  $^{207}\text{Pb}/^{204}\text{Pb}$  = 15.571–15.574, and  $^{208}\text{Pb}/^{204}\text{Pb}$  = 38.419–38.583). Lead with high  $\mu$  values ( $>9.58$ ) was derived from the upper crust [129], whereas that with values of 8.92 was derived from the mantle [183]. The sulfides and granite porphyry stock from the Lower Urgen deposit yield  $\mu$  values of 9.35–9.40 and 9.39–9.40, respectively, indicating that lead was basically from the crustal source and an extremely small amount of the mantle source. On the diagram of  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  [129], the sulfide and ore-bearing granite porphyry samples are all located between the mantle and orogen evolution curves (Figure 10a). On the diagram of  $^{208}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  [129], most sulfide and ore-bearing granite porphyry samples are distributed on the orogen evolution curve (Figure 10b). These features imply that the metal sulfides and granite porphyry at Lower Urgen have the same lead source, which has been documented in many porphyry deposits [2,3,184], and that the granitic magmatism is probably largely responsible for the molybdenum mineralization in the Lower Urgen deposit.

### 6.4. Metal Precipitation Mechanisms

Fluid immiscibility, one of the most significant ore-forming mechanisms in magmatic–hydrothermal metallogenic systems, can change the temperature, pH, and salinity of the ore-bearing fluids, thereby reducing the solubility of metals in the fluids [14,185–188]. The occurrence of fluid immiscibility is supported by the following evidence from stage 1 quartz-hosted FIs: (1) L-, S-, C1-, and C2-type FIs have intimate spatial relationships (Figure 5a–c); (2) they exhibit distinct homogenization modes; and (3) these FIs show distinct salinities and comparable homogenization temperature ranges (Figure 7a,b). Similarly, at stage 2, L-, C1-, and C2-type FIs frequently coexist, indicating that they were simultaneously captured and showed different homogenization modes (Figures 5g and 7c,d). Notably, in stages 1 and 2, C1- and C2-type FIs frequently show lower salinities but analogous homogenization temperatures than L-type FIs, which shows that fluid immiscibility occurred before their entrapment [189]. The increased salinity of the residual fluids caused by volatile separation from the ore-bearing fluids as temperature and pressure drops may be the cause of the

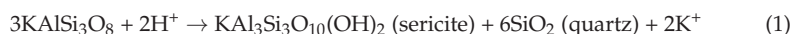
higher salinities in L-type FIs than those in C1- and C2-type FIs [185,190]. The mineralizing fluids at Lower Urgen underwent fluid immiscibility processes during stages 1 and 2, as reflected by the diagram of salinity versus homogenization temperature (Figure 12). Field evidence, such as the widespread fracture and brecciation of granite porphyry cupola and the overlying intermediate–basic volcanic rocks at Lower Urgen, suggests a dramatic pressure drop that might result in fluid immiscibility, further supporting the existence of fluid immiscibility [119,191–193]. Previous research has demonstrated that a mafic magmatic source or the magmatic–hydrothermal formation procedure of a deep-seated magma chamber often contributes significant amounts of dissolved  $\text{CO}_2$  [119,194–198]. In combination with the H–O isotopic compositions of stage 1 quartz, we speculate that the original fluids of the Lower Urgen molybdenum deposit are  $\text{CO}_2$ -rich magmatic–hydrothermal fluids. As the fluids rose, volatiles (such as  $\text{CO}_2$ ) started to separate from the fluids due to a decrease in pressure and temperature. The sudden supersaturation of the solution was caused by the release of volatiles, which also increased the pH of the solution and caused the decoupling of metal complexes. As a result of the procedure, significant amounts of molybdenite precipitated from stage 1 fluids, while chalcopyrite, pyrite, sphalerite, arsenopyrite, and galena were deposited from stage 2 fluids.



**Figure 12.** Homogenization temperature versus salinity of FIs from all stages in the Lower Urgen molybdenum deposit.

Hydrothermal mineralization frequently involves fluid–rock interaction, which is essential for the transport and deposition of metal ions, especially in an intrusive-related mineralization system [4,199–201]. Many investigations have demonstrated that changes in the physicochemical properties of fluids as a result of fluid–rock interactions affect metal solubility and mineral precipitation [202–205]. Different hydrothermal alteration types are characteristics of porphyry molybdenum mineralization, and phyllic alteration is frequently seen as a sign of prospecting [201,203,205,206], as indicated by the fact that molybdenum mineralization in the deposit is spatially related to phyllic alteration, and plagioclase and K-feldspar of the ore-bearing granite porphyry tend to be replaced by quartz and sericite in

stage 1 (Figure 4b,e). Phyllic alteration lowered the  $H^+$  contents of the hydrothermal fluids and enriched the reduced sulfur ( $S^{2-}$ ), which mixed with  $Mo^{2+}$  to generate molybdenite. The following formulas reflect the pertinent reactions:



Therefore, we provide a preliminary argument that phyllic alteration could benefit the deposition of molybdenite at Lower Urgan. Nevertheless, a more detailed explanation to this conclusion is beyond the scope of our current study and additional alteration mineralogical and geochemical research is necessary before a full understanding can be attained.

Numerous studies have shown that fluid mixing is a crucial factor in the production of base metal sulfide deposits because it can dilute and cool hydrothermal solutions, which causes enormous sulfide mineral depositions [207–211]. Mineral deposition occurs when the solubility of metal ions in the fluids surpasses saturation, and substantial deposition occurs as the solubility is dramatically decreased [208]. In the Lower Urgan deposit, the continuous fluid immiscibility in stages 1 and 2 would have increased the permeability of the host granite porphyry stock, and further accelerated meteoric water circulation. Stage 2 fluids have much lower salinity and homogenization temperatures than stage 1 fluids (Figure 12). Additionally, stage 2 fluids have more depleted  $\delta^{18}O_{\text{fluid}}$  values than stage 1 fluids (Figure 8). These features collectively demonstrate the existence of fluid mixing processes in stage 2. To summarize, fluid mixing propelled the polymetallic sulfide mineralization in stage 2 at Lower Urgan. The progressive incursion of meteoric water into the magmatic–hydrothermal system might cause considerable cooling, the instability of metal chloride complexes, and sulfide deposition.

In conclusion, stage 1 molybdenite deposition is primarily controlled through fluid immiscibility and fluid–rock interaction. The increasing injection of meteoric water into the hydrothermal system and fluid immiscibility collectively controlled the massive deposition of polymetallic sulfides in stage 2.

#### 6.5. Metallogenic Model for the Lower Urgan Magmatic–Hydrothermal System

Especially for intrusion-related magmatic–hydrothermal deposits, the development of a metallogenic model may successfully direct the investigation of the ore deposit and increase the successful rate of prospecting and prediction [4,212]. We construct the metallogenic model for the Lower Urgan molybdenum deposit upon the above discussion and previous research, as outlined below.

Due to the closure of the MOO, the surveyed region experienced an extensional environment in the Late Jurassic and Early Cretaceous, which promoted the partial melting of the lower crust and produced ore-bearing granitic magmas [25,50,213–218]. As a lithophile element, molybdenum tends to be abundant in the crust but deficient in the mantle [219]. Consequently, a potential source for molybdenum mineralization might be the lower crust under the Lower Urgan region. Metallic elements are partitioned into the melt through partial melting of the protolith. The ore-bearing granite porphyry, which represents the parental rock and served as a constant source of hot, ore-rich fluids for the generation of the hydrothermal mineralization system, was emplaced at about 142.3 Ma. The potassic and phyllic alteration zones were generated by these fluids accumulating at the cupola of the mineralization intrusion and interacting with cooling granite porphyry (Figure 2c). In the meantime, intense and widespread fluid immiscibility was created through the constant ascent and decompression of mineralizing fluids. Stage 1 fluids belong to a  $NaCl-H_2O-$

CO<sub>2</sub> system and contain bimodal salinities (5.0–11.9 and 30.1–50.8 wt% NaCl equiv.) and have medium–high temperatures (240–430 °C). Intense fluid immiscibility and fluid–rock interaction caused an increase in pH and a drop in temperature, which significantly reduced the solubility of molybdenum and aided in the precipitation of molybdenite. The molybdenum mineralization stage was characterized by widespread molybdenum-bearing quartz veinlets and disseminated molybdenite in the granite porphyry. In stage 2, massive meteoric water mixed with the evolved magmatic–hydrothermal fluids through localized regional hydraulic fractured and brecciated zones. Stage 2 fluids have salinities and homogenization temperatures of 3.0–9.1 wt% NaCl equiv. and 180–280 °C, respectively, and belong to a NaCl–H<sub>2</sub>O–CO<sub>2</sub> system. The molybdenum mineralization came to an end with the extinction of veinlet-disseminated- and vein-type quartz–molybdenite(–pyrite) ores. The constant infiltration of meteoric water diluted ore-forming fluids and decreased their temperature. This process, combined with extensive fluid immiscibility, collectively led to the large-scale decoupling of base metal complexes and promoted the massive deposition of polymetallic sulfides. Stage 3 fluids belong to a NaCl–H<sub>2</sub>O system and have salinities of 0.2 to 7.9 wt% NaCl equiv. and homogenization temperatures of 120 to 220 °C, suggesting a hydrothermal environment with low salinity and temperature. The hydrothermal fluids were governed by meteoric water as the pressure of the system was dropped. The fluids produced quartz and calcite as precipitates. The absence of ore minerals in the veins of this stage suggests that the fluids are no longer useful for mineralization, signaling the termination of the hydrothermal process in the Lower Urgen region.

## 7. Conclusions

(1) Molybdenite Re–Os dating yields two model ages of  $141.2 \pm 1.5$  and  $147.7 \pm 1.7$  Ma for the Lower Urgen molybdenum deposit. The new geochronological data indicate that the molybdenum mineralization event in the Lower Urgen area is consistent with the intensive and extensive Late Jurassic–Early Cretaceous molybdenum mineralization events in NE China.

(2) Three hydrothermal stages of the Lower Urgen molybdenum deposit can be distinguished: (i) quartz–molybdenite(–pyrite) stage—ore-forming fluids have medium–high temperatures (240–430 °C) and bimodal salinities (5.0–11.9 and 30.1–50.8 wt% NaCl equiv.) and belong to a NaCl–H<sub>2</sub>O–CO<sub>2</sub> system; (ii) quartz–polymetallic sulfide stage—ore-forming fluids have medium temperatures (180–280 °C) and low salinities (3.0–9.1 wt% NaCl equiv.) and belong to a NaCl–H<sub>2</sub>O–CO<sub>2</sub> system; and (iii) quartz–carbonate stage—fluids have low temperatures (120–220 °C) and low salinities (0.2–7.9 wt% NaCl equiv.) and belong to a NaCl–H<sub>2</sub>O system.

(3) Hydrogen–oxygen isotope results indicate that the mineralizing fluids initially had a magmatic source with the progressive incursion of meteoric water. Sulfur–lead isotopic compositions indicate that the mineralizing materials have a genetic relationship with ore-bearing granite porphyry, and sulfur and lead are magmatically derived.

(4) Fluid immiscibility and fluid–rock interaction are the predominant mechanisms for molybdenite deposition in stage 1. Fluid mixing and immiscibility are cooperatively accountable for the massive deposition of polymetallic sulfides in stage 2.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/min13091189/s1>, Table S1: Microthermometry data for fluid inclusions in quartz from the Lower Urgen molybdenum deposit; Table S2: Molybdenite Re–Os isochron ages for Mesozoic molybdenum deposits in NE China [26,41,43,46,48,49,52–54,57,59,61,62,64,65,67,72,73,75,79,81,83–86,143,153–156,158–165,167–171].

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## Article

# Continental Arc Flare-Ups and Crustal Thickening Events in NE China: Insights from Detrital Zircon U-Pb Dating and Trace Elements from the Heilongjiang Complex

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**Abstract:** Continental arc is characterized by alternant magmatic flare-ups and lulls. From the Permian to the Middle Jurassic period, two flare-ups with a lull developed in NE China, but the tectonic controls that caused the flare-ups remain unclear. Sedimentary rocks of the Heilongjiang Complex were derived from these magmatic rocks; thus, we employed detrital zircon U-Pb dating and trace elements analyses to unravel the regional tectono-magmatic evolution. Eu anomaly,  $(Dy/Yb)_N$  and Th/U ratios of the detrital zircons and Sr/Y and  $(La/Yb)_N$  of the regional granitoids together indicate the occurrence of two episodes of crustal thickening during the two flare-ups, accompanied with a westward migration of magmatism. We propose that the Permian flare-up was caused by the shallowing subduction from the east, which thickened the upper plate and enhanced the deep crustal melting. During the Middle Triassic period, the mantle wedge was expelled by the flat slab and thickened crust, leading to the magmatic lull. However, the westward subduction of the back-arc oceanic plate occurred before the lull, gradually producing the Jurassic magmatic flare-up and crustal thickening. Closure of the back-arc ocean caused by the outboard Paleo-Pacific oceanic plate subduction was important in the formation of the episodic magmatic flare-ups and crustal thickening in NE China.

**Keywords:** continental arc; arc magma tempo; detrital zircon; accretionary orogen

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## 1. Introduction

Continental arc shows periodicity. Although a continental arc have persisted for hundreds of millions of years, its flux significantly varied and showed alternate magmatic flare-ups ( $70\text{--}90\text{ km}^3\text{ km}^{-1}\text{ Myr}^{-1}$ ) and lulls ( $<20\text{ km}^3\text{ km}^{-1}\text{ Myr}^{-1}$ ) [1]. Each flare-up or lull lasted for several tens of millions of years, consisting of the “continental arc tempo” [2]. However, which tectonic process triggered this tempo remains unclear and this limits our understanding of the continental arc magmatism. Because arc magmatism and differentiation were the key to generate continental crust, unravelling the arc tempo will directly help to understand how the continent was formed and evolved [3].

The orogenic cyclicity, or periodicity was defined along the eastern Pacific margin, the American Cordillera [3]. Taking Sierra Nevada as an example, although continental arc magmatism was first initiated in the early Mesozoic era, there were only two main flare-ups, occurring in the Middle to Late Jurassic and the mid-Cretaceous periods, respectively [4]. It was noted that the two flare-ups were closely associated with strong regional compression, crustal thickening, and landward migration of arc magmatism. Based on the data from both the North and South American Cordillera, Decellas et al. (2009) suggested that these aforementioned associations were widespread in the Andes, Sierra Nevada, Canada Coastal

Mountains, and other parts of the American Cordilleran belt; after the landward migration of the arc magmas, they waned and migrated back toward the trench before the next round of flare-up, crustal thickening, and landward migration [3]. Ducea (2001) pointed out a key factor in this orogenic cyclicity, that is, each magmatic flare-up corresponded to more evolved Nd isotopic features (isotope “pull-down”) [5]. Therefore, it is indicated that increasing magmatic flux was somehow related to the involvement of enriched, mature continental materials.

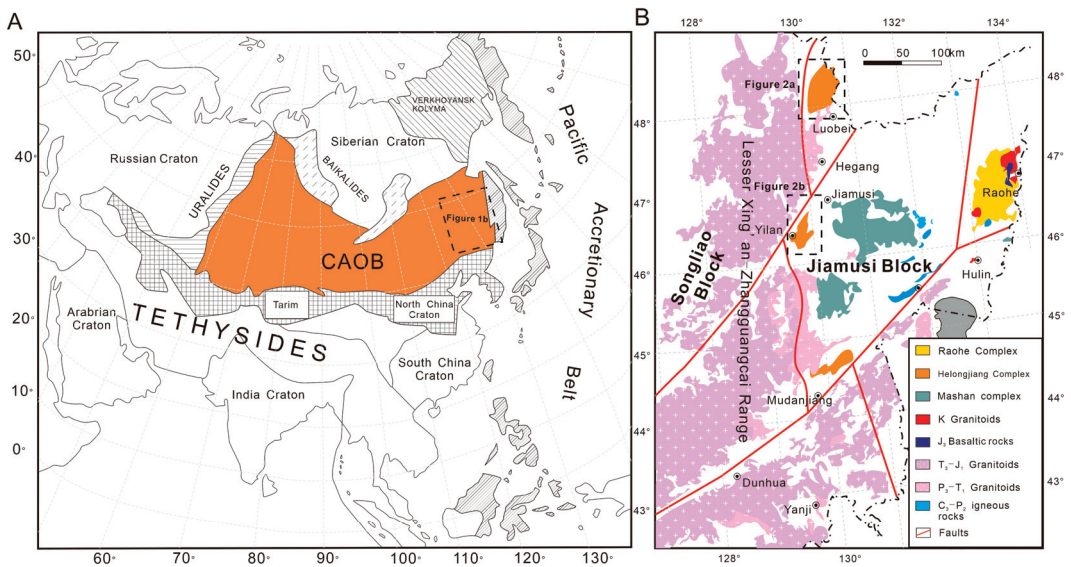
Although many tectonic models were proposed, controversies exist in many aspects [1]. First, some studies suggested that the landward arc migration was caused by slab angle shallowing [6], but some others believed that crustal thickening with magmatic addition and regional compression could migrate the arc without slab shallowing [7]. Second, why did the magmas show enriched isotopes during flare-ups? An early explanation was that the isotopes formed due to the “under-thrusting” of the rear-arc continental crust deep into the arc source, which supplied fertile and mature materials to the magmas [3,5]. Recent research proposed that the arc magmas were more enriched simply because they moved to the ancient continental interior and the addition of rear-arc materials was not necessary [8]. Some studies even suggested that it was the mantle input that triggered the magmatic flare-ups based on the juvenile zircon Hf isotopes [9]. Third, which tectonic mechanism drive the cyclicity? Many studies indicate that the crustal thickening transformed the lower continental arc crust to eclogites, and they finally foundered into the mantle, thereby thinning the crust [3,4]. Afterwards, regional compression thickened the crust again and the orogen evolved to the next cycle. According to this viewpoint, cyclicity is self-driven, influenced only by the internal factors of the orogen matter. However, other studies have suggested that external factors dominate the orogeny, such as the change in slab angle, subduction rate, and so on [1,6].

During the Early Permian to Middle Jurassic, N-S trending calc-alkaline magmatic belts developed in NE China (Figure 1), representing long-lived continental arc activities [10–13]. These arc magmas also show typical landward migration trends [11,14], similar to the situations in the American Cordillera, providing us with an opportunity to test the contested views regarding the orogenic cyclicity. However, some important geological parameters, such as crustal thickness, have been largely changed due to the surface processes for >150 Myr; most geological records were also superposed or changed due to the tectonic activities, especially the multiple episodes of regional compression, shearing, and extension.

The Heilongjiang Complex is a Mesozoic accretionary complex in NE China and represents the remnants of the Mudanjiang Ocean [15], a fossil oceanic basin between the Jiamusi and Songliao blocks, with sedimentary materials deposits mainly from the nearby continental arc magmatic rocks [13]. Recently, trace elements with coupled U-Pb ages of detrital zircons become a useful tool to indicate the tectonic evolution of continental arcs [16]. This is because many volcanic rocks and shallow plutonic rocks have been eroded, and many parts of a now-exhumed arc are covered with sediments or vegetations, making them inaccessible for sampling. But zircons could survive both surface erosion and several rounds of recycling low- to middle-grade (hydro-)thermal alteration.

In this study, we employed U-Pb dating and trace elements analyses of detrital zircons from the Heilongjiang Complex, integrated with published data from regional magmatic rocks and detrital zircons, in order to explore the evolution of continental arcs in NE China. We propose a tectonic model to explain the continental arc tempos in NE China and compare the geodynamic mechanism with the American Cordillera.





**Figure 1.** (A) Tectonic position of the study area (after [17]); (B) simplified geological map of the eastern Heilongjiang Province (after [14]). Our samples were collected from the Heilongjiang Complex, near Luobei and Yilan.

## 2. Geological Setting and Sampling

The study area is located in NE China, east of the Songliao Basin, tectonically including the eastern Songliao and Jiamusi blocks (Figure 1B).

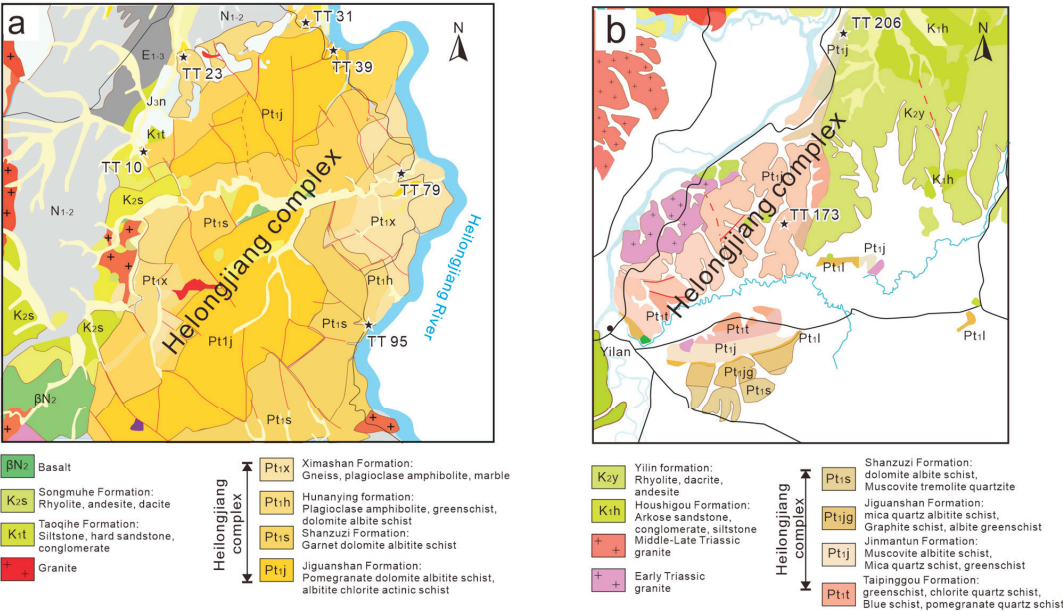
The Songliao Block include the Lesser Xing'an-Zhangguangcai Range along the eastern margin, and most other parts are covered by the post-Cretaceous strata in the Songliao Basin. Previous studies suggested that the basement of the Songliao Basin is juvenile crust and mainly contains the Paleozoic to Mesozoic meta-volcanic, meta-sedimentary rocks, and granitic gneisses. However, recent studies reported ages of ca. 1.8 Ga from meta-gabbros and meta-granitic breccias from the drill holes [18]. From the Middle Jurassic, the Songliao Basin experienced initial rifting, post-rifting subsidence, and basin inversions [19,20]. The most important volcanism in the basin occurred in the Early Cretaceous (c. 135–100 Ma) [12,21]. The Lesser Xing'an-Zhangguangcai Range is located along the eastern Songliao Block (Figure 1B), and mainly consisted of granitoids with various ages [10,22], including the Early Paleozoic (c. 510–470 Ma), Early Permian (280–290 Ma), Late Permian to Early Triassic (c. 260–240 Ma), Late Triassic to Early Jurassic (220–170 Ma), and middle Cretaceous (c. 100 Ma). The most widespread magmatic episode occurred in the Late Triassic to Early Jurassic [22].

The Bureya-Jiamusi-Khanka Block is cut by the north branches of the Tan-Lu Fault, namely the Dunhua-Mishan and Jiamusi-Yilan faults (Figure 1B); the Jiamusi Block is the central part bounded by the two faults. (Figure 1B). The oldest rocks in the Jiamusi Block have ages ranging from c. 891 to 898 Ma [23]; an almost similar age (c. 933 Ma) is reported in the Bureya Block as well [24]. Thus, the Neoproterozoic could be the basement age of this united continental block. However, the most important basement of the block was formed during the late Pan-African period (c. 500 Ma) [17,25], including granulite-facies metasedimentary and minor meta-mafic rocks, accompanied by the Early Paleozoic granitoids [25]. Along the eastern Jiamusi and Khanka blocks, there are some Paleozoic volcanic and sedimentary strata. The main lithologies are the Early Paleozoic marbles, terrigenous clastic rocks, and the Late Paleozoic volcanic rocks with intervening terrigenous clastic rocks. Calc-alkaline arc-like andesites and dacites firstly occurred in the Early

Permian, indicating the early-stage continental arc in the region [26]. From the Early Permian to the earliest Triassic, N-S trending granitoids with associated volcanic rocks were generated and migrated throughout the whole block from east to west, mainly consisting of calc-alkaline granitoids [11]. However, there are very few magmatic records from the late Early Triassic to Jurassic in the Jiamusi block, although these ages have been reported along the western Bureya and Khanka blocks [27]. Volcanic rocks with minor plutonic rocks increased in the Early Cretaceous and are most abundant from the late Early to early Late Cretaceous in the Jiamusi block, and mainly show intra-plate affinities [12,22].

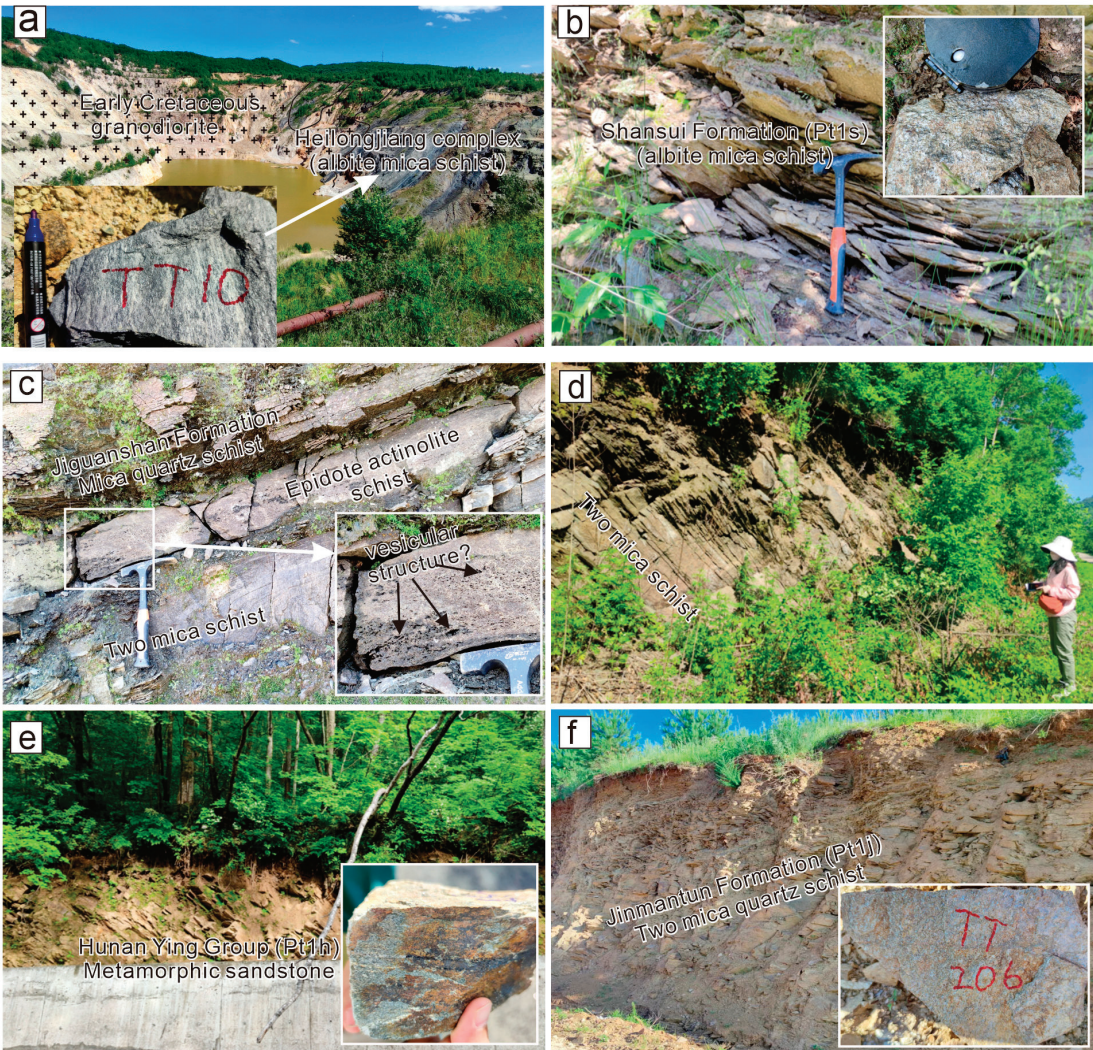
There are several fragments of Mesozoic accretionary complexes along the western margin of the Jiamusi block (Figure 1B), which are named as the Heilongjiang Complex, representing a lost ocean (the Mudanjiang Ocean) between the Songliao and Jiamusi blocks [15]. The Heilongjiang Complex is composed of mica schist, marble, quartzite, greenschist, blueschist, and amphibolite. Most published data show that the protolith age of the blueschist is Early Permian to Triassic (c. 285 to 213 Ma), whereas the high-pressure metamorphic age ranges from c. 210 to 170 Ma [15]. However, a blueschist sample from Yilan yields a concordant zircon U-Pb age of 142 Ma, which is the only Cretaceous protolith age of rocks from the Heilongjiang Complex so far [28]. There are also some other accretionary complexes exposed in the region, such as the N-S trending Zhangguangcai Complex along the eastern Songliao block [29]. It consists of amphibolite, biotite-plagioclase-gneiss, marble, schist, and meta-volcanic rocks. The metamorphic ages range from the Paleozoic to the Early Mesozoic [29].

Eight meta-sedimentary rock samples were collected from the two areas of the Heilongjiang Complex, near Luobei and Yilan, respectively (Figures 1B and 2). These samples are exposed as strongly deformed matrix (Figures 3 and 4), within which metamorphic basaltic rocks (such as greenschist) were observed and they are commonly intruded by later-stage magmatic rocks (Figure 3). Details of the samples are listed in Table 1, including the sample numbers, GPS locations, and lithologies.



**Figure 2.** Geological maps of the sampling locations (after local 1:200,000 geological map). See Table 1 for details of the samples. (a) Map of the Jiayin-Luobei area and (b) the Jiamusi-Yilan area.





**Figure 3.** Typical outcrops of the sampling locations. (a) Gold mine near Wulaga, with the Early Cretaceous granodiorite intruding into the Heilongjiang Complex; (b) the Shanzuizi Group (albite mica schist) in Jiayin; (c) the Jiguanshan Group (two mica schist) near the mouth of the Jiayin river and there are residual vesicles in the greenschist layer; (d,e) show mica schist and meta-sandstone to the north of Luobei; (f) the Jinmantun Group (two mica quartz schist) near Jiamusi.



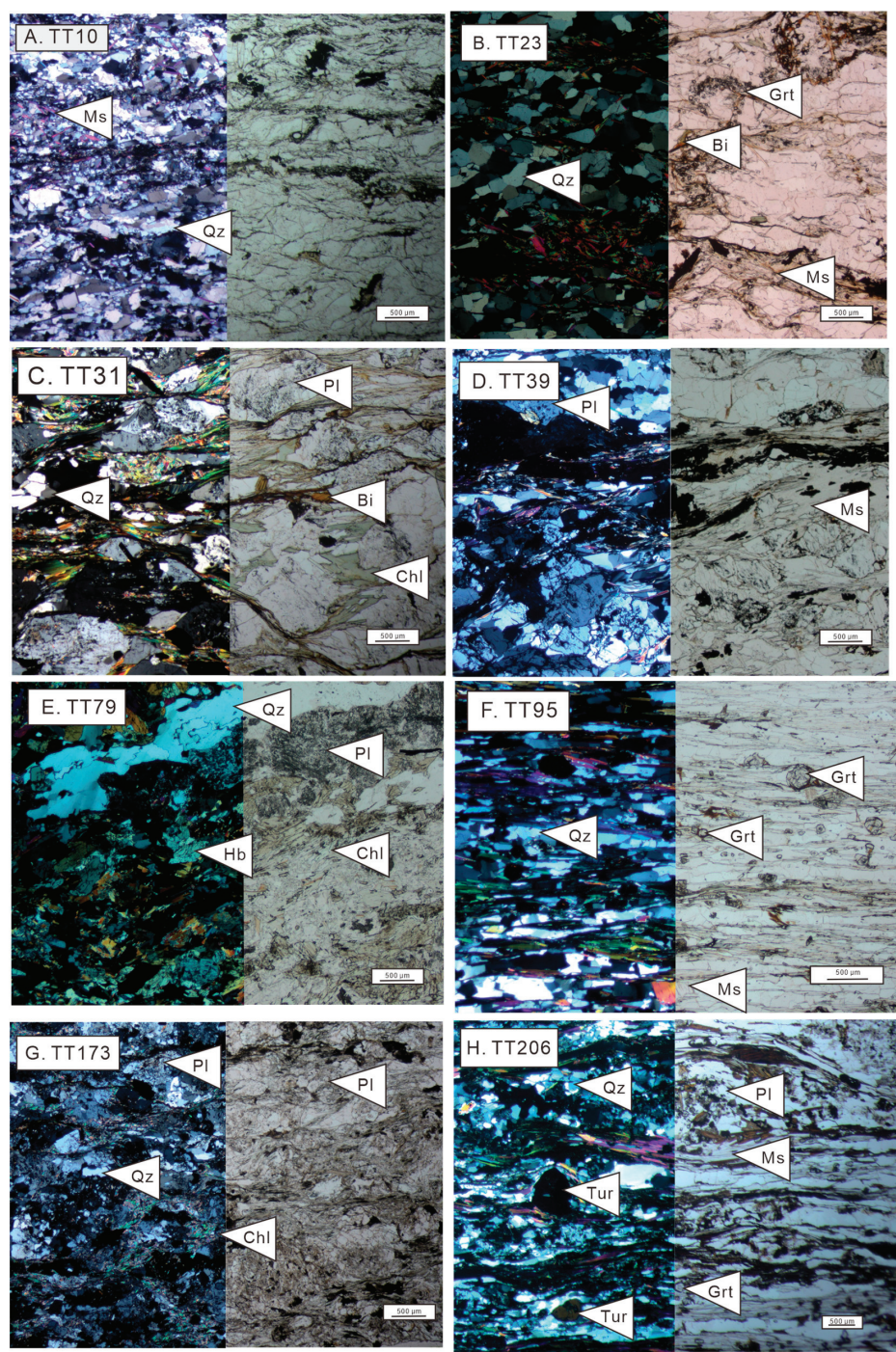


Figure 4. Thin sections of the 8 meta-sedimentary rocks in this study.

Table 1. Sample information of meta-sedimentary rocks from the Heilongjiang Complex.

| Sample Number | GPS Location                     | Area          | Descriptions                                                                                                                                     |
|---------------|----------------------------------|---------------|--------------------------------------------------------------------------------------------------------------------------------------------------|
| TT10          | E 130°15'2.9"<br>N 48°22'34.4"   | Jiayin-Luobei | Grey, mica schist; Qz (>85%) + muscovite mica (5%–10%) + opaque mineral (3%–5%).                                                                 |
| TT23          | E 130°19'18.6"<br>N 48°28'29.9"  |               | Grey, garnet two-mica quartz schist; Qz (65%) + muscovite mica (15%) + biotite (5%) + opaque mineral (3%); accessory minerals: garnet, chlorite. |
| TT31          | E 130°33'14.9"<br>N 48°30'44.8"  |               | Grey greenish, biotite greenschist; highly deformed; Plagioclase (55%) + Qz (15%) + chlorite (25%) + biotite (5%).                               |
| TT39          | E 130°36'35"<br>N 48°28'46.4"    |               | Grey, mica schist; Plagioclase (35%) + Qz (35%) + muscovite mica (25%) + opaque mineral (5%).                                                    |
| TT79          | E 130°44'15.6"<br>N 48°19'58.3"  |               | Dark grey, hornblende greenschist; deformed; Plagioclase (55%) + chlorite (20%) + hornblende (15%) + Qz (10%).                                   |
| TT95          | E 130°40'0.7"<br>N 48°09'6.5"    |               | Yellowish, garnet mica schist; highly deformed; Qz (75%) + muscovite mica (20%) + garnet (5%).                                                   |
| TT173         | E 129°52'23.7"<br>N 46°27'8"     | Yilan-Jiamusi | Dark grey, quartz greenschist; highly deformed; Plagioclase (70%) + Qz (15%) + chlorite (15%).                                                   |
| TT206         | E 129°58'4.59"<br>N 46°40'14.32" |               | Light grey, garnet muscovite mica schist; highly deformed; plagioclase (40%) + Qz (35%) + muscovite mica (20%) + tourmaline (3%) + garnet (2%).  |

We first selected detrital zircons from these samples, and then carried out U-Pb dating and trace elements analyses. See the Table S1 for details of the results, Table S2 for the compiled whole-rock geochemical data, and Table S3 for the methods used in this study. According to the temporal variations of zircon geochemical features, combined with the geochemical and geochronological data from the regional magmatic rocks, we discuss the tectonic evolution of the two episodes of continental arc in NE China.

3. Results

Most zircons from our eight samples show inherited cores with oscillatory zonation, indicating their magmatic origins (Figure 5). The internal zonation patterns in the cores differ from each other, e.g., some zoning intervals are wide and some others are narrow (Figure 5). This is because they are detrital zircons which were derived from various source rocks with different magmatic evolution history. However, almost all the grains are characterized by very thin bright rims in the cathode luminescence (CL) images. The rims have irregular boundaries with the magmatic zircon cores (Figure 5), probably caused by fluid-assisted hydrothermal alteration in low temperature metamorphism [30].

Nighty concordant ages yielded in sample TT10 (Figure 6a), ranging from 165 to 527 Ma. Zircons have length/width ratios varying from 1:1 to 4:1, and the lengths range from 80 to 200 μm (Figure 4). The age groups are divided into four categories: 509–527 Ma (2.2%), 436–458 Ma (3.3%), 216–269 Ma (12.1%), and 165–206 Ma (82.4%). The final group constitutes the major age peak (c. 182 Ma) in this sample, whereas the other three groups show very weak peak ages at 253 Ma, 455 Ma, and 509 Ma, respectively. According to the youngest age at c. 165 Ma and the youngest peak age at c. 182 Ma, the maximum depositional age of sample TT10 is the Middle Jurassic.

Zircons from sample TT23 show similar sizes and shapes to those from sample TT10. Nineteen-eight concordant results were obtained (Figure 6b), ranging from 153 Ma to 1874 Ma. More than 90% zircons have ages from 153 to 241 Ma, showing a major peak at c. 176 Ma. The maximum depositional age of sample TT23 should be the Middle Jurassic, based on the youngest zircon grain age at c. 153 Ma.





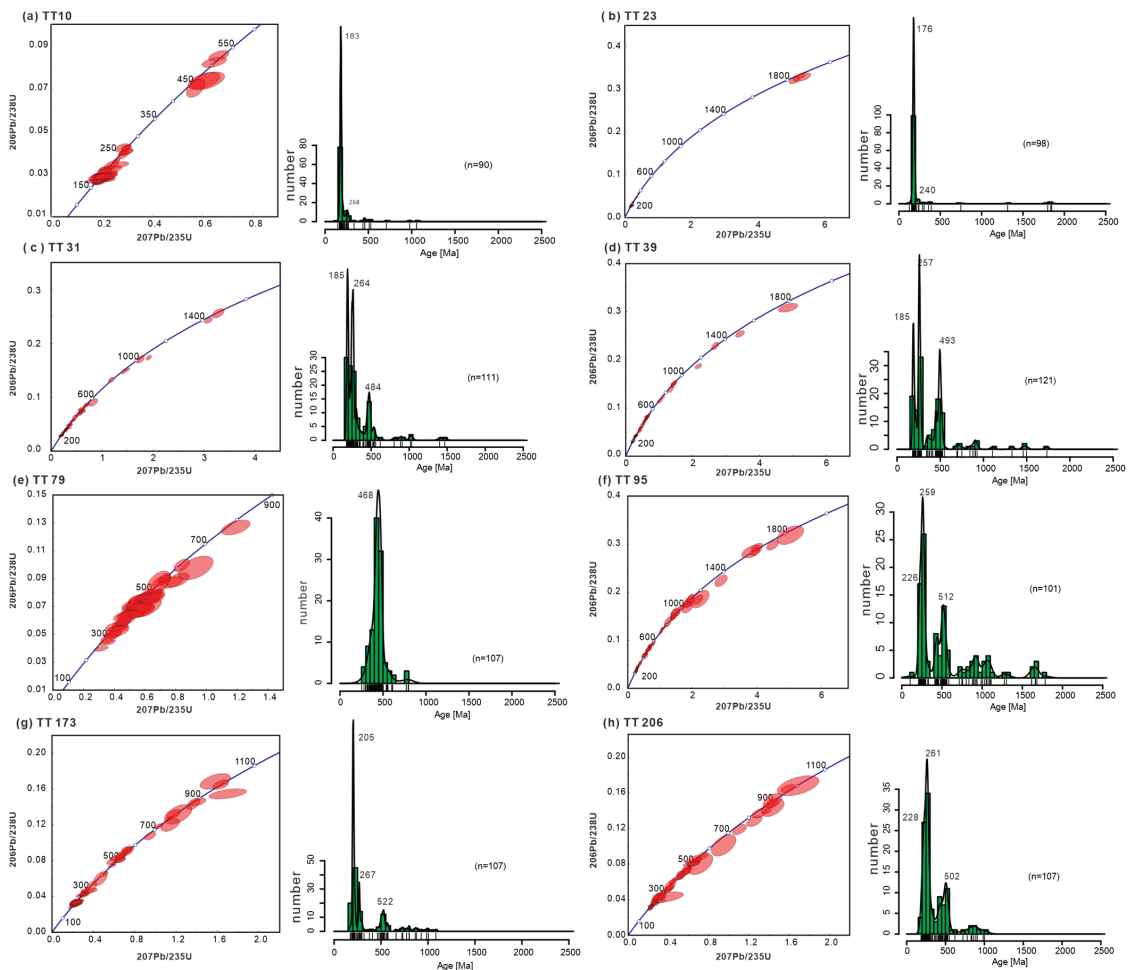
**Figure 5.** CL images of the analyzed zircons from the 8 meta-sedimentary rocks. Please see the main text for descriptions. Red circles denote the laser spots during the geochronological analyses.

In sample TT31, zircon grains are slightly larger than those from the former two samples, with lengths ranging from 100 to 300  $\mu\text{m}$  (Figure 5). There are 111 concordant ages in sample TT31 (Figure 6c). Three age populations are subdivided from c. 176 to 1474 Ma: 444–486.6 Ma (13.5%), 240.9–272.8 Ma (28.8%), and 176.1–206.1 Ma (27.9%). This sample shows two major peaks at c. 185 and 263 Ma, respectively, with a minor peak at c. 485 Ma. According to the youngest peak age at c. 185 Ma, the maximum depositional age of sample TT10 is the Early Jurassic.

Zircons from sample TT39 show angular shapes and various sizes; their lengths range from 50 to 250  $\mu\text{m}$  (Figure 5). They yield 121 concordant ages, varying from c. 181 to 1785 Ma (Figure 6d), showing three major groups: 443–527 Ma (28.9%), 235.9–284.1 Ma (32.2%), and 181–209 Ma (18.1%). The age spectrum is similar to sample TT31, that is, it has two major peaks at 185 and 257 Ma, respectively, with a weak peak at about 490 Ma. The maximum depositional age of sample TT10 should be the Early Jurassic, according to the youngest peak age at c. 181 Ma.

Zircons from sample TT79 are different from other samples because no low temperature alteration can be recognized. This sample probably experienced higher metamorphic grade because some zircons have metamorphic overgrowth rims (Figure 5). One hundred and seven concordant ages from sample TT79 (Figure 6e) were obtained. They range from 251 to 769 Ma, and thus, sample TT79 is the only one with no Mesozoic age peak in this study. The ages show a quasi-continuous distribution, and the most important age population is 339 to 556 Ma (87%) with a peak age at c. 468 Ma. Although some younger (Permian to Middle Triassic) and older (Proterozoic) ages exist, they are insignificant, indicating that the maximum depositional age of sample TT79 should be in the Early Triassic.

With similar shapes and sizes (lengths from 80 to 200  $\mu\text{m}$ ) to other samples (Figure 5), zircons from sample TT95 have wider hydrothermal altered rims and yielded 101 concordant ages, which vary from 221 to 1818 Ma and is subdivided into four groups (Figure 6f): 500–539 Ma (12.7%), 422–461 Ma (8.8%), 236–289.8 Ma (28.4%) and 218–228.6 Ma (10.8%). There are three major peak ages in this sample, 226 Ma, 259 Ma, and 512 Ma. According to the ages of the youngest zircon grain at c. 221 Ma and peak at c. 226 Ma, the maximum depositional age of this sample is the Late Triassic.



**Figure 6.** Detrital zircon U-Pb dating results of samples in this study. For each sample, the concordant diagram is shown in the left, and the histogram with a KDE curve is in the right. The figure was illustrated using IsoplotR [31] and refers to [32,33].

The hydrothermal rims of zircons are thin in sample TT173. One hundred and seven grains yielded concordant ages between 177 and 1004 Ma in this sample (Figure 6g), which show three major age populations, 501–537 Ma (10.2%), 250–296 Ma (14.0%) and 177–225 Ma (57.9%) corresponding to three major peak ages at 522, 267, and 205 Ma, respectively. The maximum depositional age of sample TT193 should be the earliest Jurassic, according to the youngest several grains which have ages from 177 to 199 Ma.

The low temperature alteration was remarkable in sample TT206 because of the wide rims with irregular complicated internal structures (Figure 5). We obtained 107 concordant ages from this sample, which range from 185 Ma to 999 Ma (Figure 6h). Three age groups can be recognized in this sample, that is, 829–906 Ma (4.7%), 486–529 Ma (14.0%) and 202–296 Ma (57.0%). Age peak at c. 261 Ma is the most important one relative to the other two at c. 228 Ma and 502 Ma, respectively. Although the youngest age peak is 228 Ma, the maximum depositional age of this sample should be the Early Jurassic, because there are six grains showing ages from 200 to 185 Ma.

## 4. Discussion

### 4.1. Types of Detrital Zircon Age Spectra and Provenance Analysis

We recognize three types of age spectra from the 8 meta-sedimentary rock samples in this study. The first one is a unimodal type, including samples TT10 and TT23 (Figure 6). Each of them only contains one major peak having ages of the Early Jurassic, 183 Ma and 176 Ma, respectively. Generally, this kind of age spectrum should be related to the intra-oceanic island arc [34] because oceanic arc-related basins are usually separated from the ancient continents by deep trench, abyssal plain, or middle ocean ridge. These positive/negative topographic anomalies are similar to the communication between oceanic arc-related basins and the old continents. Thus, sediments in these basins are mainly from the juvenile island arc, showing a unimodal peak pattern. However, this is not the case in the Heilongjiang Complex because the zircon grains with ages from Paleozoic to Neoproterozoic cannot be ignored in both samples (TT10 and TT23), indicating that they contain materials not only from the young arc, but also from the old continental basement. The depositional environment is not intra-oceanic arc, but near a continental arc. The second type is trimodal type, showing three major peak ages at the Late Triassic to Early Jurassic, Late Permian to Early Triassic, and Early Paleozoic. The three age peaks of this “trimodal” type can be recognized in the first type (unimodal). However, in the latter type, the Late Triassic to Early Jurassic age group is much more important than any other ages. In the second type, however, the Late Permian to Early Triassic and Early Paleozoic age groups are increasingly significant. The two post-Paleozoic age populations are contrasting. In sample TT173, the Late Triassic to Early Jurassic peak is much higher, but in other cases, the Late Permian to Early Triassic is equally (sample TT31) or even more (samples TT39, TT95, and TT206) important. The third type of age spectrum only contains sample TT79. It is special because the Mesozoic ages are quite fewer in this sample than in all other ones.

The three types of the detrital zircon age spectrum match the magmatic records in the Jiamusi block and the Lesser Xing'an-Zhangguangcai Range, suggesting the source region should be the continental blocks on both sides. For example, the most common age in the Jiamusi block is the Early Paleozoic (c. 530 to 450 Ma), representing the late Pan-African granulite-facies metamorphism and its accompanying or later-stage felsic magmatism [25]. Thus, the third type (sample TT79) probably suggests that it mainly accepted the sediments from the east side, the Jiamusi block, with only very minor materials from the west. Along the western margin of the Jiamusi block, numerous granitic gneisses and weakly deformed granulites are exposed and show I-type geochemical features. Their ages continuously vary from c. 275 to 245 Ma, with a peak age at 260–250 Ma. This age population is quite common in most samples in this study (samples TT31, TT39, TT95, TT173, and TT206), indicating the important contribution of the western Jiamusi block to the Heilongjiang Complex. However, the Late Triassic to Middle Jurassic (c. 210–170 Ma) magmatism is almost undetectable in the Jiamusi block but occur as the most important ages in the Lesser Xing'an-Zhangguangcai Range [10,22]. Thus, the first and second types of age spectrum should be largely containing materials from this range, namely the eastern Songliao block because age peaks at 170–210 Ma are usually high as or higher than those at 250–260 Ma (Figure 6).

Therefore, our provenance analyses indicate that the Heilongjiang Complex mainly contains deposits of terrigenous materials from both sides, that is, the Jiamusi and Songliao blocks. Although all these samples were collected from the Heilongjiang Complex, the relative contributions of the two blocks differ. Some samples (the first type) mainly consisted of materials from the west side, for example, the samples TT10 and TT23; other samples (the second type) accepted materials from both sides, including samples TT31, TT39, TT95, TT173, and TT206; the sediments of only one sample (TT79, the third type) was mainly supplied by the Jiamusi Block. The provenance complexity of the Heilongjiang Complex is consistent with the nature of the “non-Smith strata” of the accretionary complex. Accretionary complexes are formed after the closure of fossil oceanic basins and thus near the suture zones. They show a complicated “block-in-matrix” structure. Although they are mainly composed of meta-sedimentary rocks, the original sequence has been disturbed.

Rocks that have quite different provenance and metamorphic history are stacked together after the emplacement of the accretionary complex.

#### 4.2. Two Crustal Thickening Events in NE China Revealed by Zircon and Whole-Rock Geochemistry

The provenance analysis result—the detrital zircons in this study are mainly derived from the Songliao and Jiamusi blocks—indicates that the zircon trace elements can reflect the geochemical variations of their sources [16], the regional magmatic rocks. This provides a basis to our following discussions on magmatic and tectonic evolution.

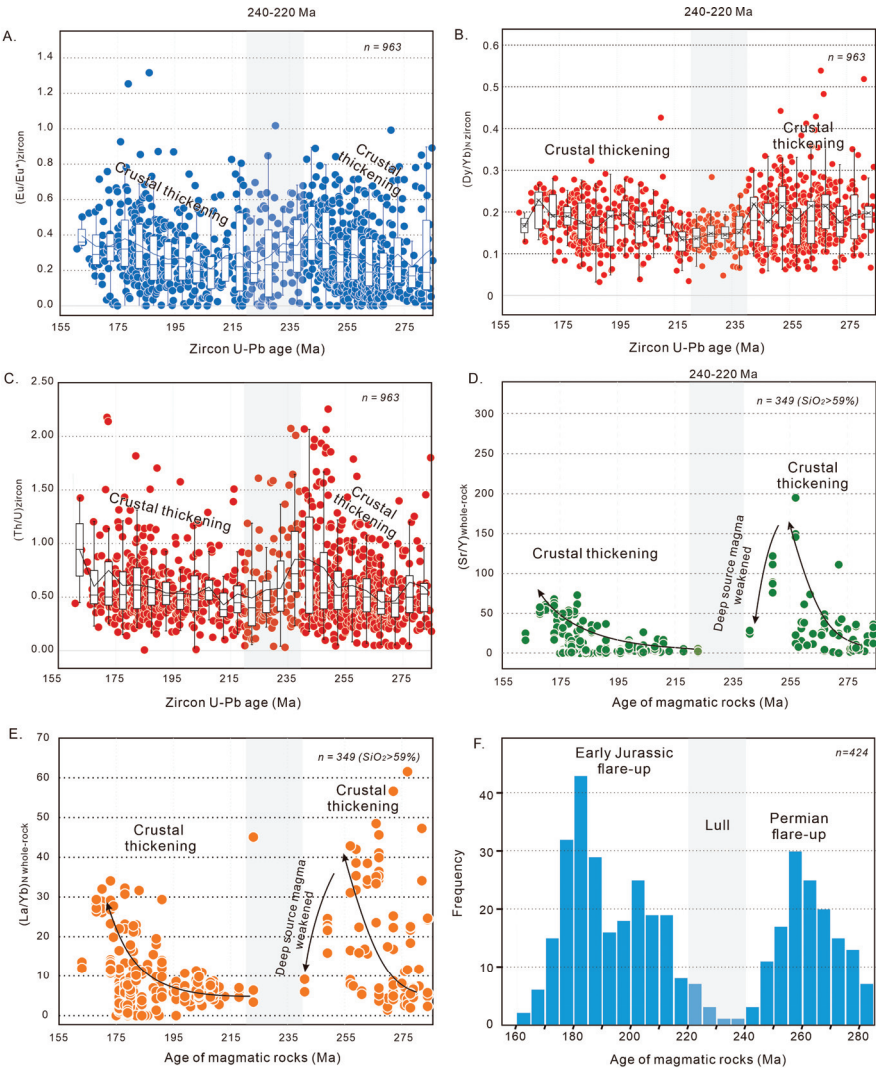
Zircon trace elements are strongly controlled by the magma compositions from which they crystallize, which further record the temperature and pressure conditions influenced by tectonics. For example, zircon Eu anomaly ( $\text{Eu}_N / \sqrt{\text{Gd}_N \times \text{Sm}_N}$ ; the subscript N means normalized to chondrites) [35] is used together with the whole-rock Sr/Y and La/Yb ratios [36] of felsic magmatic rocks to discuss the crustal thickness. The hypothesis is that crustal magmas are usually formed either by differentiation or crustal partial melting [37]. Both processes tend to occur at depths where mantle-derived stall, such as Moho. During the formation of these crustal magmas, the stability fields of some minerals are mainly associated with pressure, such as garnet (rich in HREEs and Y), plagioclase (rich in Sr and  $\text{Eu}^{2+}$ ), and amphibole (rich in middle to heavy REEs). Under higher pressure, amphibole and garnet tend to crystallize and plagioclase will break down. Thus, higher/lower whole-rock Sr/Y and La/Yb ratios indicate higher/lower pressure of felsic magmas, or deeper/shallower Moho depth [16]. Instable plagioclase under high pressure will release more Eu into the magma and increase the magmatic Eu anomaly, which will finally produce zircons with higher Eu anomaly values than those formed under lower pressure [35]. Accordingly, we will discuss the variation of magmatic formation depth by employing these geochemical proxies, based on both our new detrital zircon data and previously published data. Using the compiled geochronological and geochemical data from the regional magmatic rocks, we discuss the tectonic evolution of this region and its implications for the continental flare-ups along the active continental margin.

Detrital zircon trace elements reveal two crustal thickening events (Figure 7A–C), which coeval with the regional magmatic flare-up events: the first one lasted from the Early Permian to Early Triassic and the second mainly occurred in the Early Jurassic (Figure 7F). The median value of  $\text{Eu}/\text{Eu}^*$  increased from  $<0.2$  at c. 280 Ma to 0.5 at c. 245 Ma (Figure 7A) and decreased back to 0.2 in the Middle Triassic. Afterwards, the median value of  $\text{Eu}/\text{Eu}^*$  again increased slowly to 0.4 at c. 180 Ma. This increase indicates that the crust was probably thickened during the two episodes of magmatic flare-ups, leading to the breakdown of plagioclase in the source and the higher zircon  $\text{Eu}/\text{Eu}^*$  values in the magmas. During the magmatic lull from the Middle to Late Triassic, the crust thinned, facilitating the stabilization of plagioclase in the source region.

Similar to the  $\text{Eu}/\text{Eu}^*$  values, the  $(\text{Dy}/\text{Yb})_N$  values in the detrital zircons are also low during the magmatic lull but higher in the flare-ups (Figure 7b). The median of the  $(\text{Dy}/\text{Yb})_N$  values fluctuated around 0.2 in the Permian and slightly increased from 0.17 to 0.2 in the Late Triassic to Early Jurassic. In the Middle to Late Triassic, it decreased to near 0.15. This means that the middle REEs were depleted relative to the heavy REEs in the magmatic lull, indicating that stabilization of amphiboles weakened and thus the crust probably thinned.

Zircon Th/U ratio is commonly used to distinguish the magmatic or metamorphic origins of zircons [38], with the former being usually higher than 0.1 and the latter being lower. In this study, almost all the zircons ( $<290$  Ma) have Th/U ratios  $>0.1$ , indicating their magmatic origins and thus the temporal change of this value should not be related to any metamorphic processes. In the intermediate to felsic magmas, monazite and allanite are common accessory minerals controlling the Th and U budgets. Specially, Th is more compatible in these minerals than U and thus their fractionation will lead to low Th/U ratio in other minerals. Some studies indicate that the early-stage crystallization of Th-rich

minerals relative to zircon occurs in low-temperature magmas, whereas these minerals are instable in high-temperature magmas [39]. Thus, high Th/U ratio probably indicates high magmatic temperature. During the crustal thickening event, the deep crust becomes warmer when the geothermal gradient remains constant; a thicker crust is able to keep the magma reservoir warm, accelerating the Th/U ratios, similar to the examples in the Cretaceous Sikhote-Alin arc magmas [40] and Mesozoic Andes [16,41]. In this study, higher Th/U ratio corresponds to higher zircon Eu/Eu\*, whole-rock Sr/Y, and (La/Yb)<sub>N</sub>, probably representing the crustal thickening events. The low zircon Th/U ratios during the Middle to Late Triassic may have resulted from the crustal magmas produced in shallower crust and thus in lower temperatures.



**Figure 7.** Trace elements geochemical data (shown in different colors) from the regional magmatic rocks and detrital zircons in this study. Part of the detrital zircon data are from [13]. (A–C) show Eu anomaly, Th/U and Dy/Yb ratios of zircons varying with zircon ages, respectively; (D,E) show whole-rock Sr/Y and (La/Yb)<sub>N</sub> ratios varying with rock ages, respectively; (F) age histogram of magmatic rocks (Permian to Jurassic).

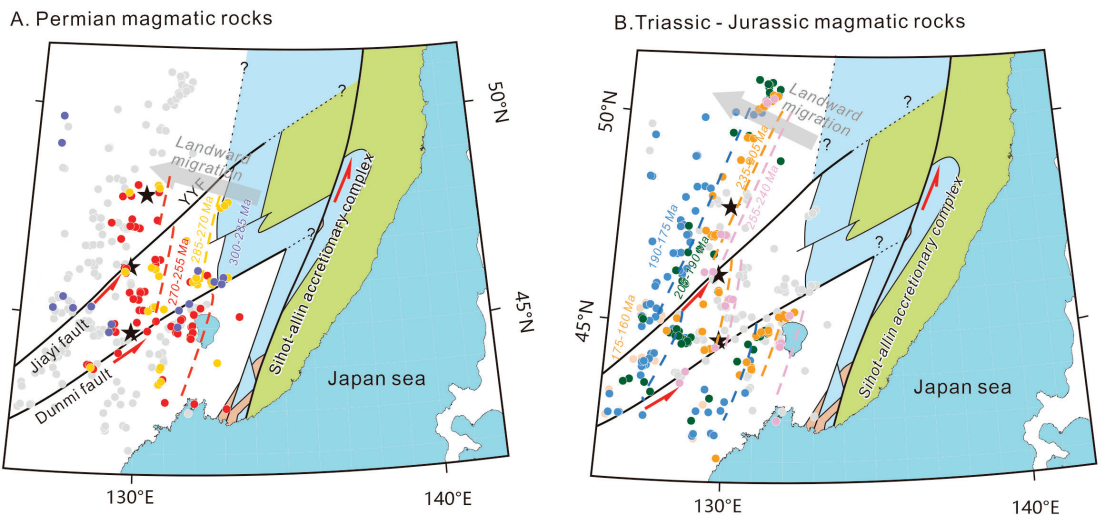


Whole-rock trace elements of the compiled magmatic rocks show consistent trends with the zircon  $\text{Eu}/\text{Eu}^*$ ,  $(\text{Dy}/\text{Yb})_N$  and  $\text{Th}/\text{U}$  ratios. Two crustal thickening events are revealed by high  $\text{Sr}/\text{Y}$  and  $(\text{La}/\text{Yb})_N$  ratios (Figure 7D,E). The first occurred in the Permian, during which the whole-rock  $\text{Sr}/\text{Y}$  ratios increased from 10–40 to  $>150$ , and the  $(\text{La}/\text{Yb})_N$  ratios also increased from  $<10$  to  $>40$ . The second lasted from the Late Triassic to Early Jurassic when the  $\text{Sr}/\text{Y}$  ratios increased from  $<10$  to  $>50$ , whereas the  $(\text{La}/\text{Yb})_N$  ratios increased from about 5 to 35. The good coherence between the two ratios indicates that the source of these felsic magmatic rocks changed from low pressure to high, indicating that the crust was possibly thickened at that time [42]. It should be noted that during the Middle to Late Triassic, both ratios decreased remarkably, suggesting that the deep magma source (high pressure) was shut down and only the shallow-level (low pressure) magmas were active.

In a word, trace elements of both the whole rock and detrital zircon reveal two events of crustal thickening in NE China during the Permian and Early Jurassic, respectively. Each thickening event was coeval with a continental flare-up (Figure 7F). Between them, the volume of deep source magmas reduced with the shallow ones remaining active, accompanied by an important magmatic lull (Figure 7F).

#### 4.3. Tectono-Magmatic Evolution in NE China: Not a “Cyclic Orogen”

The tectono-magmatic evolution in NE China shares similarities with the proposed “cyclic orogen”, such as in the American Cordillera [3]. The most important fact is that crustal thickening was accompanied by continental arc flare-ups and landward arc migration (Figure 8). During the Permian flare-up, the arc-related andesite and other volcanic rocks in the Erlongshan Formation was distributed along the eastern margin of the Jiamusi block in the Early Permian. At the end of the Permian, most magmatism had migrated to the Yilan-Mudanjang alignment and the migrating distance was about 180 km (Figure 8A). During the Late Triassic to Middle Jurassic, the magmatic rocks migrated westwards from Hegang-Yilan-Mudanjang to Tieli-Jilin, and the distance approximated to 150 km (Figure 8B).



**Figure 8.** Spatial distribution of regional magmatic rocks. (A,B) show the westward younger trends of the Permian and Triassic-Jurassic calc-alkaline magmatic rocks (continental arc), respectively. Black stars show the positions of Luobei, Yilan, and Mudanjang from north to south. The supposed extensions of the major faults are shown by dashed lines with question marks.

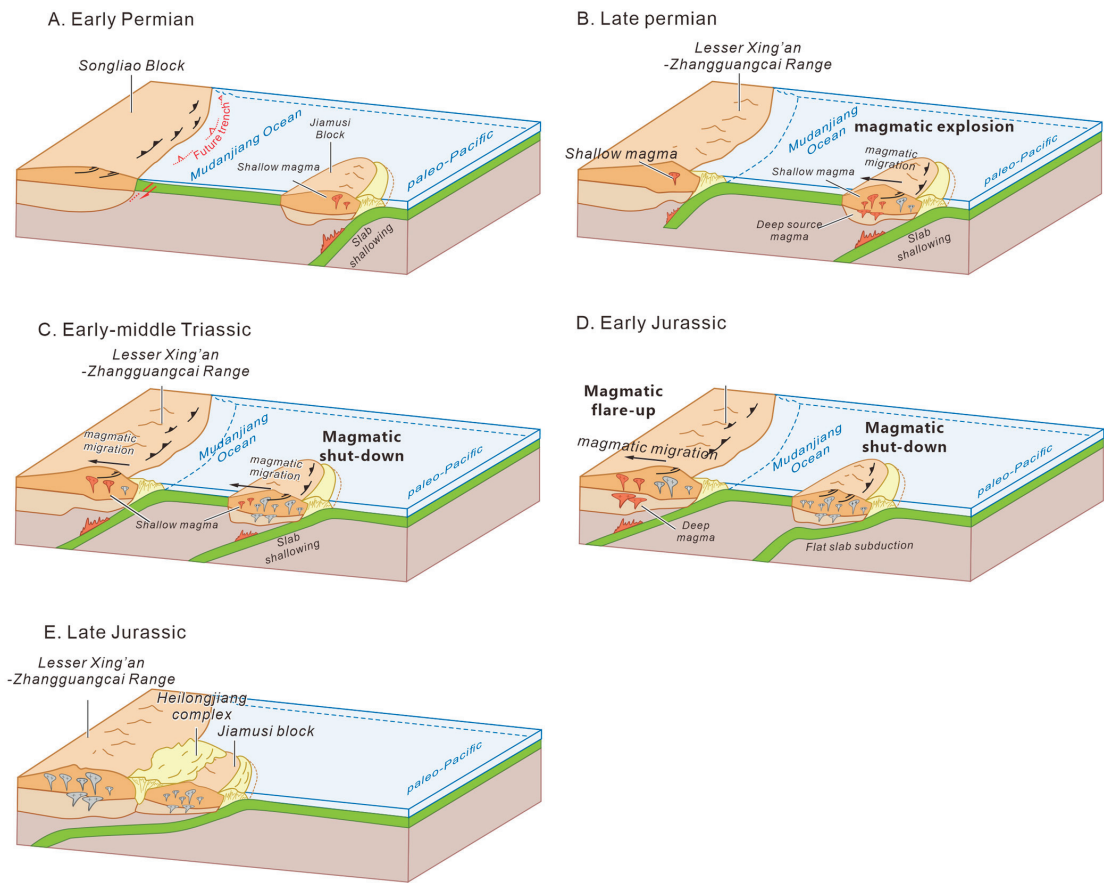
However, there are significant differences between the cases in NE China and the American Cordillera. The first is the nature of the arc magmatic migration. In NE China, the two migrations were independent from each other, that is, during the magmatic lull the magmas did not move back to the trench (east) but consistently migrated landward (westward) (Figure 8). However, in the American Cordillera, continental arc fronts tended to migrate towards the trench during the lulls and moved landwards again when the magmatic flare-ups were onset [3,5]. This difference indicates that the twice orogenic events in NE China, marked by the two magmatic flare-ups and crustal thickening events, were not two orogenic episodes within a single “cyclic orogen”. The second difference is that regional extension was active in NE China during the orogenic events, evident from the opening of the Mudanjiang Ocean and regional A-type and bimodal volcanism [10]. In the Heilongjiang Complex, metamorphic oceanic crustal fragments were preserved as exhumed blocks within the strongly deformed matrix, such as MORB and OIB-like blueschist and greenschist, representing the opening of the Mudanjiang Ocean and island arc within it [15]. The protolith ages of these remnants of the oceanic crust range from c. 210 Ma to 290 Ma. In the Late Triassic, A-type and bimodal volcanic rocks were reported in the Lesser Xing’an-Zhangguangcai Range and Khanka block [10], indicating the occurrence of intra-continental extension during that period.

#### *4.4. Tectonic Implications in NE China: Two Orogenic Events during the Closure of the Mudanjiang Ocean*

According to the similarities and differences between magmatism in NE China and the American Cordillera, we propose a new model in our study area in order to explain the coupling between magmatic flare-up, landward migration, and crustal thickening (Figure 9).

During the early Permian, the eastern Jiamusi margin experienced a transition from a passive continental margin to an active one [26]. This transition produced a series of arc-related volcanic rocks with sedimentary strata (Figure 9A), aligning from north to south near Baoqing. Since then, the oceanic plate within the Panthalassa Ocean began to subduct beneath the Jiamusi block and triggered the first orogenic event in NE China. The slab dip angle became shallower as the oceanic plate subducted and thus resulted in the landward migration of the calc-alkaline magmatism in the Jiamusi block. The coupling between the overriding and subducting plates was strengthened, and thus the crust was thickened (Figure 9B). Crustal thickening caused warmer lower crust and deeper Moho in the region, facilitating deep crustal melting and resulted in more voluminous magmas in the Permian, namely the first magmatic flare-up. However, the asthenospheric mantle wedge could be largely expelled by the shallowing slab and thickening arc crust, and thus the arc magmatic source weakened after it migrated to the western margin of the Jiamusi block (Figure 9C). Deep source melting also vanished, causing the descending trend in the whole-rock Sr/Y, (La/Yb)<sub>N</sub>, and zircon Eu/Eu\*, Th/U, and (Dy/Yb)<sub>N</sub> ratios.

From the Early Triassic, the Mudanjiang Oceanic plate probably began to subduct westwards and produced calc-alkaline magmatism in the Lesser Xing’an-Zhangguangcai Range, the second continental arc flare-up (Figure 9D). Magmatism also moved westwards during the Middle Triassic to Middle Jurassic, probably related to the shallowing subducting slab dip, or associated with the removal of the fore-arc crust by subduction erosion. Regional extension may have existed in the arc or back-arc region during the Middle-Late Triassic, making the regional tectonics complicated than our schematic tectonic model. The closure of the Mudanjiang Ocean occurred after the Early Jurassic (the maximum depositional ages of most samples in this study), which should be the reason why the Early Jurassic magmatic flare-up ended abruptly at c. 170 Ma (Figure 9E) without remarkable decrease in the values of the whole-rock Sr/Y, (La/Yb)<sub>N</sub>, and zircon Eu/Eu\* ratios.



**Figure 9.** Tectono-magmatic evolution in the eastern Heilongjiang Province. It illustrates the two episodes of continental arc magmatic flare-ups and crustal thickening history.

**5. Conclusions**

The Heilongjiang Complex mainly received sediments from the both sides, including the Songliao block (the Lesser Xing'an-Zhangguangcai Range) and Jiamusi block, recording abundant geochemical information of the Permian to Middle Jurassic magmatism in NE China.

Trace elements from the detrital zircons ( $Eu/Eu^*$ ,  $Th/U$ , and  $(Dy/Yb)_N$  ratios) and regional magmatic rocks (whole-rock  $Sr/Y$ ,  $(La/Yb)_N$ ) both indicate two crustal thickening events in the Permian and Early Jurassic, respectively. Crustal thickening was accompanied by magmatic flare-up and landward migration.

The two crustal thickening events and flare-ups are independent of each other, forming two orogenic events in NE China. The Permian crustal thickening event was caused by shallowing subducting slab angle and thus triggered magmatic flare-ups. The shallow slab subduction enhanced plate coupling and caused the westward subduction of the Mudanjiang Oceanic plate, generating the second flare-up in this region and the crustal thickening event.

Closure of the back-arc basin or marginal sea (the Mudanjiang Ocean) by the subduction of the Paleo-Pacific oceanic plate (Izanagi plate) could lead to several arc magmatic flare-ups and crustal thickening events, as revealed by our study. This is probably a com-

mon process in the accretionary orogens and contributed to the continental growth along active continental margins.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13091121/s1>, Table S1. Detrital zircon U-Pb dating and trace elements results; Table S2. Data for Figure 7d,e; Table S3. Analytical methods. References [43,44] are cited in the Supplementary Materials.

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

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

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## Article

# Middle Silurian–Middle Devonian Magmatic Rocks in the Eastern Segment of the Northern Margin of the North China Craton: Implications for Regional Tectonics

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**Abstract:** This paper presents a detailed study including LA-ICP-MS zircon U-Pb dating, geochemical, zircon Hf isotope, and whole rock Sr-Nd isotope analysis of magmatic rocks from the Yitong County, Jilin Province, NE China. These data are used to better constrain the Middle Silurian–Middle Devonian tectonic evolution in the eastern segment of the northern margin of the North China Craton (NCC). Zircon U-Pb dating results show that the Ximangzhang tonalite formed in the Late Silurian ( $425 \pm 6$  Ma); the basalt, andesite, and metamorphic olivine-bearing basalt in the Fangniugou volcanic rocks formed in the Middle Silurian ( $428 \pm 6.6$  Ma) and Middle Devonian ( $388.4 \pm 3.9$  Ma, and  $384.1 \pm 4.9$  Ma). The Late Silurian tonalites are characterized by high  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  and low  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{FeOT}$ , and  $\text{TiO}_2$ , with an A/CNK ratio of 0.91–1.00, characteristic of calc-alkaline I-type granite. They are enriched in Rb, Ba, Th, U, and K, and depleted in Nb, Sr, P, and Ti, with positive  $\epsilon_{\text{Nd}}(t)$  (+0.35) and  $\epsilon_{\text{Hf}}(t)$  (+0.44 to +6.31) values, suggesting that they mainly originated from the partial melting of Meso–Neoproterozoic accretionary lower crustal material (basalt). The Middle Silurian basalts are characterized by low  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{TiO}_2$ , and  $\text{Na}_2\text{O}$  and high  $\text{Al}_2\text{O}_3$ ,  $\text{FeOT}$ , and  $\text{K}_2\text{O}$ , enriched in Rb, Ba, Th, U, and K and depleted in Nb, Ta, Sr, P, and Ti, indicative of shoshonitic basalt. The Late Silurian tonalites have positive  $\epsilon_{\text{Nd}}(t)$  (+4.91 to +6.18) values and primarily originated from depleted mantle magmas metasomatized by subduction fluids, supplemented by a small amount of subducted sediments and crustal materials. The Middle Devonian volcanic rocks exhibit low  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{Na}_2\text{O}$  and high  $\text{K}_2\text{O}$ , and  $\text{MgO}$ , enriched in Rb, K, and LREEs and depleted in Nb, Ta, Sr, and HREEs, characteristic of shoshonitic volcanic rocks. Their  $\epsilon_{\text{Nd}}(t)$  (+2.11 to +3.77) and  $\epsilon_{\text{Hf}}(t)$  (+5.90 to +11.73) values are positive. These characteristics indicate that the Middle Devonian volcanic rocks primarily originated from depleted mantle magmas metasomatized by subduction fluids, with the addition of crustal materials or subducted sediments during their formation. Based on regional geological data, it is believed that the study area underwent the following evolutionary stages during the Silurian–Devonian period: (1) active continental margin stage of southward subduction of the Paleo–Asian Ocean (PAO) (443–419 Ma); (2) arc-continent collision stage (419–405 Ma); (3) post-collision extension stage (404–375 Ma); (4) active continental margin stage, with the PAO plate subducting southward once again (375–360 Ma).

**Keywords:** Silurian; Devonian; magmatic rocks; geochronology; geochemistry; petrogenesis; the eastern segment of the northern margin of the North China Craton

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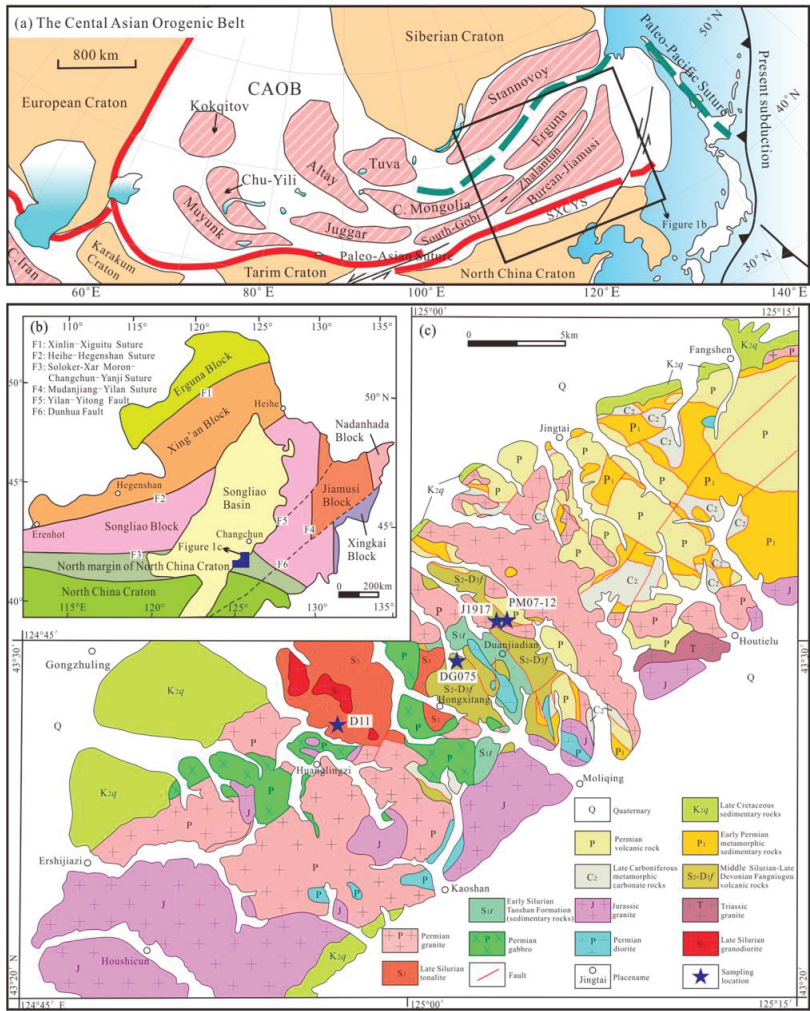


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## 1. Introduction

The Central Asian Orogenic Belt (CAOB), situated between the North China, Tarim, and Siberian plates [1–6], represents the largest accretionary orogenic belt of the Phanerozoic. The CAOB is noted for its extensive crustal growth and significant mineralization

potential during the same period [7–10]. The formation of the CAOB involved the subduction of the Paleo–Asian Ocean (PAO) and the amalgamation of terranes, consisting of a series of microcontinents, island arcs, accretionary complexes, ophiolites, forearc/back-arc basins, oceanic plateaus, and seamounts [1,4,11]. With a highly complicated geological tectonic evolution [12], the CAOB serves as a critical area for studying the processes of collision and amalgamation of micro-continents, continental accretion, and ocean-continent transitions [6,13–17]. There is a consensus among scholars that the PAO closed along the Solonker–Xar Moron–Changchun–Yanji Suture (SXCYS) on the southeastern margin of the CAOB (Figure 1a) [4,6,12,13,18–29].



**Figure 1.** (a) Tectonic division of the Central Asian Orogenic Belt and adjacent regions (modified after [22]), and the position of Figure 1b (black color square); (b) Tectonic division of NE China (modified from [12]); (c) Geological sketch map of the Yitong area in Jilin Province (modified from [29]).

The northern margin of the North China Craton (NCC) is located at the southeastern margin of the CAOB (Figure 1a,b), north of the Bayan Obo–Chifeng–Kaiyuan fault and south of the SXCYS. This area primarily encompasses the Bainaimiao arc and the Ondor Sum subduction–accretionary complex [20,30,31]. The Bainaimiao arc extends approximately

1300 km from Baoerhantu to Bayan Obo, Bainaimiao, and Chifeng in Inner Mongolia to eastern Faku in Liaoning Province to northeastern Gongzhuling and Yanbian in Jilin Province [32]. At present, there are still different opinions on the basement properties, subduction polarity, and tectonic setting of the Bainaimiao arc. One suggests affinity of the arc basement with the NCC and the other proposes affinity with other continental blocks. It is also suggested that the Bainaimiao arc belt and the Ondor Sum subduction-accretionary complex constitute a trench-arc-basin system formed by the southward subduction of the PAO [15,20,33–41]; however, some argue for its formation through the northward subduction of the South Bainaimiao Ocean, accreting to the NCC via arc-continent collision [32,42–48]. Consequently, the Bainaimiao arc belt has been regarded as a Japan-style island arc [37,49,50], Andean-type continental margin arc [20,51], or exotic terrain [42]. In addition, there is controversy about the formation age of the Bainaimiao arc, suggested to be Middle Neoproterozoic [50,52,53] or Ordovician–Silurian [32,51,54,55].

Previous research was predominantly focused on the central and western regions of Inner Mongolia, while the northern margin of the NCC from northern Liaoning Province to central Jilin Province has received less attention [32,43,45,56,57]. Moreover, the northern Liaoning Province to central Jilin Province region, which was originally classified as Early Paleozoic, has now been classified as Late Paleozoic or Early Mesozoic [12,19,51,58–66]. Therefore, it remains uncertain whether the Bainaimiao arc belt can extend over the Songliao Basin into northeastern China [12,58,59,67]. With the deepening of research, some Ordovician–Devonian rocks have been discovered in recent years in northern Liaoning Province and central to eastern Jilin Province [43,44,48,56,64,68–71], providing valuable information for further understanding of tectonic evolution. The Silurian–Devonian rocks in Yitong County, Jilin Province, which document a continuous evolutionary history from the Silurian to the Permian, are particularly crucial for exploring the tectonic framework and accretionary processes along the eastern segment of the northern margin of the NCC. In this study, zircon U–Pb chronological, petrographical, geochemical, zircon Hf-isotope, and whole-rock Sr–Nd isotope analyses were conducted (Table 1), and the properties and tectonic setting of the source area of the Silurian–Devonian magmatic rocks in Yitong area are discussed. These data provide new evidence for the magmatic-tectonic evolution of the northern margin of the NCC in the Silurian–Devonian.

Table 1. The simplified list of the volcanic and intrusive rock samples in this study.

| Age            | Lithology                             | GPS                        | Samples No.                                                                                            |
|----------------|---------------------------------------|----------------------------|--------------------------------------------------------------------------------------------------------|
| 425 ± 6 Ma     | Tonalite                              | E124°56′07″,<br>N43°27′42″ | Zircon U–Pb and Hf Isotope: D11<br>Whole-Rock: D11-1-1, D11-1-2,<br>D11-1-3, D11-1-4<br>Sr–Nd: D11-1-1 |
| 428 ± 6.6 Ma   | Basalt                                | E125°01′31″,<br>N43°29′37″ | Zircon U–Pb: DG075<br>Whole-Rock: DG075-1, DG075-2,<br>DG075-3, DG075-4<br>Sr–Nd: DG075-1, DG075-2     |
| 388.4 ± 3.9 Ma | Andesite                              | E125°03′24″,<br>N43°30′29″ | Zircon U–Pb and Hf Isotope:<br>J1917<br>Whole-Rock: J1917-2, J1917-5<br>Sr–Nd: J1917-2, J1917-5        |
| 384.1 ± 4.9 Ma | Metamorphic<br>olivine-bearing basalt | E125°04′12″,<br>N43°30′28″ | Zircon U–Pb: PM07-12<br>Whole-Rock: PM07-9-2,<br>PM07-9-4, PM07-9-5                                    |

2. Geological Setting and Samples

2.1. Geological Setting

The study area is located in the northwest of Yitong County, Jilin Province, Northeast China (Figure 1c). It is adjacent to the Yitong Basin to the east and the Songliao Basin to the west, belonging to the southeast margin of the CAO and the eastern margin of the

NCC. This area mainly contains the Lower Silurian Taoshan Formation, Upper Silurian–Upper Devonian Fangniugou volcanic rocks, Upper Carboniferous metamorphic carbonate rocks, Lower Permian metamorphic clastic rocks, and Permian volcanic rocks. The main lithology of the Taoshan Formation consists of sandstone, siltstone, silty mudstone, and silty slate, interbedded with marlstone, and contains gracilite. Intrusive rocks include the Late Ordovician–Late Silurian tonalite and granodiorite; Middle–Late Permian granodiorite, monzonite, quartz monzonite, and gabbro; Early Triassic monzogranite; and Early–Middle Jurassic syenite granite, granodiorite, monzogranite and quartz diorite.

Fangniugou volcanic rocks, established as an informal mapping unit [72], primarily consist of intermediate to acidic volcanic rocks considered to have formed during the Ordovician. In recent years, scholars have obtained zircon U–Pb ages of  $426 \pm 4.8$  Ma [29],  $402 \pm 4$  Ma [68],  $419 \pm 3$  Ma [43],  $425 \pm 4$  Ma,  $390 \pm 4$  Ma [44], and  $375.5 \pm 4.6$  Ma [29] from the Fangniugou volcanic rocks, suggesting that they were formed during the Late Silurian to Late Devonian period.

In the northeast of the Taoshan Formation, the Fangniugou volcanic rocks are exposed with a suite of metamorphic carbonates, clastic rocks, and volcanic rocks, which formed during the Carboniferous to Permian [32,45] (Figure 1c). The Paleozoic geological units in the study area are composed of a series of tectonic slices, which were formed during the Silurian to Permian, and gradually became younger from southwest to northeast. Reflected in the process of oceanic crust subduction, various geological bodies of different ages and environments were, in turn, collaged laterally, and then transformed by later tectonic events.

## 2.2. Sample Descriptions

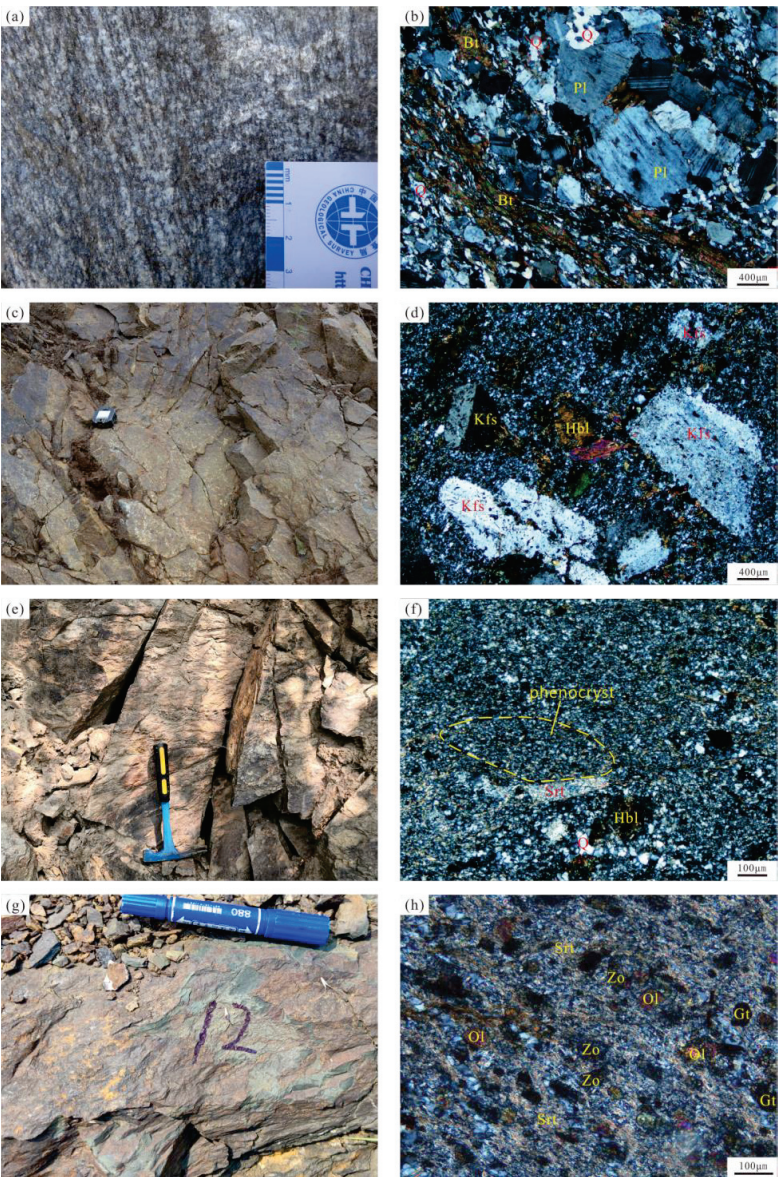
The tonalite (D11) is gray in color, with a mylonitic structure and a fine-grained granitic texture (Figure 2a,b). The sample shows a typical mineral assemblage of plagioclase (~55 vol.%), quartz (~25 vol.%), biotite (~20 vol.%), and minor accessory minerals (~5 vol.%; e.g., allanite, epidote).

The basalt (DG075) is dark gray in color and shows a porphyritic texture with 27% phenocrysts (Figure 2c,d). The phenocrysts are mainly alkali feldspar (15%) and hornblende (12%). The matrix (73%) is predominantly microcrystalline and includes hornblende, alkali feldspar, and plagioclase.

The andesite (J1917) is gray in color and shows a porphyritic texture with 8% phenocrysts (Figure 2e,f). The phenocrysts are composed of plagioclase (5%) and hornblende (3%). Plagioclase undergoes alteration such as sericitization and chloritization. The matrix (92%) is predominantly microcrystalline and includes biotite, chlorite, sericite, felsic minerals, etc.

The metamorphic olivine-bearing basalt (PM07-12) is greenish–gray in color, with a porphyroblastic texture and massive structure (Figure 2g,h). The porphyroblasts are zoisite (6%), garnet (3%), and olivine (3%). The matrix (88%) is predominantly microcrystalline and includes zoisite, sericite, and plagioclase.





**Figure 2.** Field photographs and microphotographs of the Middle Silurian–Middle Devonian magmatic rocks from the Yitong area. (a,b) Tonalite (Sample D11); (c,d) Basalt (Sample DG075); (e,f) Andesite (Sample J1917); (g,h) Metamorphic olivine-bearing basalt (Sample PM07-12). In the figure, 12 represents the layer number of profile 07). Abbreviations: Qz, Quartz; Pl, Plagioclase; Kfs, K-feldspar; Srt, Sericite; Bi, Biotite; Hbl, hornblende; Ol, olivine; Ep, epidote; Zo, Zoisite; Grt, Garnet.

### 3. Analytical Methods

#### 3.1. Whole-Rock Composition Analyses

Geochemical analyses of the rock samples were conducted at the Northeast China Supervision Inspection Center of Mineral Resources, Ministry of Natural Resources, Shenyang Center of Geological Survey, China Geological Survey, Shenyang, China, using

contamination-free equipment. Major elements were quantified via X-ray fluorescence spectrometry (XRF), with errors in precision and accuracy of  $\pm 5\%$ . Trace elements were measured using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), with errors in precision and accuracy of less than 10%.

### 3.2. LA-ICP-MS Zircon U-Pb Dating

LA-ICP-MS Zircon U-Pb dating was performed at the Key Laboratory of Mineral Resources Evaluation in Northeast Asia, Ministry of Natural Resources, Jilin University, Changchun, China. The process utilized a COMPEX Pro type ArF excimer laser ablation system from the Coherent Company (Saxonburg, PA, USA) and an Agilent 7900 type ICP-MS (Agilent Technologies, Inc., Santa Clara, CA, USA). The laser spot diameter was set at 32  $\mu\text{m}$ . High-purity helium served as the carrier gas, and argon was used as the auxiliary gas. Isotopic ratio corrections employed standard zircons 91500 and PLE, while the international standard NIST610 corrected the contents of Th, U, Pb, and other elements [73]. The procedures followed for these analyses are elaborated in Yuan et al. [74]. Age determinations were conducted using Isoplot software (version 3.0).

### 3.3. Zircon Lu-Hf Isotopic Analyses

Zircon Lu-Hf isotopic analyses were carried out at the Tianjin Institute of Geology and Mineral Resources. This process utilized a Thermo Fisher Neptune type Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) and a 193 nm laser ablation system (NEW WAVE193nm FX), with a laser spot size of 50  $\mu\text{m}$  (Thermo Fisher Scientific, Waltham, MA, USA). The methodologies applied, including isotopic fractionation corrections, are based on the techniques described by Geng Jianzhen et al. [75] and Wu Fuyuan et al. [17].

### 3.4. Whole-Rock Sr-Nd Isotopic Analyses

Whole-rock Sr-Nd isotopic analyses were conducted at the Analytical and Testing Research Center of the Beijing Research Institute of Uranium Geology. These analyses utilized an ISOPROBE-T thermal ionization mass spectrometer (Isotopx LTD., Cheshire, UK). The isotopic ratios for Sr and Nd were standardized using the values  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$  and  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ .

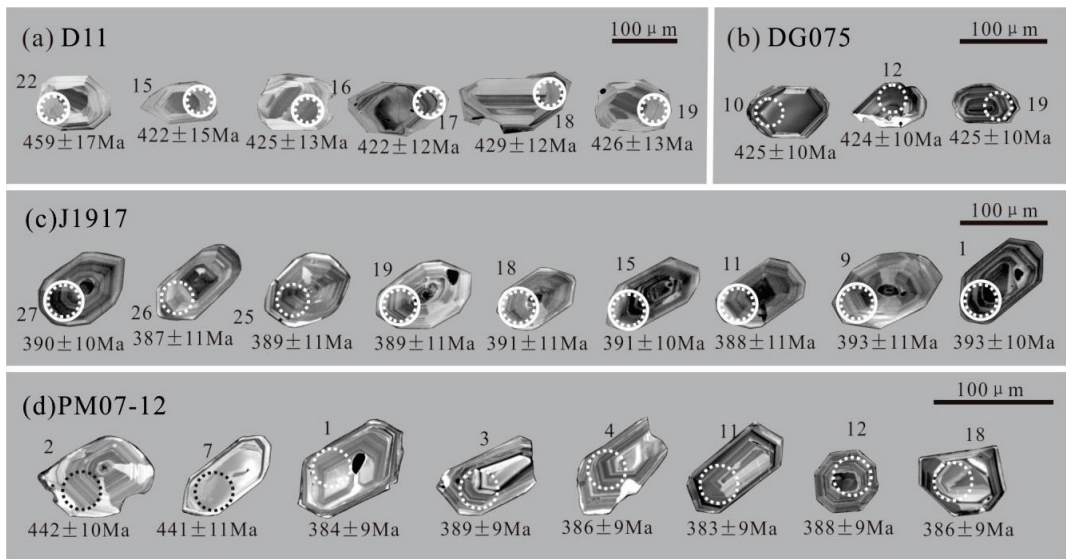
## 4. Analysis Results

### 4.1. Zircon U-Pb Geochronology

The zircon U-Pb dating results are shown in Supplementary Table S1.

Sample D11 is a tonalite from the Ximangzhang pluton. Twenty-five zircon grains from this sample were dated, with most results lying on or near the concordia line. These zircons are mostly granular and short columnar, with grain sizes of 100–200  $\mu\text{m}$  and length/width ratios of 1:1 to 3:2. The cathodoluminescence (CL) images (Figure 3a) show that these zircon grains have typical zonal textures and Th/U ratios of 0.36–0.77, suggesting a magmatic origin. Of these, 17 zircon grains have  $^{206}\text{Pb}/^{238}\text{U}$  ages of 420–437 Ma, with a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $425 \pm 6$  Ma (mean squared weighted deviation (MSWD) = 0.12) (Figure 4a), representing the best estimate for emplacement time of the tonalite. Another 8 zircon grains have  $^{206}\text{Pb}/^{238}\text{U}$  ages of 445–459 Ma, with a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $451 \pm 10$  Ma (MSWD = 0.08).

Sample DG075 is a basalt from the Fangniugou volcanic rocks. These zircons are short columnar, with grain sizes of 50–100  $\mu\text{m}$  and length/width ratios of 2:1 to 3:2. The CL images (Figure 3b) show that these zircon grains have typical zonal textures and Th/U ratios of 0.41–0.75, suggesting magmatic zircons. Twenty zircon grains were analyzed in this study. Most results deviated from the concordia line, but all data could fit a line, showing a lower intercept age of  $428 \pm 6.6$  Ma (MSWD = 0.77) (Figure 4b), which represents the best estimate for the eruption time of the basalt.

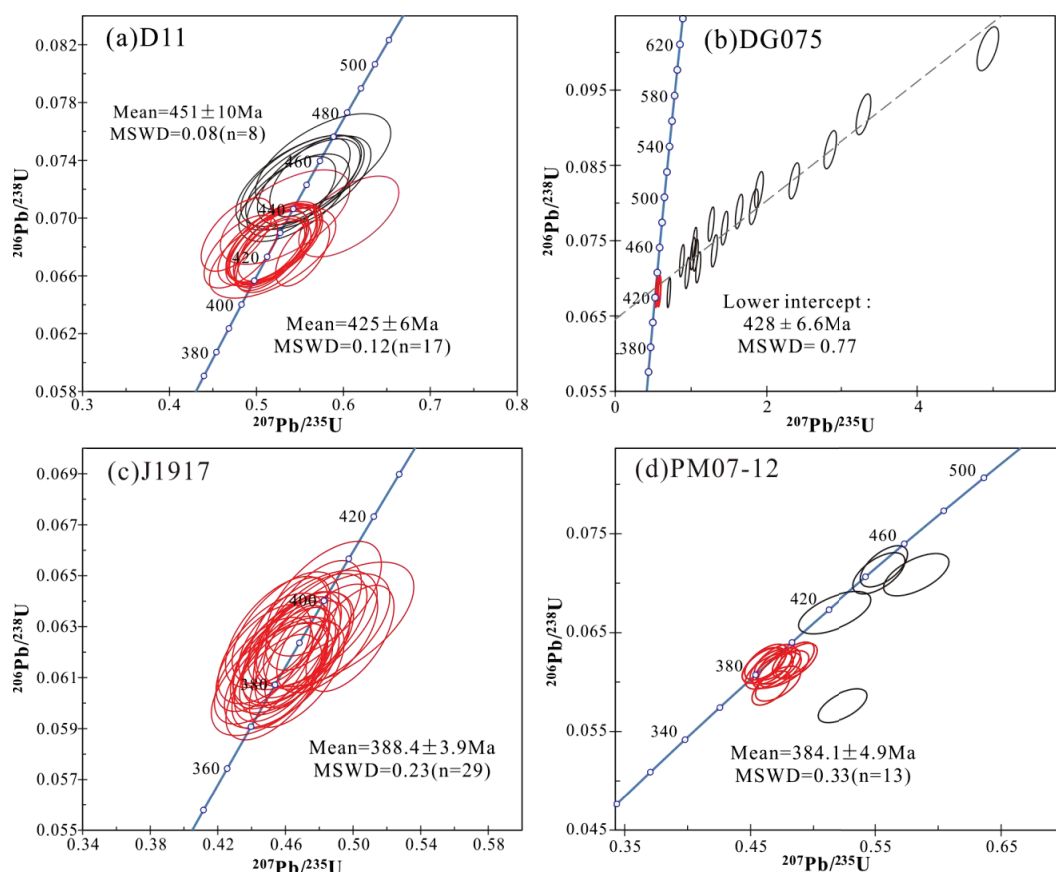


**Figure 3.** Representative CL images of zircons from the Middle Silurian–Middle Devonian magmatic rocks in the Yitong area. (a) CL image of zircons from sample D11. (b) CL image of zircons from sample DG075. (c) CL image of zircons from sample J1917. (d) CL image of zircons from sample PM07-12. The solid line circle is the Hf isotope analysis point; the dotted line circle is the U-Pb age analysis point. The numbers show the ages of the zircons (Ma) and the  $\epsilon_{\text{Hf}}(t)$  values.

Sample J1917 is an andesite from the Fangniugou volcanic rocks. These zircons are tabular and short columnar, with grain sizes of 50–100  $\mu\text{m}$  and length/width ratios of 1:1 to 2:1. The CL images (Figure 3c) show that these zircon grains have typical zonal textures and Th/U ratios of 0.56–1.47, suggesting magmatic zircons. Twenty-nine zircon grains in this sample were dated, with all results lying on or near the concordia line. The analyses give a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $388.4 \pm 3.9$  Ma (MSWD = 0.23) (Figure 4c), representing the best estimate for the eruption time of the andesite.

Sample PM07-12 is a metamorphic olivine-bearing basalt, from the Fangniugou volcanic rocks. These zircons are tabular and short columnar (Figure 3d), with grain sizes of 50–120  $\mu\text{m}$  and length/width ratios of 1:1 to 3:1. The CL images show that these zircon grains have typical zonal textures and Th/U ratios of 0.45–1.35, suggesting magmatic zircons. Eighteen zircon grains in this sample were dated, with all results lying on or near the concordia line. Of these, 13 zircon grains have  $^{206}\text{Pb}/^{238}\text{U}$  ages of 372–389 Ma, with a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $384.1 \pm 4.9$  Ma (MSWD = 0.33) (Figure 4d), representing the eruption time of the basalt. Another 4 zircon grains have  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $446 \pm 10$  Ma,  $442 \pm 10$  Ma,  $441 \pm 11$  Ma, and  $418 \pm 11$  Ma, most likely representing xenocrystic zircon ages.





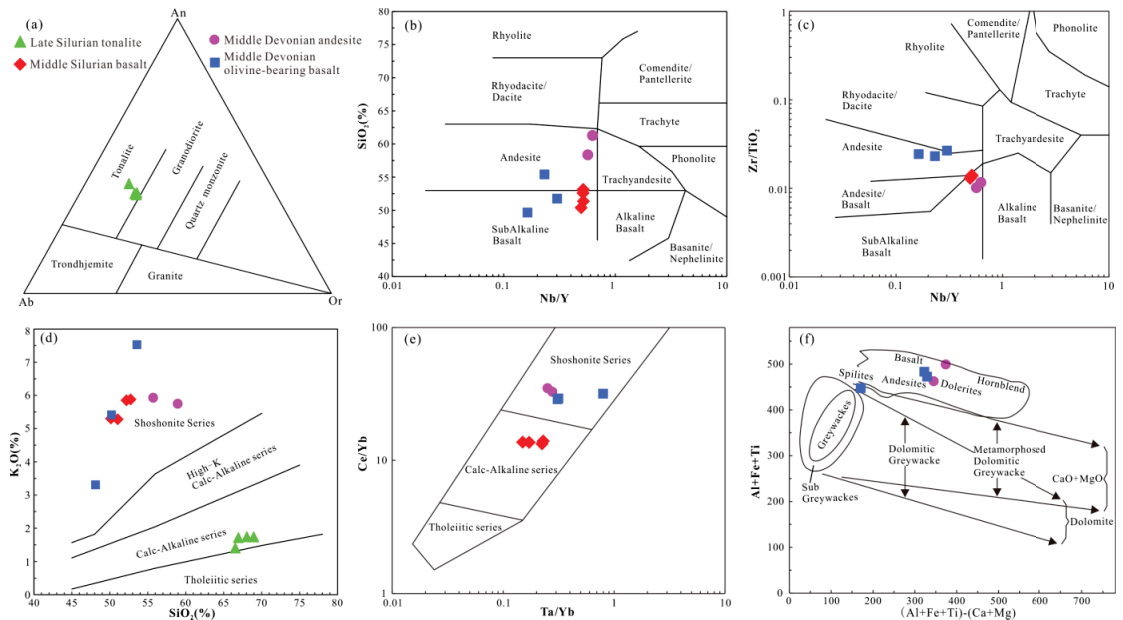
**Figure 4.** Zircon U-Pb concordia diagrams from the Middle Silurian–Middle Devonian magmatic rocks in the Yitong area. (a) Zircon U-Pb concordia diagrams from sample D11. (b) Zircon U-Pb concordia diagrams from sample DG075. (c) Zircon U-Pb concordia diagrams from sample J1917. (d) Zircon U-Pb concordia diagrams from sample PM07-12. Data-point error ellipses are 1 sigma. Age errors are 95% confidence.

#### 4.2. Whole-Rock Major and Trace Elements Analysis

The whole-rock major and trace elements analysis results are shown in Supplementary Table S2.

The  $K_2O/Na_2O$  ratios of Late Silurian tonalite (D11) samples are 0.44–0.59, indicating that they are relatively enriched in Na and depleted in K. Their  $A/CNK$  ratios range from 0.91 to 1.00, showing metaluminous signatures. In the An-Ab-Or classification diagram (Figure 5a), data for the samples are located within the field of tonalite. As revealed by the rock series discrimination diagram (Figure 5d), the samples all fall into the calc-alkaline zone. The samples have relatively higher  $\Sigma REE$  contents (167.38–180.81 ppm), exhibiting LREE enrichment ( $La_N/Yb_N = 2.40$ – $3.32$ ) with slightly negative Eu anomalies ( $Eu/Eu^* = 0.77$ – $0.84$ ) (Figure 6a). According to the parameters proposed by Irber [76] and Monecke [77],  $Ce_N/Ce^*$  and  $Pr_N/Pr^*$  of the tonalites are slightly less than 1, T1 is slightly greater than 0, and t1 is slightly less than 1 (Table S2), indicating that the first group of rare earth elements (La, Ce, Pr, and Nd) show a weak W-type tetrad effect.  $Tb_N/Tb^*$ ,  $Dy_N/Dy^*$ ,  $Tm_N/Tm^*$ , and  $Yb_N/Yb^*$  are significantly greater than 1, T3 is greater than 0, t3 and t4 are greater than 1 (Table S2), all indicating that the third group (Ga, Tb, Dy, and Ho) and the fourth group (Er, Tm, Yb, and Lu) of rare earth elements show a significant M-type tetrad

effect. The trace element spider plot illustrates that the samples are relatively enriched in Rb, Ba, Th, U, and K (LILEs), and depleted in Nb, Sr, P, and Ti (HFSEs) (Figure 6b).

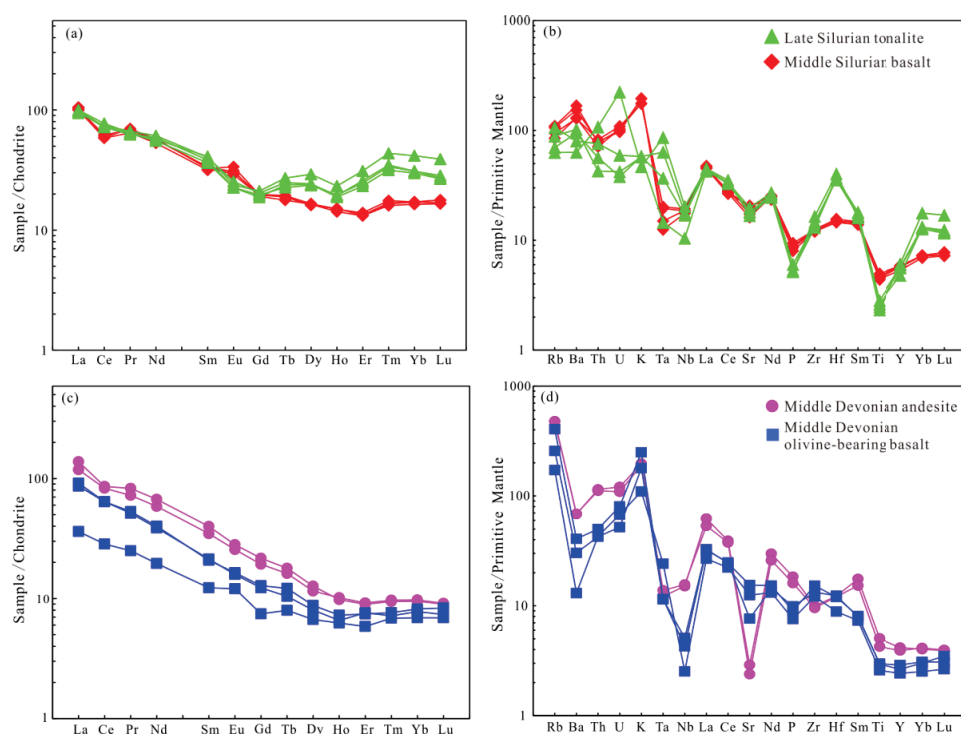


**Figure 5.** (a) An–Ab–Or [78], (b)  $\text{SiO}_2$  versus Nb/Y [79], (c)  $\text{Zr}/\text{TiO}_2$  versus Nb/Y [79], (d)  $\text{K}_2\text{O}$  versus  $\text{SiO}_2$  [80], (e)  $\text{Ce}/\text{Yb}$  versus  $\text{Ta}/\text{Yb}$  [81], and (f)  $\text{Al} + \text{Fe} + \text{Ti}$  versus  $(\text{Al} + \text{Fe} + \text{Ti}) + (\text{Ca} + \text{Mg})$  [82] diagrams for the Middle Silurian–Middle Devonian magmatic rocks in the Yitong area.

The  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratios of Middle Silurian basalt (DG075) samples are 1.24–1.57, indicating that they are relatively enriched in K and depleted in Na. Their A/CNK ratios range from 0.58 to 0.64, showing metaluminous signatures. Their Rittmann index  $\sigma$  (9.70–11.75) suggests peralkaline characteristics. The basalt samples dominantly plot in the shoshonite series field (Figure 5d). In the  $\text{SiO}_2$  vs. Nb/Y and  $\text{Zr}/\text{TiO}_2$  vs. Nb/Y diagrams (Figure 5b,c), the data for the samples are located within the field of sub-alkaline basalt. They fall within the calc-alkaline series on the  $\text{Ce}/\text{Yb}$  vs.  $\text{Ta}/\text{Yb}$  diagram (Figure 5e) due to their low Ce content. The samples have relatively higher REE contents (145.15–152.30 ppm), exhibiting LREE enrichment ( $\text{La}_N/\text{Yb}_N = 5.89\text{--}6.16$ ) with positive Eu anomalies ( $\text{Eu}/\text{Eu}^* = 1.10\text{--}1.29$ ) and negative Ce anomalies ( $\text{Ce}/\text{Ce}^* = 0.68\text{--}0.74$ ) (Figure 6a). The trace element spider plot illustrates that the samples are relatively enriched in Rb, Ba, Th, U, and K (LILEs), and depleted in Nb, Ta, Sr, P, and Ti (HFSEs) (Figure 6b).

The  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratios of Middle Devonian andesite (J1917) samples are 57.74–150.66, indicating that they are enriched in K and depleted in Na. Their A/CNK ratios range from 2.03 to 2.10, showing peraluminous signatures. The andesite samples plot in the shoshonite series field (Figure 5d,e) and in the andesite and sub-alkaline basalt regions on the  $\text{SiO}_2$  vs. Nb/Y and  $\text{Zr}/\text{TiO}_2$  vs. Nb/Y diagrams (Figure 5b,c). The samples have relatively higher REE contents (171.29–188.49 ppm), exhibiting LREE enrichment ( $\text{La}_N/\text{Yb}_N = 12.15\text{--}14.54$ ) with no Eu anomalies ( $\text{Eu}/\text{Eu}^* = 0.91\text{--}0.95$ ) and negative Ce anomalies ( $\text{Ce}/\text{Ce}^* = 0.78\text{--}0.87$ ) (Figure 6c). The trace element spider plot illustrates that the samples are relatively enriched in Rb, Th, U, and K (LILEs) and depleted in Nb, Ta, Sr, Zr, and HREEs (Figure 6d).



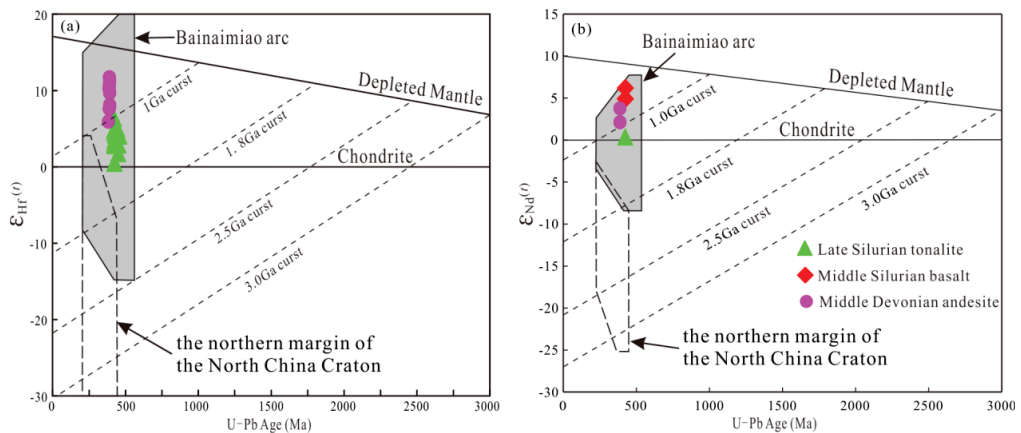


**Figure 6.** Chondrite-normalized REE patterns (a,c) (normalizing values after Boynton [83]), and primitive-mantle-normalized trace element spider diagrams (b,d) (normalizing values after Sun and Mc Donough [84]) for the Middle Silurian–Middle Devonian magmatic rocks in the Yitong area.

The  $K_2O/Na_2O$  ratios of the Middle Devonian metamorphic olivine-bearing basalt (PM07-12) samples are 13.25–24.14, indicating that they are enriched in K and depleted in Na. According to the  $(Al + Fe + Ti)$  vs.  $(Ca + Mg)$  diagram (Figure 5f), the samples predominantly classify within the regions of basalt and basaltic andesite volcanic rocks, suggesting that the protolith was an intermediate to mafic volcanic rock. Their  $A/CNK$  ratios range from 0.84 to 1.07, showing metaluminous–weakly peraluminous signatures. The andesite samples plot in the shoshonite series field (Figure 5d) and in the sub-alkaline basalt and andesite regions on the  $SiO_2$  vs.  $Nb/Y$  and  $Zr/TiO_2$  vs.  $Nb/Y$  diagrams (Figure 5b,c). The samples have relatively lower REE contents (93.52–106.89 ppm), exhibiting LREE enrichment ( $La_N/Yb_N = 9.77$ – $10.23$ ) with positive Eu anomalies ( $Eu/Eu^* = 1.12$ – $2.12$ ) and no Ce anomalies ( $Ce/Ce^* = 0.92$ – $1.02$ ) (Figure 6c). The trace element spider plot illustrates that the samples are relatively enriched in Rb and K and depleted in Ba, Th, U, Nb, Ta, Sr, P, Ti, and HREEs (Figure 6d).

#### 4.3. Zircon Lu-Hf Isotopes

Based on LA-ICP-MS zircon U-Pb dating of Late Silurian tonalite and Middle Devonian andesite in the Yitong area, this study conducted in situ zircon Hf isotope analysis of some zircons from the dated samples (Figure 7a). The analytical results are shown in Supplementary Table S3.



**Figure 7.** (a)  $\epsilon_{\text{Hf}}(t)$  versus U-Pb age for zircons [85], and (b)  $\epsilon_{\text{Nd}}(t)$  versus U-Pb age for zircons [86] of the Middle Silurian–Middle Devonian magmatic rocks in the Yitong area.

Sixteen zircons from Late Silurian tonalite sample D11 that represented the younger group gave  $\epsilon_{\text{Hf}}(t)$  values of +0.44–+6.31. They show single-stage Hf model ages ( $T_{\text{DM1}}$ ) and two-stage Hf model ages ( $T_{\text{DM2}}$ ) of 790–1027 Ma and 1005–1379 Ma, respectively. Ten zircons from Middle Devonian andesite sample J1917 gave  $\epsilon_{\text{Hf}}(t)$  values of +5.90–+11.73. They show single-stage Hf model ages ( $T_{\text{DM1}}$ ) and two-stage Hf model ages ( $T_{\text{DM2}}$ ) of 552–796 Ma and 636–1001 Ma, respectively.

#### 4.4. Whole-Rock Sr-Nd Isotopes

Measured and age-corrected initial isotopic ratios of Sr and Nd are presented in Supplementary Table S4. The Sm, Nd, Rb, and Sr contents of these rocks are given in Supplementary Table S2.

The Late Silurian tonalite sample has initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ( $I_{\text{Sr}}$ ) of 0.70646 and  $\epsilon_{\text{Nd}}(t)$  values of +0.35. In contrast, the Middle Silurian basalt samples possess lower initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ( $I_{\text{Sr}} = 0.70499\text{--}0.70508$ ) and distinctly higher positive  $\epsilon_{\text{Nd}}(t)$  values (+4.91 to +6.18) (Figure 7b and Figure 9d). The Middle Devonian andesites have positive  $\epsilon_{\text{Nd}}(t)$  values of +2.11 to +3.77, but initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ( $I_{\text{Sr}} = 0.66800\text{--}0.67546$ ) are too low to have any genetic significance. All samples exhibit positive  $\epsilon_{\text{Nd}}(t)$  values, which is consistent with the Bainaimiao arc magmatic rocks in the CAO (Figure 7b). The Middle Silurian basalts and Middle Devonian andesites have Neoproterozoic Nd model ages ( $T_{\text{DM1}} = 647\text{--}956$  Ma;  $T_{\text{DM2}} = 663\text{--}964$  Ma), whereas the Late Silurian tonalite has Mesoproterozoic Nd model age ( $T_{\text{DM1}} = 1119$  Ma;  $T_{\text{DM2}} = 1138$  Ma).

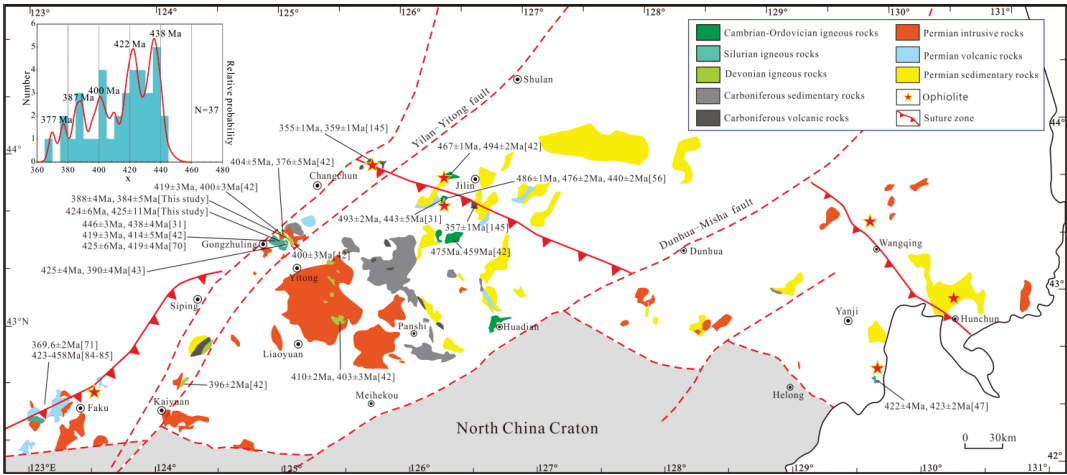
## 5. Discussions

### 5.1. Silurian to Devonian Magmatism in the Eastern Section of the Northern Margin of the NCC

Previous studies [29,32,43,44,48,68], indicate that the  $424 \pm 6$  Ma Ximangzhang pluton underwent multiple episodes of magmatism during the Late Ordovician to Early Silurian (448–438 Ma), Late Silurian (425–419 Ma), and Early Devonian (414 Ma), forming a magmatic complex. The Fangniugou volcanic rocks emerged in the Middle Silurian to the Late Devonian, which was marked by multiple volcanic episodes at 428–425 Ma, 419 Ma, 404–400 Ma, 390–384 Ma, and 375 Ma.

In recent years, Cambrian–Devonian geological bodies have been reported successively from the eastern section of the northern margin of the NCC in Faku-Kaiyuan, Liaoning Province, and Gongzhuling-Liaoyuan-Zhangjiatun-Yanbian, Jilin Province (Figure 8) [29,43, 44,48,56,64,68–70]. The Early Paleozoic magmatism in this region extended from the Late Cambrian to the Late Silurian, with peaks observed at 494 Ma, 486 Ma, 475 Ma, 467 Ma,

459 Ma, 438 Ma, and 422 Ma. These peaks resemble those of the Early Paleozoic Bainaimiao arc belt magmatic rocks [32], suggesting that the subduction-accretionary complex belt in the Faku-Yanji area is an extension of the Bainaimiao arc belt in the east. Combined with previous data, the Silurian magmatism in the northern margin of the NCC ranges from 443 to 419 Ma, and the Devonian magmatism ranges from 414 to 375 Ma (Table 2). The Silurian (443~419Ma) magmatism is frequent and distributed along the north margin of the NCC in an east–west direction, mainly exposed in the Faku, Gongzhuling, Yitong, Zhangjiatun, and Yanbian areas. The lithology is mainly intermediate-acid magmatic rocks, including andesite, quartz diorite, tonalite, granodiorite, rhyodacite, granite, rhyolite, etc. [29,32,43,44,48,56,57,87,88]. Mafic rocks are rarely exposed, only found in the Yitong area, as shoshonitic basalt. The Devonian (414–375 Ma) magmatism is weaker, exposed in Faku, Changtu, Gongzhuling, and Liaoyuan, with lithology mainly including granodiorite, rhyolite, rhyolitic tuff, dacite, monzogranite, etc., as well as a small amount of basalt and basaltic andesite [29,43,68–71,89].



**Figure 8.** Distribution of Paleozoic magmatic rocks and strata from the Faku–Yanji area in the eastern segment of the northern margin of the NCC [17,29,31,42,43,47,56,70,71,84,85,89–91].

**Table 2.** Geochronological data for the Silurian–Devonian magmatic rocks in the eastern segment of the northern margin of the NCC.

| Rocks                  | Sampling Location       | Method    | Ages (Ma) | References |
|------------------------|-------------------------|-----------|-----------|------------|
| Tonalite               | E126°17′41″, N43°41′21″ | LA-ICP-MS | 443 ± 5   | [56]       |
| Tonalite               | Zhangjiatun             | LA-ICP-MS | 440 ± 2   | [57]       |
| Quartz diorite         | E124°56′15″, N43°27′38″ | LA-ICP-MS | 438 ± 4   | [32]       |
| Granodiorite           | E123°14′51″, N42°32′59″ | LA-ICP-MS | 438 ± 4   | [32]       |
| Tonalite               | E123°14′27″, N42°32′41″ | SHRIMP    | 437 ± 3   | [87]       |
| Granite                | E123°13′59″, N42°33′56″ | LA-ICP-MS | 436 ± 2   | [32]       |
| Granodiorite           | E123°14′17″, N42°32′25″ | LA-ICP-MS | 436 ± 3   | [32]       |
| Granodiorite           | E123°13′18″, N42°33′28″ | LA-ICP-MS | 434 ± 3   | [32]       |
| Granodiorite           | E123°13′55″, N42°32′20″ | SHRIMP    | 433 ± 3   | [88]       |
| Granodiorite (adakite) | E123°02′47″, N42°31′20″ | SHRIMP    | 432 ± 3   | [87]       |
| Andesite               | E125°01′51″, N43°28′00″ | LA-ICP-MS | 426 ± 4.8 | [29]       |
| Dacite                 | E125°08′51″, N43°28′04″ | LA-ICP-MS | 425 ± 4   | [44]       |
| Tonalitic mylonite     | E124°58′29″, N43°29′40″ | LA-ICP-MS | 425 ± 6   | [29]       |
| Basalt                 | E125°01′31″, N43°29′37″ | LA-ICP-MS | 428 ± 6.6 | This study |
| Tonalite               | E124°56′07″, N43°27′42″ | LA-ICP-MS | 424 ± 6   | This study |

Table 2. Cont.

| Rocks                  | Sampling Location       | Method    | Ages (Ma) | References                |
|------------------------|-------------------------|-----------|-----------|---------------------------|
| Felsic mylonite        | E123°10′50″, N42°35′05″ | SHRIMP    | 423 ± 5   | [88]                      |
| Tonalite               | E129°41′11″, N42°33′28″ | LA-ICP-MS | 423 ± 2   | [48]                      |
| Tonalite               | E129°40′37″, N42°33′12″ | LA-ICP-MS | 422 ± 4   | [48]                      |
| Rhyolite               | E125°02′37″, N43°29′38″ | LA-ICP-MS | 419 ± 3   | [43]                      |
| Granodiorite           | E124°56′03″, N43°27′44″ | LA-ICP-MS | 419 ± 3   | [43]                      |
| Tonalite               | E124°56′15″, N43°28′04″ | LA-ICP-MS | 419.5 ± 4 | [29]                      |
| Granodiorite           | E124°58′32″, N43°29′40″ | LA-ICP-MS | 414 ± 5   | [43]                      |
| Rhyolitic tuff         | E125°26′44″, N43°01′59″ | LA-ICP-MS | 410 ± 2   | [43]                      |
| Rhyolitic tuff         | E125°27′50″, N43°02′15″ | LA-ICP-MS | 403 ± 3   | [43]                      |
| Basalt                 | Faku                    | LA-ICP-MS | 405 ± 5   | Shi et al.<br>(unpublish) |
| Rhyolitic tuff         |                         |           |           |                           |
| rhyolitic crystal tuff | E125°00′51″, N43°31′52″ | LA-ICP-MS | 404 ± 4.5 | [29]                      |
| rhyolitic crystal tuff |                         |           |           |                           |
| Dacite                 | E125°01′40″, N43°53′11″ | SHRIMP    | 402 ± 4   | [68]                      |
| Monzogranite           | E124°57′29″, N43°31′04″ | LA-ICP-MS | 400 ± 2   | [43]                      |
| Monzogranite           | E124°54′22″, N42°07′15″ | LA-ICP-MS | 396 ± 2   | [43]                      |
| Rhyolite               | E124°59′39″, N43°28′27″ | LA-ICP-MS | 390 ± 4   | [44]                      |
| Biotite monzogranite   | E124°16′44″, N42°48′08″ | LA-ICP-MS | 389 ± 2   | [70]                      |
| Rhyolite crystal tuff  | E124°27′13″, N42°54′15″ | LA-ICP-MS | 385 ± 2   | [70]                      |
| Andesite               | E125°03′24″, N43°30′29″ | LA-ICP-MS | 388 ± 4   | This study                |
| Metamorphic            |                         |           |           |                           |
| olivine-bearing basalt | E125°04′12″, N43°30′28″ | LA-ICP-MS | 384 ± 5   | This study                |
| Monzogranite           | E124°15′47″, N42°49′01″ | LA-ICP-MS | 377 ± 2   | [70]                      |
| Rhyolite               | E125°01′20″, N43°32′00″ | LA-ICP-MS | 375.5 ± 5 | [29]                      |
| High-Mg andesite       | E123°33′19″, N43°39′13″ | LA-ICP-MS | 369.6 ± 2 | [89]                      |

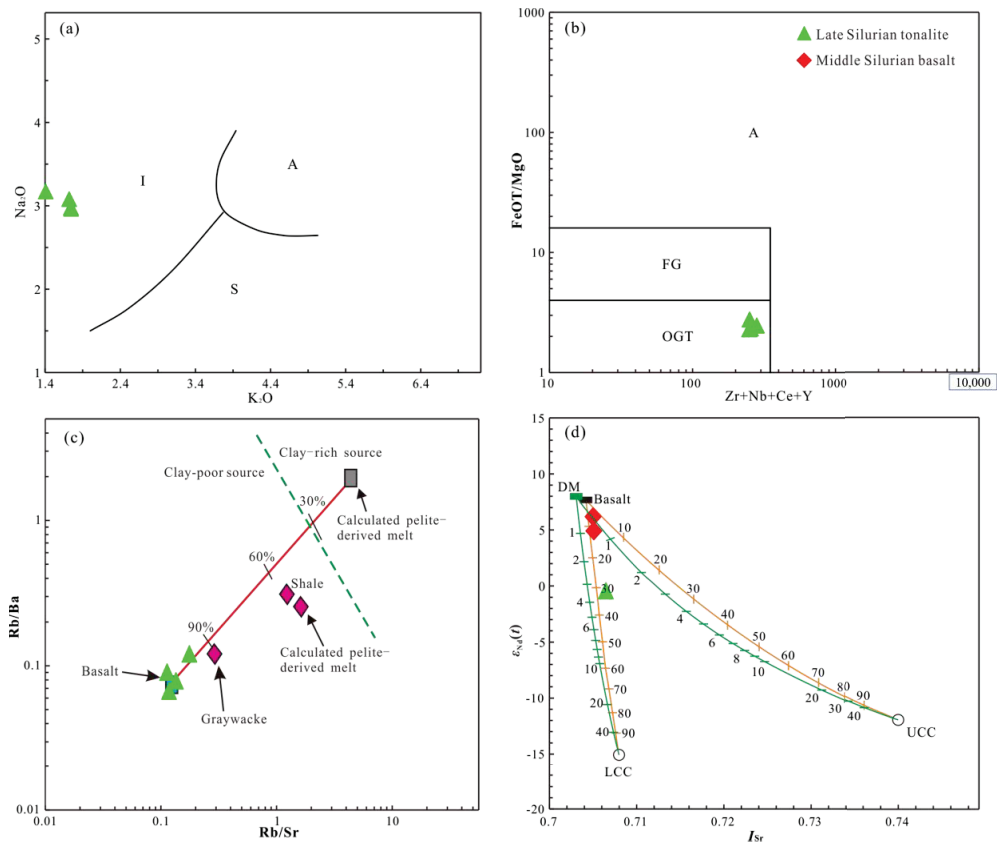
5.2. Petrogenesis and Source Characteristics

5.2.1. Middle–Late Silurian Magmatic Rocks

The Middle–Late Silurian magmatic rocks display relatively weak metamorphism and deformation, with a low loss on ignition (LOI = 0.50–0.75), indicating minimal alteration effects. These geochemical characteristics make them well-suited for investigating their petrogenesis and source features.

The Late Silurian tonalites have high contents of SiO<sub>2</sub> and Na<sub>2</sub>O, and low contents of K<sub>2</sub>O, MgO, FeOT, and TiO<sub>2</sub>, with an A/CNK ratio of 0.91–1.00, indicative of I-type granites. In the Na<sub>2</sub>O vs. K<sub>2</sub>O diagram (Figure 9a), the tonalite samples fall within the zone of the I-type granite. Additionally, in the petrogenetic discrimination diagrams (Figure 9b), all tonalite samples fall within the zone of unfractionated granitoids. These characteristics are consistent with those of metaluminous calc-alkaline I-type granitoids. They exhibit enrichment in Rb, Ba, Th, U, and K (LILEs) and depletion in Nb, Sr, P, and Ti (HFSEs), displaying magmatic arc features [19,92,93]. The explanations for the tetrad effect of rocks include mineral crystallization [94,95], late-stage magma-fluid interactions [76,96,97], or inheritance from the parental magma [76,97]. According to published papers [29,43], the Ximangzhang tonalites do not exhibit tetrad effects, indicating that this characteristic is not a feature of its primary magma. The low Zr/Hf (12.81–14.99) and Y/Ho (15.41–18.83) ratios in tonalites cannot be explained by mineral crystallization [98,99]. Crust-derived magmas that have undergone significant magma-hydrothermal exchange typically exhibit lower Zr/Hf ratios (<20) [76]. The Nb/Ta ratio (4.11–12.49, average 7.38) in tonalite is similar to the differentiated continental crust (11) [100]. Therefore, the REE anomalies may be caused by magma-fluid interactions. Increasing La concentrations correspond with a rise in the La/Sm ratio, indicative of partial melting processes during their formation. The absence of pronounced Sr and Eu anomalies further supports the partial melting of plagioclase in the source material. The tonalites have low Cr (24.70–30.82 ppm) and Ni (5.34–6.56 ppm) content and Mg# (39.26–43.79) values, indicating a crustal source. Their

La/Sm ratios between 3.72 and 4.34 (average 3.98) suggest a moderate degree of crustal contamination, given that ratios above 4.5 typically indicate strong contamination, while those below 2 suggest primary compositions [101]. Additionally, the tonalites display high Ba/Th (48.35–196.86, average 117.57) and Ba/La (14.27–24.49, average 19.79) ratios, but low Th content (3.63–9.13 ppm) and Th/Yb ratios (0.56–1.05), implying that slab-derived fluids primarily influenced the source of these Late Silurian magmatic rocks [102], with lesser contributions from sediments or melts. The Rb/Ba vs. Rb/Sr diagram (Figure 9c) shows that the source material for the tonalite is predominantly basalt. The  $\epsilon_{Nd}(t)$  vs.  $I_{Sr}$  diagram (Figure 9d) indicates that the magmas are composed of approximately 70–75% basalt and 25–30% lower continental crust. The  $\epsilon_{Nd}(t)$  value of tonalite is +0.35, with a two-stage model age of 1138 Ma, and zircon  $\epsilon_{Hf}(t)$  values ranging from +0.44 to +6.31, with a two-stage model age ranging from 1005.0 to 1379.5 Ma. These characteristics indicate that the tonalite predominantly originated from partial melting of Mesoproterozoic accreted lower crustal material (basalt), and magma ascent was accompanied by contamination with lower crustal material.



**Figure 9.** (a) Na<sub>2</sub>O versus K<sub>2</sub>O diagram [103], (b) FeOT/MgO versus (Zr + Nb + Ce + Y) diagram [104], (c) Rb/Ba versus Rb/Sr diagram (The red solid line represents the mixing curve between basalt- and pelite-derived melts; The green dashed line divides strongly peraluminous granites derived mostly from clay-poor sources from those formed mostly from clay-rich source rocks.) [105], and (d)  $\epsilon_{Nd}(t)$  versus  $I_{Sr}$  diagram [105] for the Middle Silurian–Middle Devonian magmatic rocks in the Yitong area. FG: fractionated granitoid; OGT: unfractionated granitoid; I: I-type granitoid; S: S-type granitoid; A: A-type granitoid; DM: depleted mantle; LCC: lower continental crust; UCC: upper continental crust.



The Middle Silurian basalts have low contents of  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{TiO}_2$ , and  $\text{Na}_2\text{O}$  and high contents of  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{CaO}$ , and  $\text{K}_2\text{O}$ , with a  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio of 1.24–1.57. Notably, these basalts contain primarily K-feldspar phenocrysts, with  $\sigma$  values ranging from 9.70 to 11.75, and CIPW norm calculations indicating the presence of nepheline ( $\text{Ne} = 7.41\text{--}10.69$ ), but alkaline minerals are absent in thin section observations. Positioned within the subalkaline basalt region in the  $\text{SiO}_2$  vs.  $\text{Nb}/\text{Y}$  and  $\text{Zr}/\text{TiO}_2$  vs.  $\text{Nb}/\text{Y}$  diagrams (Figure 5b,c), these samples are identified as shoshonitic rocks rather than typical alkaline rocks. The ratios of incompatible elements, largely unchanged by fractional crystallization, remain constant during the partial melting of the mantle, thereby serving as indicators of magma source characteristics [106]. Geochemical analysis reveals an average  $\text{Lu}/\text{Yb}$  ratio of 0.15–0.16, closely aligned with the typical mantle-derived magmatic value of 0.14–0.15 [107], and an average  $\text{Nb}/\text{Ta}$  ratio of 19.80, approaching the mantle standard of 17.5 [84,106], affirming their mantle-derived magmatic nature. Positive  $\varepsilon_{\text{Nd}}(t)$  values ranging from +4.91 to +6.18 further affirm a mantle origin. Additionally, high ratios of  $\text{La}/\text{Ta}$  ( $37.94\text{--}60.22 > 22$ ) and  $\text{La}/\text{Nb}$  ( $2.27\text{--}2.47 > 1.7$ ), alongside low  $\text{Zr}/\text{Ba}$  (0.12–0.16) and  $\text{La}/\text{Ba}$  (0.03–0.04) ratios, point to a genesis within the lithospheric mantle, modified by subduction processes [108–112]. These basalts also exhibit high  $\text{Ba}/\text{Th}$  (128.08–177.84) and  $\text{Ba}/\text{La}$  (27.88–36.84) ratios and lower  $\text{La}/\text{Sm}$  (4.78–5.03) and  $\text{Th}/\text{Yb}$  (1.69–1.97) ratios, indicative of a mantle-derived magmatic source predominantly influenced by slab dehydration [102]. They are enriched in Rb, Ba, Th, U, K, and LREE, yet depleted in Nb, Ta, Sr, P, and Ti, characteristic of island arc magmatic rocks [19], suggesting an origin from the lithospheric mantle that has been metasomatized by subduction fluids [113]. Furthermore, relatively low Cr (67.60–70.51 ppm), Ni (38.95–40.13 ppm), and Co (17.96–19.97 ppm) contents and  $\text{Mg\#}$  (32.15–34.95) values suggest a significant evolutionary process during its formation [114], such as fractional crystallization of olivine or pyroxene, or crustal contamination. Their average  $\text{Rb}/\text{Sr}$  ratio of 0.16 distinctly reflects a mixed mantle-crust source, consistent with the typical mantle-crust mixed source magmatic  $\text{Rb}/\text{Sr}$  ratio range of 0.05–0.50 [106]. Island arc volcanic rocks often exhibit a characteristic negative anomaly in Ce concentrations [115]. The samples have negative Ce anomaly (0.68–0.74) and low  $\text{Ce}/\text{Th}$  ratios (6.97–7.89), further suggesting the incorporation of subducted sediment melts into the source. The  $\varepsilon_{\text{Nd}}(t)$  vs.  $I_{\text{sr}}$  diagram (Figure 9d) indicates that the magma mainly originated from a depleted mantle with some crustal material addition. The Nd isotope single-stage model age ( $T_{\text{DM1}}$ ) ranges from 647 to 758 Ma, which represents the mixed age of juvenile crust and older crust, suggesting the presence of a Proterozoic crystalline basement in the study area. Collectively, these features indicate that the Middle Silurian basalts primarily originated from depleted mantle magmas metasomatized by subduction fluids, supplemented by a small amount of subducted sediments and crustal materials.

### 5.2.2. Middle Devonian Volcanic Rocks

The Middle Devonian volcanic rocks have undergone weak metamorphism and deformation with a slightly higher loss on ignition ( $\text{LOI} = 2.94\text{--}4.78$ ). Therefore, to discern the rock origins and source characteristics, less mobile lithogenic elements along with rare earth elements and high field strength elements, which are less affected by metamorphism and alteration, are primarily utilized [116].

The Middle Devonian volcanic rocks have low  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{Na}_2\text{O}$  content and high  $\text{K}_2\text{O}$  content, and a high  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio with a wide range of variation in  $\text{Al}_2\text{O}_3$  content (ranging from 13.65 to 17.50 wt%). In the  $\text{SiO}_2$  vs.  $\text{Nb}/\text{Y}$  and  $\text{Zr}/\text{TiO}_2$  vs.  $\text{Nb}/\text{Y}$  diagrams (Figure 5b,c), these volcanic rocks primarily fall into the subalkaline basalt and andesite zones, indicating that the K-rich and Na-poor characteristics of the samples are a result of alteration. The samples are enriched in LILEs such as Rb, K, and LREEs and are depleted in Nb, Ta, Sr, and HREEs, showing geochemical characteristics similar to those of arc volcanics [117–121].

The  $\text{Zr}/\text{Hf}$  ratio of these volcanic rocks (28.74–49.78, average 38.59) is close to that of mantle-derived magmas (39) [122]; their average  $\text{Lu}/\text{Yb}$  ratio (0.14–0.17) is also close to

the average mantle-derived magma value (0.14–0.15) [107], affirming their mantle-derived magmatic nature. The volcanic rocks have positive  $\varepsilon_{\text{Nd}}(t)$  values (+2.11 to +3.77), also indicating mantle-derived magma. Additionally, high ratios of La/Ta (18.57–85.64, average 52.79 > 22) and La/Nb (3.29–10.22 > 1.7), alongside low Zr/Ba (0.22–1.50) and La/Ba (0.08–0.20) ratios, point to a genesis within the lithospheric mantle, modified by subduction processes [108–112].

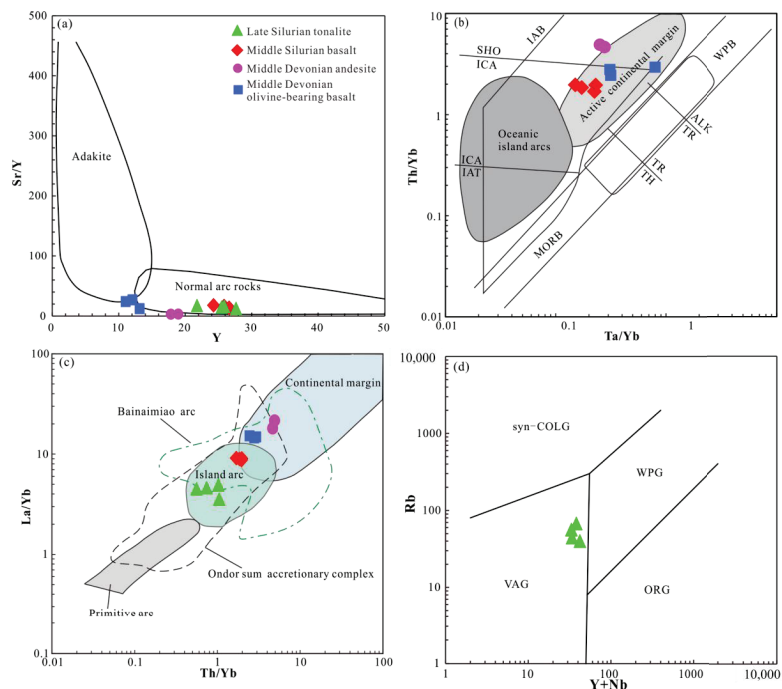
It is generally believed that the fluids or melts formed during the subduction of oceanic crust and sediments metasomatize the overlying mantle wedge, resulting in partial melting and the formation of island arc magma [123,124]. The addition of subduction zone fluids significantly lowers the Ce/Pb and Nb/U ratios of magmas originating from depleted mantle [125]. The Middle Devonian volcanic rocks have Nb/U (1.27–4.86) and Ce/Pb (0.66–10.30) ratios lower than those of typical depleted mantle (Nb/U =  $47 \pm 10$ , Ce/Pb =  $25 \pm 5$ ) [126], suggesting the addition of subduction zone fluids to the magma source. Sample J1917 has low Ce/Th ratios (7.07–7.13) and a Ce negative anomaly (0.78–0.87), suggesting the addition of subducted sediment melts to the source. Sample PM07 has higher Ce/Th ratios (10.36–11.98) and no Ce anomaly (0.92–1.02), suggesting no addition of reduced sediment melts in the source. The volcanic rocks have low Cr (2.35–10.09 ppm) and Ni (2.74–3.96 ppm) content and Mg# values (21.24–47.39), suggesting they may have undergone fractional crystallization of olivine and pyroxene, or crustal contamination [114]. Typically, the addition of crustal material leads to an increased abundance of LILEs (Rb, Ba, Th, etc.) and decreased content of HFSEs (Nb, Ta, Ti, etc.). Important indicators of crustal contamination include  $(\text{Th}/\text{Nb})_{\text{PM}} \gg 1$  [127],  $\text{La}/\text{Nb} > 1$  [128], and  $\text{La}/\text{Sm}$  values (>4.5) [101]. The Middle Devonian volcanic rocks exhibit  $(\text{Th}/\text{Nb})_{\text{PM}} = 7.12$ –17.02,  $\text{La}/\text{Nb} = 3.29$ –10.22, and  $\text{La}/\text{Sm} = 5.42$ –6.29, suggesting a limited degree of crustal contamination.

In the  $\varepsilon_{\text{Hf}}(t)$  vs.  $t$  and  $\varepsilon_{\text{Nd}}(t)$  vs.  $t$  diagrams (Figure 7a,b), the Middle Devonian volcanic rock samples fall within the  $\varepsilon_{\text{Hf}}(t)$  and  $\varepsilon_{\text{Nd}}(t)$  ranges of the Bainaimiao arc. The volcanic rocks have  $\varepsilon_{\text{Nd}}(t)$  values of +2.11 to +3.77 and zircon  $\varepsilon_{\text{Hf}}(t)$  values of +5.90 to +11.73, falling between the chondritic and depleted mantle evolution lines (Figure 7a,b), suggesting that their source mainly originated from depleted mantle; the decoupling of  $\varepsilon_{\text{Nd}}(t)$  and  $\varepsilon_{\text{Hf}}(t)$  indicates crustal contamination. The Nd isotope  $T_{\text{DM2}}$  ranges from 823 to 956 Ma, and the Hf isotope  $T_{\text{DM2}}$  ranges from 636.0 to 1001.4 Ma, representing the mixing ages of juvenile crust and Proterozoic crust, indicating the presence of a Proterozoic crystalline basement in the study area. These characteristics indicate that the Middle Devonian volcanic rocks primarily originated from depleted mantle magmas metasomatized by subduction fluids, with the addition of crustal materials or subducted sediments during their formation.

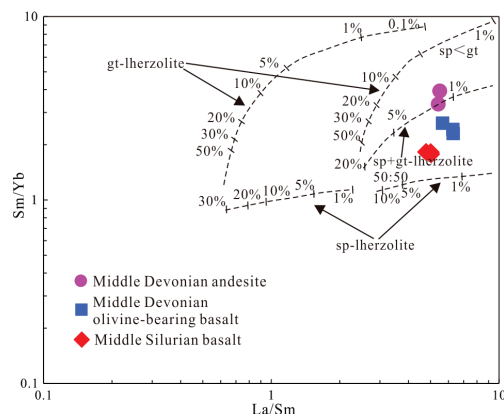
### 5.3. Tectonic Setting

In the study area, the Middle–Late Silurian magmatic rocks are mainly composed of basalt, andesite, tonalite, granodiorite, dacite, and rhyolite, which is similar to a typical island arc magmatic rocks assemblage. These rocks are enriched in Rb, Ba, Th, U, and K, while being depleted in Nb, Ta, Sr, P, and Ti, a signature suggesting formation in a subduction zone environment [92,129]. In the Sr/Y vs. Y and La/Yb vs. Th/Yb diagrams (Figure 10a,c), the tonalite and basalt samples fall within the zone of a typical island arc. Additionally, in the Rb vs. (Y + Nb) diagram (Figure 10d), the tonalite samples fall within the zone of a volcanic-arc granite. In the Th/Yb vs. Ta/Yb diagram (Figure 10d), the basalt samples fall within the active continental margin field. These Middle–Late Silurian magmatic rocks (428–419 Ma) share isotopic and geochemical traits with the earlier Late Ordovician to Early Silurian tonalite and quartz diorite (446 Ma, 438 Ma) [29,32]. Notably, the tonalite, characterized by low Sr and high Yb, formed at a depth similar to standard crustal thickness of about 30–40 km [130], suggesting that no arc-continent collision occurred during this period. Therefore, this study suggests that the Middle–Late Silurian magmatic rocks formed in an active continental margin environment.

The Middle Devonian volcanic rocks are marked by low  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Sr}$ , and  $\text{Y}$  but are rich in  $\text{K}_2\text{O}$ . In the  $\text{Sr}/\text{Y}$  vs.  $\text{Y}$  diagram (Figure 10a), these samples fall within the zone of the typical island arc. In the  $\text{Th}/\text{Yb}$  vs.  $\text{Ta}/\text{Yb}$  diagram (Figure 10d), the samples fall within the active continental margin field, exhibiting characteristics of the calc-alkaline to shoshonitic series. The  $\text{La}/\text{Yb}$  vs.  $\text{Th}/\text{Yb}$  diagram (Figure 10c) further underscores their affinity with a mature continental arc. Furthermore, the Early Devonian rhyolitic tuff ( $404 \pm 4.5$  Ma) in the study area, showing the features of typical A2-type granite, formed in a post-collisional extension setting [29]. In the  $\text{La}/\text{Sm}$  vs.  $\text{Sm}/\text{Yb}$  diagram (Figure 11), the Middle Silurian and Middle Devonian volcanic rock samples can be derived from spinel-garnet lherzolite (Figure 11), with degrees of partial melting ranging from 1 to 5%, and magma source depths estimated between 60 and 80 km [131]. The Middle Silurian volcanic rocks can be derived from spinel lherzolite, whereas the Middle Devonian rocks are more likely derived from spinel-garnet lherzolite (spinel:garnet = 1:1), suggesting an increase in crustal thickness during the Middle Devonian. The collision of the Late Silurian Bainaimiao arc with the NCC led to the subsequent formation of a series of alkaline series magmatic rocks [31,86,132–138]. Combined with the Middle Devonian magmatic rocks in the northern Liaoning Province to central Jiling Province having characteristics of I- and A-type granites [43], this suggests that the study area was an extensional environment after the arc-continent collision during the Middle Devonian period.



**Figure 10.** Tectonic environment discriminant diagrams for the Middle Silurian–Middle Devonian magmatic rocks in the Yitong area. (a)  $\text{Sr}/\text{Y}$  versus  $\text{Y}$  diagram [139]; (b)  $\text{Th}/\text{Yb}$  versus  $\text{Ta}/\text{Yb}$  diagram [81]; (c)  $\text{La}/\text{Yb}$  versus  $\text{Th}/\text{Yb}$  diagram [140]; (d)  $\text{Rb}$  versus  $(\text{Y} + \text{Nb})$  diagram [141]. MORB: mid-ocean ridge basalts; N-MORB: normal MORB; E-MORB: enriched MORB; WPB: within-plate basalt; OIB: ocean island basalts; OIT: ocean island tholeiitic; OIA: ocean island alkaline; SHO: shoshonite; CAB: calc-alkaline basalts; ICA: island-arc calc-alkaline basalts; IAT: island-arc tholeiitic; IAB: island-arc alkaline basalts; VAG: volcanic-arc granite; Syn-COLG: syn-collision granite; WPG: within plate granite; ORG: ocean-ridge granite.



**Figure 11.** La/Sm-Sm/Yb diagram [141,142] for the Middle Silurian and Middle Devonian magmatic rocks in the Yitong area.

#### 5.4. Silurian–Devonian Tectonic–Magmatic Evolution in the Eastern Section of the Northern Margin of the NCC

Based on previous studies and the division of tectonic evolution, the magmatic and tectonic progression of the eastern section of the northern margin of the NCC from the Silurian to Devonian can be delineated into four primary stages:

##### 5.4.1. Active Continental Margin (443–419 Ma)

Early Paleozoic magmatism along the eastern segment of the northern margin of the NCC commenced in the Late Cambrian and persisted through the Late Silurian. The rock assemblages and peak ages of this Early Paleozoic magmatism align closely with those observed in the central-western segment of the northern margin of the NCC, indicating that the eastern magmatism is a continuation of the Bainaimiao arc [29,32]. Between the Late Cambrian and Middle Ordovician (493–458 Ma), the magmatic rocks are mainly composed of peridotite, pyroxenite, gabbro, high-Mg andesite, pyroxene andesite, quartz diorites, etc., representing the initial stages of subduction [43] within an intra-oceanic arc environment [57], and can be compared with the Ondor Sum subduction-accretionary complex. These early magmatic rocks are primarily located around areas such as Xiaosuhe, Zhangjiatun, Toudaogou, and Huadian, positioned northeastern of the study area, closer to the Changchun Yanji suture zone. Subsequent magmatism (446–419 Ma) is mainly composed of adakitic diorite, andesite, quartz diorites, granodiorites, tonalites, rhyolitic dacites, granites, and rhyolites. These rocks are similar to active continental margin rock assemblages and belong to the calc-alkaline to high-K calc-alkaline series, displaying mature island arc rock characteristics [43]. Silurian magmatic rocks are enriched in LREEs and LILEs, yet are depleted in HFSEs such as Nb, Ta, and Ti, mirroring the geochemistry of arc volcanic rocks. Discrimination diagrams suggest that these Silurian magmatic rocks were produced within an active continental margin setting. Due to subsequent strong modification, rocks from the Late Cambrian and Middle Ordovician are limited and scattered in exposure. Therefore, the position of the immature arc of the Late Cambrian and Middle Ordovician is not very clear. In general, the immature arc of the Late Cambrian and Middle Ordovician is located on the northeast side of the volcanic arc with an age of 446–419 Ma. They can be compared with the Bainaimiao Arc and Ondor Sum subduction-accretionary complex.

South of the Changchun–Yanji Suture zone, the study area records a continuous evolution process from the Late Ordovician to the Permian period. From southwest to northeast, Late Ordovician to Late Silurian intrusive rocks, Silurian to Devonian volcanic and clastic rocks, Late Carboniferous to Early Permian carbonate and clastic rocks, and

Permian metamorphic volcanic rocks are exposed sequentially. Based on rock assemblages, protolith formation, and geochemical characteristics, they can be divided into a Late Ordovician to Late Devonian arc-basin system and a Late Carboniferous to Late Permian arc-basin system. The Paleozoic geological bodies in the area are generally distributed in a northwest direction, and geological bodies of different ages are mostly in tectonic contact, reflecting the process of transpression during the southward subduction of the PAO. In summary, we suggest that the Silurian magmatic rocks in the area formed in an active continental margin environment during the southward subduction of the PAO.

#### 5.4.2. Arc-Continent Collision (419–405 Ma)

The northern margin of the NCC and the Bainaimiao arc show different evolutionary histories and basement properties during the Early Paleozoic era [86]. Currently, many workers believe that the NCC and the Bainaimiao arc underwent an arc-continent collision at the end of the Early Paleozoic and the beginning of the Late Paleozoic [32,42–48]. The Xibiehe Formation and Zhangjiatun Formation, exposed in central Inner Mongolia to central Jilin Province, are considered to be post-collision molasse, unconformably overlying Early Paleozoic units [143]. The Xibiehe Formation in the Jiefangyingzi area of Chifeng City was deposited in the Early Devonian (with tuff interlayer ages of  $405 \pm 2$  Ma); the Zhangjiatun Formation in central Jilin Province was deposited after  $404 \pm 14$  Ma and  $409 \pm 8$  Ma [43]. Detrital zircon geochronology from the Xibiehe Formation indicates that the arc-continent collision occurred during the Late Silurian to the Early Devonian [86]. Moreover, along the Chifeng-Kaiyuan fault, syn-collisional magmatic rocks have been dated to between 419 and 411 Ma [13,15,144,145]. Therefore, the arc-continent collision should have occurred in the Early Devonian (419–405 Ma).

#### 5.4.3. Post-Collisional Extension (404–375 Ma)

During the Devonian period, the northern margin of the NCC and the central to the western section of the Bainaimiao arc show the development of an alkaline magmatic belt from 400 to 380 Ma [31], comprising mafic-ultramafic rocks, alkaline rocks, A-type granites, and bimodal volcanic rocks [31,62,133,135,137,146,147]. These features suggest that this region was in an extensional tectonic environment during the Devonian period. Devonian magmatism in the eastern section of the northern margin of the NCC (414–375 Ma) is mainly composed of basalt, basaltic andesite, andesite, granodiorite, monzonite, dacite, rhyolite, and rhyolite tuff, with notable magmatic peaks at 411 Ma, 400 Ma, 387 Ma, and 377 Ma (Figure 8). Age peaks correspond closely to those in the northern margin of NCC and the Bainaimiao arc (400 Ma, 392 Ma, 379 Ma) [31], suggesting a similar evolutionary history from the eastern to western sections of the northern margin of the NCC during the Devonian period.

In the study area, the Early Devonian rhyolitic tuff (404 Ma) shows A2-type granite geochemical characteristics and was formed in a post-collisional extensional tectonic setting [29]. The Early Devonian monzogranite (400 Ma) and Middle Devonian rhyolite (390 Ma) display adakitic geochemical characteristics, reflecting the thickening of the crust after collision [43,44]. In the Chifeng area, the Middle Devonian syenogranite (392 Ma), granite (385 Ma), and granitic porphyry (377 Ma) [132,148] are classified as A2-type granites, formed in a post-collisional or post-orogenic environment, indicating that the Middle Devonian setting was post-collisional. The intermediate and mafic volcanic rocks from the Middle Devonian (388–384 Ma) in the study area are rich in alkali elements and belong to the shoshonitic series, formed in an extensional setting. In summary, the northern margin of the NCC appears to have been in a post-collisional extensional environment during the Early to Middle Devonian (404–375 Ma).

#### 5.4.4. Active Continental Margin (375–360 Ma)

Previous research suggests that extension during this period may have continued until the end of the Devonian period [70,147–149] or the Early Carboniferous period [150].



Studies on ophiolites and volcanic rocks indicate that southward subduction of the PAO commenced in the Late Devonian to Early Carboniferous. The discovery of Late Devonian calc-alkaline I-type rhyolite in the Yitong area ( $375.5 \pm 4.6$  Ma) [29] and high-K calc-alkaline I-type granite in the Changtu area ( $377 \pm 2$  Ma) [70] suggests that the PAO plate began to subduct southward during the Late Devonian. Late Devonian high-Mg andesite (370 Ma) in the Faku area, formed in a back-arc rift environment, supports that the PAO underwent southward subduction at this time, leading to the initiation of continental rifting in the Faku area and the development of a post-arc basin [71]. Song et al. [151] based on ophiolites exposed in the CAO, proposed the existence of two major oceanic expansion/subduction cycles between 500–410 Ma and 360–220 Ma. Xie et al. [152] suggested that the Heishan mafic-ultramafic intrusive rock ( $357 \pm 4$  Ma) along the northern margin of the Tarim Craton formed in an active continental margin setting. In summary, this paper posits that the PAO began southward subduction during the Late Devonian (377–360 Ma), leading to the formation of a post-arc basin.

## 6. Conclusions

(1) Zircon U-Pb dating results show that the Ximangzhang tonalite formed in the Late Silurian ( $425 \pm 6$  Ma), while basalt, andesite, and metamorphic olivine-bearing basalt in the Fangniugou volcanic rocks formed in the Middle Silurian ( $428 \pm 6.6$  Ma) and Middle Devonian ( $388.4 \pm 3.9$  Ma, and  $384.1 \pm 4.9$  Ma, respectively).

(2) The Late Silurian tonalites are characterized by high  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  and low  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{FeOT}$ , and  $\text{TiO}_2$ , with an A/CNK ratio of 0.91–1.00, and thus belong to the calc-alkaline series, identified as I-type granite. They are enriched in Rb, Ba, Th, U, and K and depleted in Nb, Sr, P, and Ti, with positive  $\varepsilon_{\text{Nd}}(t)$  (+0.35) and  $\varepsilon_{\text{Hf}}(t)$  (+0.44 to +6.31) values, suggesting that they mainly originated from partial melting of Meso–Neoproterozoic era accretionary lower crustal material (basalt). The Middle Silurian basalts are characterized by low  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{TiO}_2$ , and  $\text{Na}_2\text{O}$  and high  $\text{Al}_2\text{O}_3$ ,  $\text{FeOT}$ , and  $\text{K}_2\text{O}$ , enriched in Rb, Ba, Th, U, and K and depleted in Nb, Ta, Sr, P, and Ti, indicative of shoshonitic basalt. The Late Silurian tonalite has positive  $\varepsilon_{\text{Nd}}(t)$  (+4.91 to +6.18) values and primarily originated from depleted mantle magmas metasomatized by subduction fluids, supplemented by a small amount of subducted sediments and crustal materials. The Middle–Late Silurian magmatic rocks formed in an active continental margin environment influenced by the southward subduction of the PAO.

(3) The Middle Devonian volcanic rocks exhibit low  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{Na}_2\text{O}$  and high  $\text{K}_2\text{O}$ , and  $\text{MgO}$  and enriched in Rb, K, and LREEs and depleted in Nb, Ta, Sr, and HREEs, characteristic of shoshonitic volcanic rocks.  $\varepsilon_{\text{Nd}}(t)$  (+2.11 to +3.77) and  $\varepsilon_{\text{Hf}}(t)$  (+5.90 to +11.73) values are positive. These characteristics suggest that the Middle Devonian volcanic rocks primarily originated from depleted mantle magmas metasomatized by subduction fluids, with the addition of crustal materials or subducted sediments during their formation. The Middle Devonian magmatic rocks formed in an extensional environment after the arc-continent collision.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14070641/s1>, Table S1. LA-ICP-MS zircon U-Pb data of samples from the Yitong Area; Table S2. Major element (wt.%), and trace elements (ppm) compositions of samples from the Yitong Area; Table S3. Lu-Hf isotopic compositions of zircons from the Yitong area; Table S4. Sr-Nd isotopic compositions of samples from the Yitong area.

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

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## Article

# Permian Granitic Plutons from the Northern Margin of the North China Craton: Implications for the Tectonic Evolution of the Central Asian Orogenic Belt

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**Abstract:** As the world's largest accretionary orogen, the Central Asian Orogenic Belt (CAOB) underwent continuous juvenile crustal growth in the Phanerozoic. The northern margin of the North China Craton (NCC) and its adjacent area form the eastern segment of the CAOB, which is a key area for learning about the geological evolution of the Paleo-Asian Ocean (PAO). In the Permian, the west of the northern margin of the NCC was a post-collision extensional environment, while the east was in a subduction stage. As a connecting area, the Permian evolution of the PAO in the middle of the northern margin of the NCC has not been systematically studied. In order to fill the gap and understand the continuous temporal and spatial evolutionary process of the PAO, this paper focuses on the Permian granitic rocks in the Chifeng area. Zircon U-Pb dating and the geochemical analysis of whole-rock major and trace elements were conducted to build a granite chronological framework, and to discuss the genesis and tectonic background of the granitic rocks, along with tectono-magmatic evolutionary history in the Chifeng area. The respective LA-ICP-MS zircon U-Pb dating results from eight samples are  $269 \pm 1$ ,  $268 \pm 3$ ,  $260 \pm 4$ ,  $260 \pm 1$ ,  $260 \pm 1$ ,  $255 \pm 2$ ,  $254 \pm 2$  and  $256 \pm 1$  Ma, respectively. These results, combined with previous data, revealed that the Permian granitic rocks had undergone three events of magmatism: (1) monzogranitic-syenitic phase (294–284 Ma; Ciszurlian); (2) monzogranitic phase (269–260 Ma; Guadalupian) and (3) late monzogranitic-syenitic phase (256–254 Ma; Lopingian). From the Early Permian (294–284 Ma) to the Middle Permian (269–260 Ma), granites with fine-medium-grained locally porphyritic texture and massive structure showed a high-potassium calc-alkaline series formed in a compressional setting, indicating a continuous collision between the Xing'an-Mongolian Orogenic Belt (XMOB) and the NCC. During the Late Permian-Early Triassic (256–248 Ma), granites with massive structure and medium-grained texture in the Chifeng area were magmatism dominated by A- and I-type granites of high-potassium calc-alkaline series, combined with the coeval basic rocks, which constituted a typical “bimodal” rock assemblage. This suggests that the Chifeng area was located in an extensional setting where the subducting slab broke off during the collision between the XMOB and NCC. These granitic plutons from the Permian are believed to have been generated by the subduction-collision of the Paleo-Asian oceanic crust beneath the NCC, according to emplacement time and occurrence location. Our findings provide strong evidence for Permian continuous temporal and spatial tectonic evolution and the characterization of the eventual closure of the PAO in Chifeng area at the northern margin of the NCC.

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**Keywords:** Permian granitic pluton; geochronology; geochemistry; tectonic evolution of the Paleo-Asian Ocean; northern margin of the North China Craton

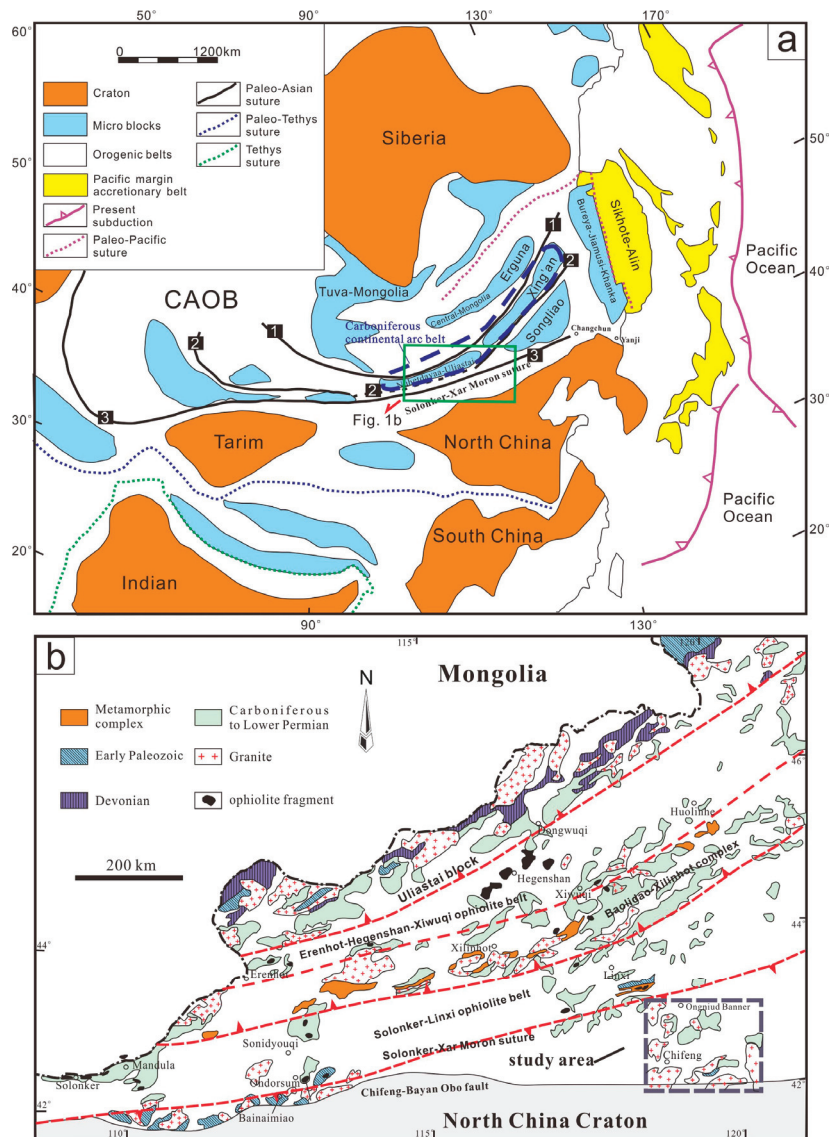
## 1. Introduction

As the world's largest Phanerozoic subduction-accretion orogen, the Central Asian Orogenic Belt (CAOB) is located between the Siberian Plate (SP) and the North China Craton (NCC). Its formation is closely related to the evolution of the Paleo-Asian Ocean (PAO) [1–3]. The CAOB adjacent to the northern margin of the NCC is also known as the Xing'an-Mongolian Orogenic Belt (XMOB), which is the orogenic belt with the longest evolutionary history and the most complicated tectonic and magmatic activities in China (Figure 1a). Its formation is related to the closure of the PAO, continental crust accretion, and extensive long-lasting tectonic–magmatic activities throughout the Phanerozoic [4,5]. As a result, the XMOB was formed by the accretion of microcontinents and Phanerozoic orogenic belts [6]. After intense continental growth and multi-stage geological evolution, the XMOB had a complex and diverse structure and crustal composition, being rich in oil and gas and metal mineral resources. Therefore, it has become a natural laboratory for scholars around the world to study continental dynamic evolution, magmatism, and ore metals [3].

The PAO has undergone a long and complex evolutionary history, as concluded from various investigations. As the mid-ocean ridge expanded and the ocean reached its maximum width, the oceanic crust began to subduct toward the continental margins on both sides. Then, the PAO basins contracted and eventually closed, leading to the collision and amalgamation of the micro-continents between the two major plates [7,8]. After the collision, it entered the post-orogenic stage of stress relaxation, and a series of complex continental crust transformation events began to occur, including extension, structural collapse, and lithosphere delamination [9–11]. Increasing data show that the Solonker-Xar Moron-Changchun-Yanji Suture (SXCYS) is the final location where the two major plates collided and joined [7,12–16]. Currently, the focus of debate is the time of collision and suturing, including the following four main points of view:

- (1) Based on the analysis of sedimentary petrography, mixed accumulation of ophiolite, formation of stratigraphic deposition, and contact between the Carboniferous strata and ophiolite, it has been proposed that the northern margin of the NCC and the XMOB collided and collaged in the early Late Paleozoic, resulting in the complete subduction of the PAO [17,18]. Since the Late Carboniferous and after the SP and NCC were united through the XMOB, the study area has been characterized by intracontinental rifting magmatic and sedimentary activities [17,18]. It is believed that the Permian basin is a new rift basin with extension-related volcanic activities [17]. Some scholars also believe that the PAO closed before the Early Permian based on magmatism [19,20].
- (2) Based on the study on the Early-Middle Permian alkaline granites in the northern margin of the NCC, it is assumed that the time limit for the final merging of the northern margin of the NCC and the XMOB to be the Early-Middle Permian [10,13,21,22].
- (3) Some scholars consider that the subduction of the PAO occurred in the Late Paleozoic, and its closure took place in Late Permian to Early Triassic times based on (I) paleomagnetism, mixing of paleontological groups, and biological extinction events suggesting that the PAO closed at the end of the Permian [2,23,24]. (II) Geochronological and geochemical data of magmatism show that a post-collision extensional environment can be interpreted for the Early Triassic. Therefore, the closure of the PAO was delimited as Late Permian [4,8,12,25–29]. (III) Oceanic Carboniferous basalts and Permian fossil content were discovered in the north of the Xar Moron River [30,31]. The reefs and marine fossils of the late Permian and the P/T unconformity surface exposed in Balin Right Banner, Inner Mongolia, and Jiutai County, Jilin, proved that the PAO closed at the end of the Late Permian [32]. (IV) Ophiolite suites obducted in

- the Late Permian–Early Triassic in the island arc/back-arc environment, indicating the two plates likely collided in this period [7,33–36]. (V) The zircon U–Pb age of the Permian clastic deposits in Balin Left Banner showed the final collision and merged time of the two plates were likely later than 266 Ma [37].
- (4) Other researchers believe that the collision between the the NCC and SP occurred at the end of the Late Permian and lasted for a long time until the Late Triassic, based on the Middle Permian–Middle Triassic syn-collision granite [28,38] and Late Triassic post-orogenic granite [8,16,29,31,39,40].



**Figure 1.** (a) Schematic tectonic map showing main tectonic subdivisions of central and eastern Asia and location of northeast China (modified from Li, 2006) [4]; (b) simplified geological map of central Inner Mongolia of the CAOB showing different tectonic units (modified from [7,8]).



The Chifeng area of Inner Mongolia, located at the junction of the XMOB and the northern margin of the NCC, is a key area to study the attributes, boundaries, collision and merging, and magmatic-tectonic evolution of the two tectonic units [17]. In recent years, geologists have identified multiple phases of granite assemblages from the Early Paleozoic to Mesozoic in southeastern Inner Mongolia: high-potassium, calc-alkaline series rock assemblages formed in an active continental margin environment [5,8,9,15,41,42]; potassium feldspar granites and monzogranite with syn-collision properties formed in a compressional environment [9,31,41]; and bimodal volcanic rocks and alkaline complex assemblages formed in a post-orogenic extensional environment [13,37,39]. These granites were formed in different magmatic-tectonic evolutionary stages during the PAO's closure and are controlled by different geodynamic backgrounds. Scholars have established the Triassic evolution model of the PAO by systematically studying the Triassic granitic rocks exposed in the Chifeng area [8]. However, the evolutionary process of the PAO in the Permian remains unclear. This study of the Permian granitic rocks exposed in the Chifeng area of the central-northern margin of the NCC, based on detailed field geological surveys, petrography, and geochemical and geochronological data, aims to shed light on the temporal and spatial tectonic–magmatic evolution of the PAO.

## 2. Geological Setting and Sample Descriptions

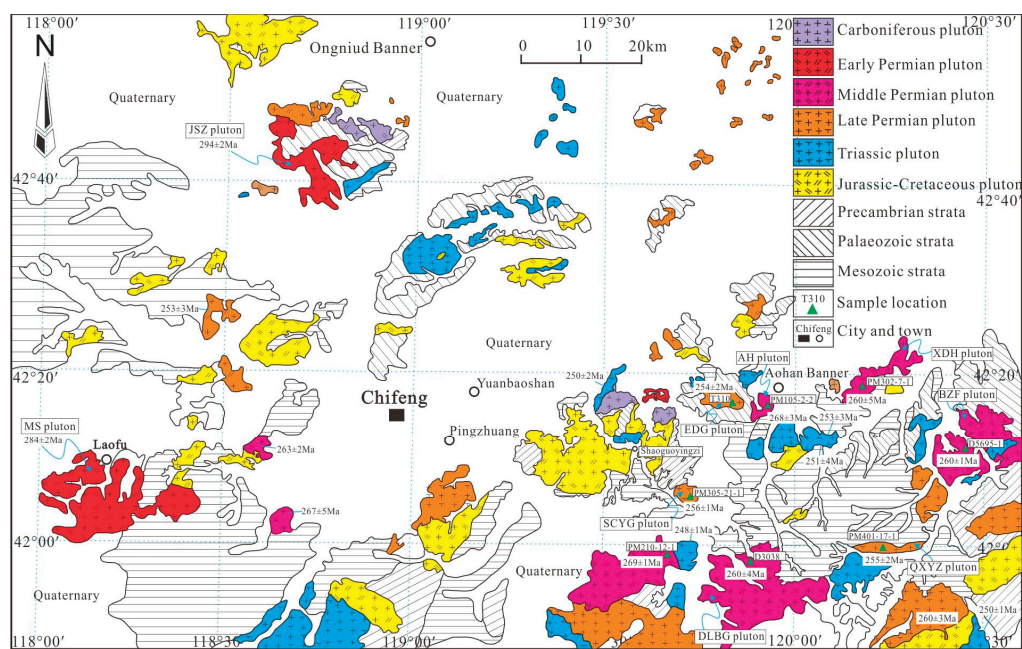
### 2.1. Geological Setting

The Chifeng area is located along the central-eastern part of the CAOBS, between the Solonker-Xar Moron-Changchun-Yanji Suture (SXCYS) and Chifeng-Kaiyuan Fault (Figure 1b). Due to the quaternary covering, the bedrock mainly is composed of granitic rocks and the strata from different epochs [8,42]. The study area is bounded by the Chifeng-Kaiyuan Fault; the northern part belongs to the CAOBS, showing Ordovician, Silurian, Carboniferous, and Permian strata (Figure 1b); and the southern part belongs to the NCC, showing Neoproterozoic metamorphic rocks and the Paleoproterozoic Baoyintu Group. During the Mesozoic, the Paleozoic basement was faulted, and the study area was transformed into an extensional basin. Continental molasse- and coal-bearing clastic rock formed in the early and Middle Jurassic; volcanic rocks formed in the Late Jurassic, and coal-bearing sediment was deposited in the Cretaceous. The graben basin formed in the Mesozoic era and changed over time due to uneven movements in the Cenozoic era. Sedimentary rocks were deposited in rivers and lakes, and basic volcanoes erupted [42].

### 2.2. Geological and Petrological Characteristics of Permian Granitoid Intrusions

There has been a lack of research on the granites in the Chifeng area. In recent years, in the process of regional geological surveys in Yuanbaoshan, Pingzhuang, Aohan Banner, and Beizifu in the east of Chifeng City, the author has disintegrated the plutons from 1:200,000 geological maps of Aohan Banner, Xiawa, and Chifeng City. Nine different Permian granitic intrusions have been identified in the Chifeng area (Figure 2), namely, the Mingshan, Jianshanzi, Aohan Banner, Daluobogou, Xiaodonghuang, Beizifu, Shangchaoyanggou, Qixieyingzi, and Erdaogou plutons. Eight samples were collected from each of these plutons for geochronological analyses (Table 1) and twenty-four samples for geochemical analyses (Figure 2).

There are only two Early Permian granitoid intrusions in the study area, the Mingshan and Jianshanzi plutons. The Jianshanzi pluton, dominated by syenogranite, located at west of the Wutonghua Town of Chifeng City (Figure 2), intrudes into the Carboniferous Jiujuzi Formation, Permian Sanmianjing and Elitu Formations, and is covered by the volcanic rocks of the Baiyingaolao and Hannuoba Formations [22]. The Mingshan pluton, dominated by porphyritic biotite monzogranite, located at south of Laofu Town in Chifeng City (Figure 2), intrudes into the Late Devonian granite and is covered by the Cretaceous volcanic rocks [22].



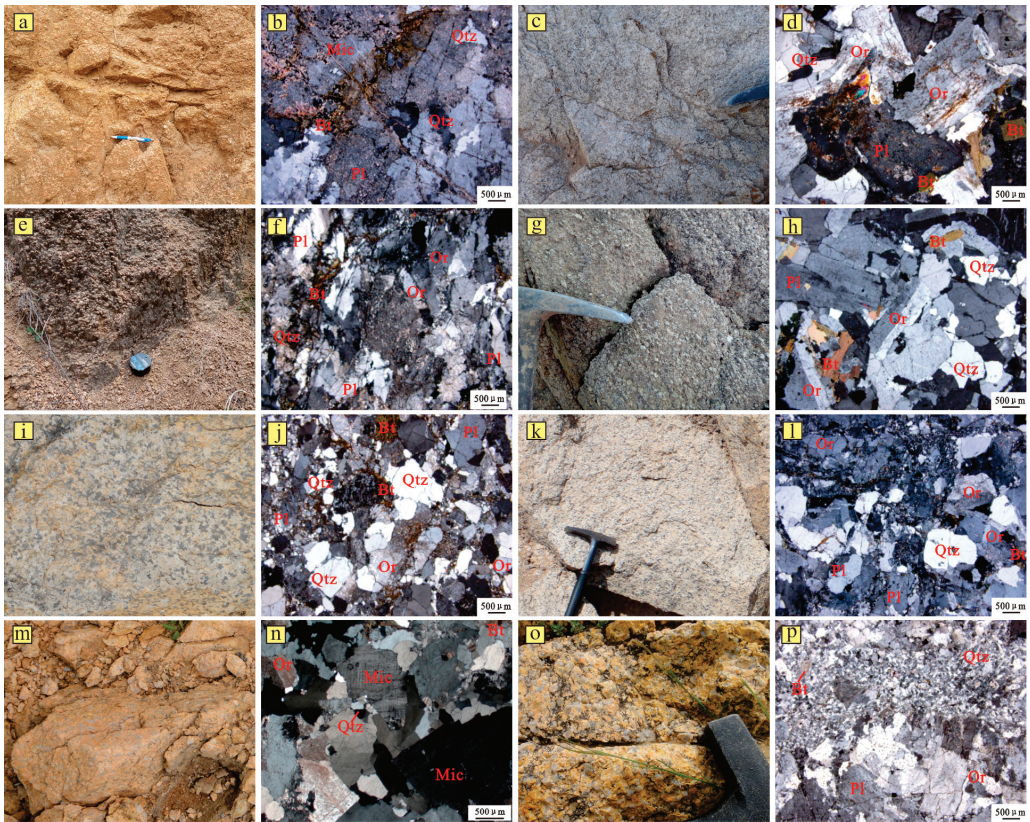
**Figure 2.** Simplified geological map of the study area in the north margin of the North China Craton showing sample locations, modified after [8]. AH–Aohan Banner, DLBG–Daluobogou, XDH–Xiaodonghuang, BZF–Beizifu, SCYG–Shangchaoyanggou, QXYZ–Qixieyingzi, EDG–Erdaogou.

**Table 1.** Location and lithology for the Permian granitic rocks of this study in the Chifeng area.

| Sample No. | Name of Intrusion       | Lithology                         | GPS Location |           |
|------------|-------------------------|-----------------------------------|--------------|-----------|
| PM210-12-1 | Daluobogou pluton       | monzogranite                      | 119°41'28"   | 42°00'06" |
| PM105-2-2  | Aohan Banner pluton     | fine-grained biotite monzogranite | 119°52'48"   | 42°17'58" |
| D3038      | Daluobogou pluton       |                                   | 119°51'53"   | 41°59'40" |
| PM302-7-1  | Xiaodonghuang pluton    | porphyry monzogranite             | 119°05'29"   | 42°19'21" |
| D5695      | Beizifu pluton          | medium-grained monzogranite       | 119°18'44"   | 42°07'51" |
| T310       | Erdaogou pluton         | medium-grained monzogranite       | 119°47'35"   | 42°18'50" |
| PM401-17-1 | Qixieyingzi pluton      | medium-grained syenogranite       | 119°08'56"   | 42°01'34" |
| PM305-21-1 | Shangchaoyanggou pluton | monzogranite                      | 119°42'24"   | 42°07'17" |

The Aohan pluton, located west of Aohan Banner (Figure 2), is covered by the rhyolitic crystal tuff of the Upper Jurassic Manketouebo Formation and the andesitic tuff of the Lower Cretaceous Yixian Formation. This granitic pluton is dominated by monzogranites (samples PM105-2-1, PM105-2-2, PM105-2-3, PM105-2-4, PM105-2-4, and PM105-4-1) with a fine-grained granite texture and massive structure (Figure 3a). These samples are composed of potassium feldspar (34 wt%±), plagioclase (30 wt%±), quartz (30 wt%±), and biotite (5 wt%±), with accessory hematite, limonite, zircon, pyrite, and apatite (1 wt%±) (Figure 3b).

The Daluobogou pluton, located 80 km east of Chifeng City (Figure 2), is covered by the volcanic and sedimentary rocks of the Lower Cretaceous Yixian Formation. This pluton is dominated by monzogranites (samples PM210-12-1, D3038-1, D3038-2, D3038-3, D3047-1, D3048-1, and D3049-1) with fine-medium-grained texture and massive structure (Figure 3c,e). These samples consist of quartz (25 wt%±), plagioclase (28 wt%±), potassium feldspar (36 wt%±), and biotite (5 wt%±), with accessory limonite, zircon, and apatite (1 wt%±) (Figure 3d,f).



**Figure 3.** Outcrop pictures and microphotographs (cross-polarized light) of magmatic rocks from the Chifeng Area showing rock textures. (a,b) Aohan Banner pluton (fine-grained monzogranite); (c,d) Daluobogou pluton (fine-grained monzogranite); (e,f) Daluobogou pluton (medium-grained monzogranite) (g,h) Xiaodonghuang pluton (porphyritic biotite monzogranite); (i,j) Beizifu pluton (medium-grained monzogranite); (k,l) Shangchaoyanggou pluton (medium-grained monzogranite); (m,n) Qixieyingzi pluton (medium-grained syenogranite) and (o,p) Erdaogou pluton (medium-grained monzogranite); Qtz: quartz; Pl: plagioclase; Mic: microcline; Or: orthoclase; Bt: biotite.

The Xiaodonghuang pluton, located at Xiaodonghuang, Sijianfang, and Tengjiawopu in the northeast of Fengshou Town Aohan Banner (Figure 2), intrudes into the Upper Carboniferous Shizuizi Formation and is covered by the rhyolite and rhyolitic crystal tuff of the Upper Jurassic Manketouebo Formation. This pluton is dominated by biotite monzogranite (sample PM302-7-1) with porphyritic texture and massive structure (Figure 3g). The matrix is phanocrystalline with medium-fine-grained granitic texture. These samples consist of quartz (25 wt%±), plagioclase (39wt%±), potassium feldspar (30 wt%±), and biotite (5 wt%±), with accessory zircon, magnetite, and titanite (1 wt%±) (Figure 3h).

The Bizifu pluton, located at Beizifu Town 30km east of the Aohan Banner (Figure 2), is intruded by the Mesozoic intrusions. This pluton is dominated by monzogranites (sample 5695-1) with massive structure and medium-fine-grained texture (Figure 3i). These samples consist of quartz (30 wt%±), plagioclase (32wt%±), potassium feldspar (34 wt%±), and biotite (3 wt%±), with accessory apatite, zircon, and titanite (1wt%±) (Figure 3j).

The Shangchaoyanggou pluton, located at Shangchaoyanggou, Yangjiaogou, and Weijiataizi in north of Jianping County (Figure 2), has fault contact with the Cretaceous Yixian Formation and the Sunjiawan Formation. This pluton is dominated by monzogranite



(sample PM305-21-1) with massive structure and fine-grained texture (Figure 3k). These samples consist of quartz (25 wt%±), plagioclase (25wt%±), potassium feldspar (44 wt%±), and biotite (5 wt%±), with accessory hematite, titanite, and zircon (1 wt%±) (Figure 3l). The minerals in this monzogranite showed a weak certain orientation in the northeast direction locally because of the influence of Nenjiang–Balihan Fault.

The Qixieyingzi pluton, located at Qixieyingzi, Jiangjiagou, and Guluyingzi in the southeast of Aohan Banner (Figure 2), is intruded by Cretaceous monzogranite and covered by volcanic rocks from the Lower Cretaceous Yixian Formation. This pluton is dominated by syenogranite (samples PM403-2-1, PM403-2-2, PM403-2-3, PM403-2-4, PM403-2-5, PM403-2-6) with massive structure and medium-grained texture (Figure 3m). These samples consist of potassium feldspar (55 wt%±), quartz (25 wt%±), plagioclase (15wt%±), and biotite (4wt%±), with accessory apatite, zircon, and titanite (1 wt%±) (Figure 3n).

The Erdaohou pluton, located at Erdaogou, Gaojiayaozi, and Sanlamayaozi 15km northwest of the Aohan Banner (Figure 2), intrudes into the Permian strata (i.e., the Sanminanjing, Elitu, and Yujiabeigou Formations) and is covered by rhyolite and andesite from the Lower Cretaceous Yixian Formation. This pluton is dominated by monzogranites (samples T310, PM103-2-1, PM103-2-3, PM103-4-2, PM103-6-1, PM103-6-2, PM103-6-4,) with massive structure and medium-grained texture (Figure 3o). These samples consist of potassium feldspar (36 wt%±), quartz (30 wt%±), plagioclase (30wt%±), and biotite (3 wt%±), with accessory zircon, magnetite, hematite, and limonite (1 wt%±) (Figure 3p).

### 3. Analytical Methods

#### 3.1. Sample Preparation

After being collected from the field, samples for geochronological analyses were cleaned, crushed, and ground. Next, zircon crystals were separated from these samples by means of conventional heavy liquid and magnetic techniques, and the separates were hand-picked and purified under a binocular microscope at Langfang Yuneng Mineral Separation Co., Ltd. (Langfang, China). Next, the zircons were selected and embedded in epoxy resin and polished, then imaged through a scanning electron microscope via cathodoluminescence (CL) to reveal their internal structures. CL images of five samples (PM105-2-2, D3038, PM302-7-1, PM401-17-1, and T310) were obtained from the Zhongnan Mineral Supervision and Testing Center of the Ministry of Land and Resources, and the others (PM210-12-1, PM305-21-1 and D5659-1) from the electron microprobe Laboratory of the Institute of Geology and Geophysics, Chinese Academy of Sciences.

#### 3.2. Zircon LA-ICP-MS U-Pb Isotope Dating

The U-Pb zircon ages for the Permian granites in the Chifeng area were obtained using an Agilent 7500a inductively coupled plasma–mass spectrometry (ICP-MS) instrument, equipped with a 193 nm ArF Excimer laser-ablation (LA) system. The spot size for the analyses was 36 µm, with an energy density of 8.5 J/cm<sup>2</sup> and repetition rate of 10 Hz. Helium was used as the carrier gas to transport the ablated material from the standard LA cells. Zircon 91500 (<sup>206</sup>Pb/<sup>238</sup>U age of 1062.4 ± 0.4 Ma (2σ) and <sup>206</sup>Pb/<sup>207</sup>Pb age of 1065.4 ± 0.3 Ma (2σ)) was used as the external standard for age calibration, while standard silicate NIST 610 glass was used to calibrate content calculations [43]. Zircon standards TEMORA (<sup>206</sup>Pb/<sup>238</sup>U age of 416.78 ± 0.33 Ma (2σ), [44]) and QH (160 ± 1 Ma) were also used as secondary standards to monitor any deviation in age measurement. Isotopic ratios and element contents were calculated using Glitter software (version 4.0; Macquarie University, Sydney, Australia), and the age calculation and concordant plots were obtained using Isoplot (v. 3.0) [45]. Common Pb was corrected using the method described by Andersen (2002) [46]. The analytical data are presented on U-Pb concordia diagrams with 1σ errors, and the mean ages are weighted means at the 95% confidence level [47]. Analyses of five samples (PM105-2-2, D3038, PM302-7-1, PM401-17-1, and T310) were conducted at the Zhongnan Mineral Supervision and Testing Center of the Ministry of

Land and Resources, and the others (PM210-12-1, PM305-21-1, and D5659-1) at the Geologic Laboratory Center, China University of Geosciences (Beijing, China). The analytical results are listed in Table S1.

3.3. Major- and Trace-Element Analyses

Next, major-, trace- and rare-earth-element (REE) analyses for 24 samples were conducted at the Northeast China Supervision and Inspection Center of Mineral Resources, Ministry of Land and Resources (Shenyang, China). After petrographic examination and removal of altered rock surfaces, the samples were crushed and ground to 74  $\mu\text{m}$  in an agate mill. Then, whole-rock major-element contents were determined using X-ray fluorescence spectrometry (XRF), yielding analytical precisions exceeding 2%. The trace-element and REE contents were determined using ICP-MS and yielded analytical precisions exceeding 5% for elements with contents of >10 ppm, exceeding 8% for elements with contents of <10 ppm, and 10% for the transition metals. The results are listed in Table S2.

4. Analytical Results

4.1. Zircon U-Pb Ages

4.1.1. Early-Middle Permian

Sample PM210-12-1 is a monzogranite with fine-grained texture collected from the Daluobogou pluton in the Machang area. Zircons within this sample are generally colorless, transparent, and mostly subhedral to euhedral columnar in shape. They have length-to-width ratios of 3:2 to 4:1. In the cathodoluminescence (CL) images (Figure 4), most grains display fine-scale oscillatory growth zoning and clear internal structure. The zoning, combined with Th/U ratios of 0.42–1.57 (Table S1), indicates a magmatic origin [48,49]. A total of 24 isotopic analyses were conducted on 24 zircons grains from this sample. Most of the analyses are concordant and define a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $269 \pm 1 \text{ Ma}$  (MSDW = 0.90) (Figure 5a), which is interpreted as the crystallization age of the monzogranite.

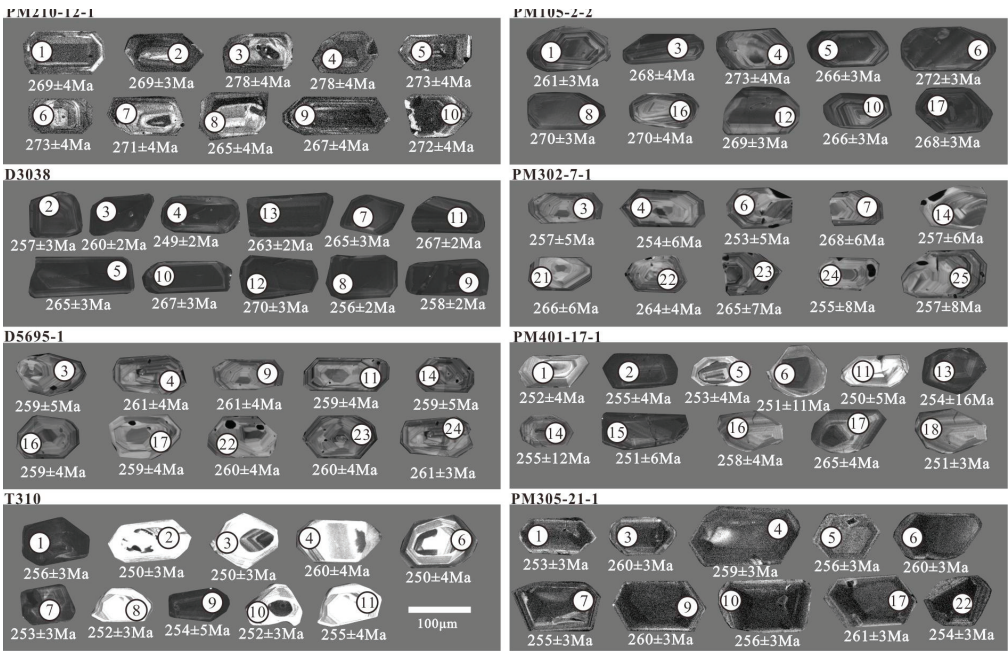
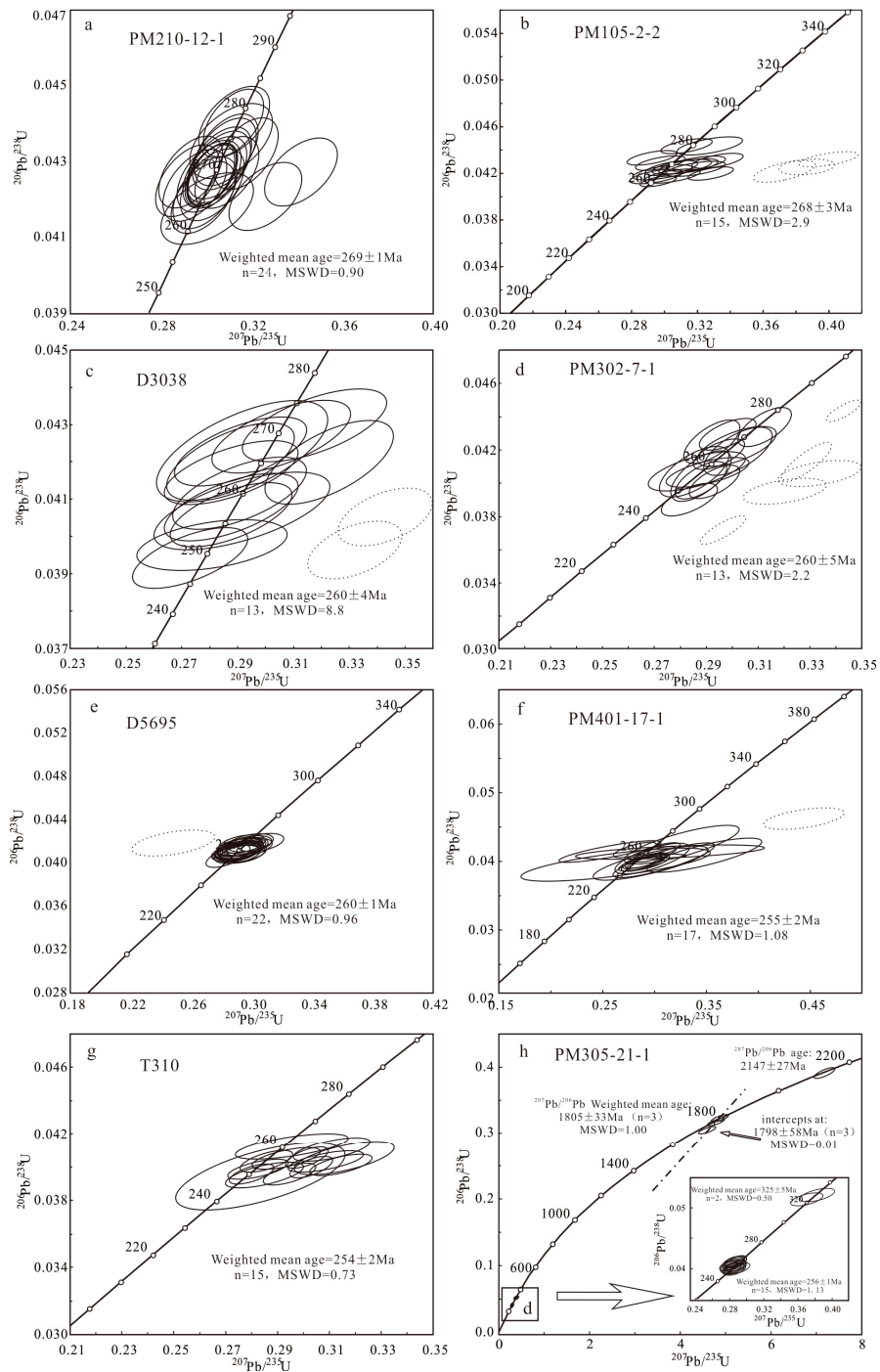


Figure 4. Cathodoluminescence (CL) images of selected zircon grains from the Permian granites in this study.





**Figure 5.** Zircon  $^{207}\text{Pb}/^{235}\text{U}$ - $^{206}\text{Pb}/^{238}\text{U}$  concordia diagrams of the Permian granites samples from this study. The dashed ellipse represents the discordant age. (a): PM210-12-1; (b): PM105-2-2; (c): D3038; (d): PM302-7-1; (e): D5695; (f): PM401-17-1; (g): T310; (h): PM305-21-1.

Sample PM105-2-2, a fine-grained biotite monzogranite, was collected from the Aohan pluton. Zircons from this sample are translucent and euhedral to subhedral or form short prisms to long columns in shape. They have length-to-width ratios ranging from 2:1 to 3:1. CL imaging reveals that most zircons are bright with fine-scale oscillatory growth zoning (Figure 4), indicating a magmatic origin [48,49]. A total of 18 analyses were made on 18 zircons, which were shown to have high Th/U ratios (0.43–0.88) (Table S1). Three analysis points were not considered in the concordia diagram due to the low confidence (less than 90%) (Figure 5b). The remaining 15 analysis points were plotted on or near the concordia line. The concordant zircon data give a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $268 \pm 3$  Ma (MSDW = 2.90), interpreted as the crystallization age of the sample.

#### 4.1.2. Late-Middle Permian

Sample D3038 is a medium-grained monzogranite from the Daluobogou pluton near the Luofugou area. The zircon grains from the sample are mostly euhedral elongate prisms with oscillatory zoning. They have length-to-width ratios of 2:1 to 4:1, and Th/U ratios of 0.52 to 1.31 (Figure 4), indicating magmatic origin [48,49]. A total of 15 analyses on 15 zircon grains were conducted. All but two of the analyses were concordant and yield a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $260 \pm 4$  Ma (MSDW = 8.8) (Figure 5c), which is regarded as the monzogranite's emplacement age.

Sample PM302-7-1, a porphyry monzogranite, was collected from the Xiaodonghuang pluton of Fengshou Village, Aohan Banner. Zircon grains from this sample are prismatic and stubby in shape, and the Th/U ratios mostly cluster around 0.43–1.38 (Table S1). A total of 23 analyses were conducted on 23 zircons; 10 analyses were excluded because of high discordancy, and the remaining 13 analysis spots yielded a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $260 \pm 1$  Ma (MSDW = 0.96) (Figure 5d), which is considered as representing the crystallization age of porphyritic monzogranite.

Sample D5695, a medium-grained monzogranite, was collected from the Beizifu pluton. Zircons from this sample are generally colorless, transparent, and euhedral in shape. In the CL images, most of them display fine-scale oscillatory zoning, with high Th/U ratios of 0.29–1.35, indicating magmatic origin [48,49]. A total of 25 spots were analyzed on 25 zircons from this sample; 3 analyses were excluded due to high discordancy, and the remaining 22 spots were concordant. The concordant zircon data give a weighted mean of  $^{206}\text{Pb}/^{238}\text{U}$  age of  $260 \pm 1$  Ma (MSDW = 0.96) (Figure 5e), interpreted as the sample's emplacement age.

#### 4.1.3. Late Permian

Sample PM401-17-1, a medium-grained syenogranite, was collected from the Qixieyingzi pluton. Zircons within sample PM401-17-1 are generally euhedral and prismatic with length-to-width ratios of 2:1–4:1. They show variable degrees of oscillatory zoning visible during CL imaging (Figure 4) and have Th/U ratios of 0.43–2.83 (Table S1), characteristic of magmatic zircons of acid rocks [48,49]. Excluding three discordant data points likely caused by lead loss, the remaining 17 analysis spots yielded a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $255 \pm 2$  Ma (MSDW = 1.08) (Figure 5f), which is interpreted to be the crystallization age of the syenogranite.

Sample T310, a medium-grained monzogranite, was collected from the Erdaogou pluton. Zircon grains within this sample are generally colorless, transparent, and short columnar in shape, with a maximum length-to-width ratio of 2:1. The CL imaging reveals that most grains have fine oscillatory zones (Figure 4). These properties, together with their relatively high Th/U ratios (0.43–2.97) (Table S1), suggest the zircons are of magmatic origin [48,49]. The results of all 15 analyses are consistent and define a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $254 \pm 2$  Ma (MSDW = 0.73) (Figure 5g), which is interpreted as the time of crystallization of the monzogranite.

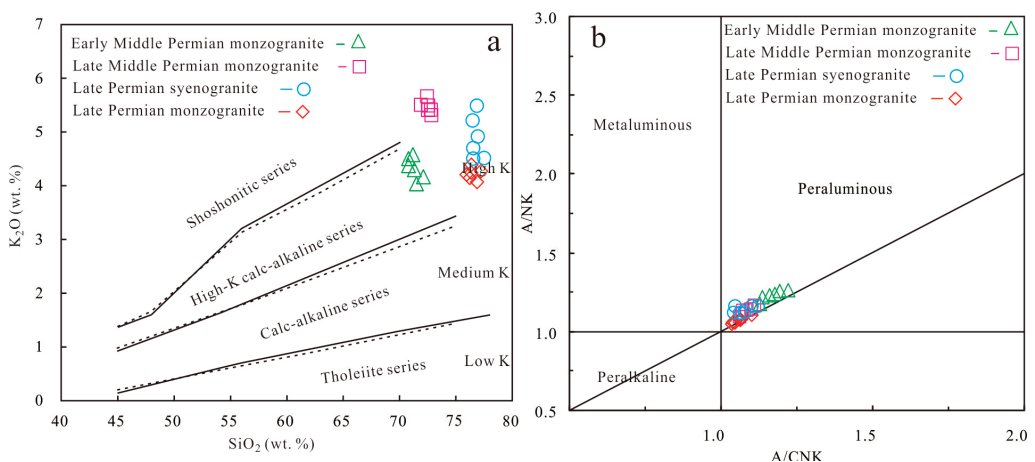
Sample PM305-21-1 is a monzogranite collected from the Shangchaoyanggou pluton. Zircons from this sample are generally euhedral and prismatic with length-to-width ratios

of 2:1 to 3:1. In the CL images, most grains display fine-scale oscillatory growth zoning (Figure 4), with high Th/U values of (0.28–1.92) (Table S1). A total of 23 spots were analyzed on 23 zircons from this sample; 2 analyses were excluded due to high discordancy, and the remaining 21 analysis points were plotted on or near the concordant line, and gave four groups of ages (Figure 5h). The first group comprises one analysis (No. 16) with a  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $2147 \pm 27$  Ma, representing a middle Paleoproterozoic magmatic event. The second group consists of three analyses (Nos. 11, 18, 20), yielding a weighted mean  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $1,805 \pm 33$  Ma, which is consistent with their upper intercept age of  $1798 \pm 58$  Ma, representing late Paleoproterozoic magmatic activity. The third group comprises two analyses (Nos. 14 and 15), yielding a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $352 \pm 5$  Ma (MSDW = 0.50) (Figure 5h). The fourth group comprises 15 analyses, yielding a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $256 \pm 1$  Ma (MSDW = 1.13). The youngest age of  $256 \pm 1$  Ma is interpreted to be the emplacement age of the monzogranite, whereas the other three ages (ca. 2147, 1805, and 352 Ma) are interpreted to represent the crystallization ages of captured zircon entrained by the granitic magma.

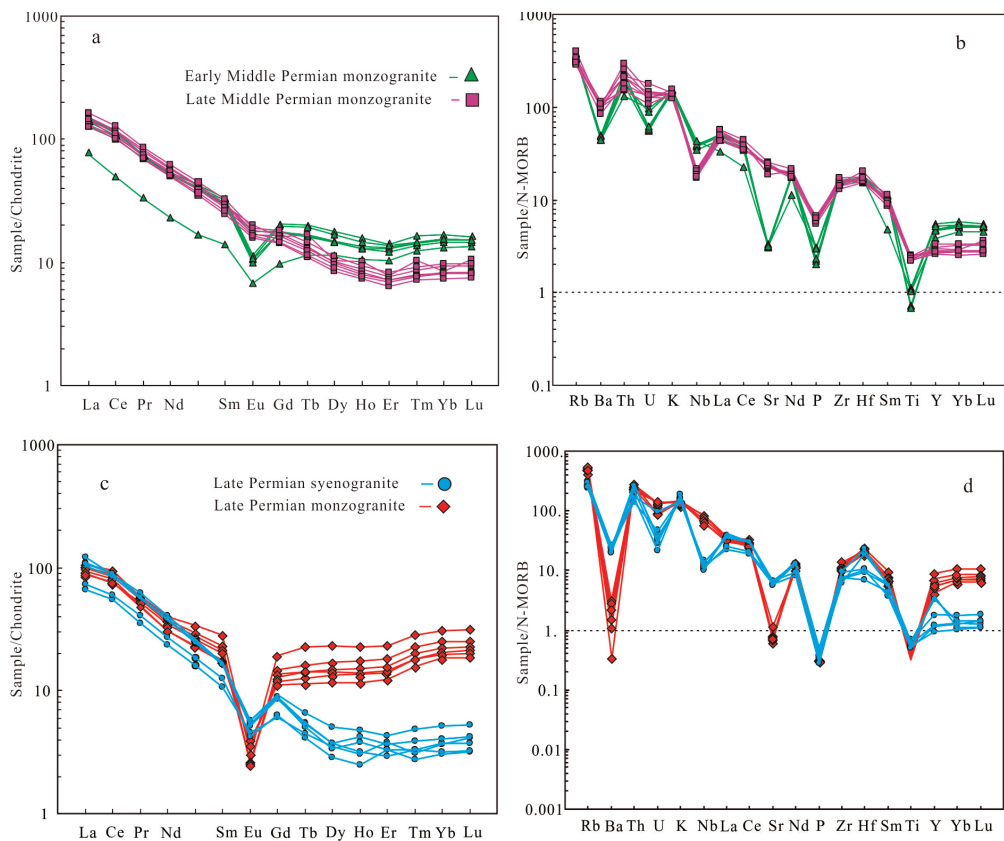
#### 4.2. Major and Trace Element Geochemistry

##### 4.2.1. Early-Middle Permian Monzogranite

The monzogranites are high in  $\text{SiO}_2$  (72.00–73.37 wt%),  $\text{K}_2\text{O}$  (4.32–4.70 wt%), and  $(\text{Na}_2\text{O} + \text{K}_2\text{O})$  (14.17–14.62 wt%), with  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratios of 0.88–1.01, yet low in  $\text{TiO}_2$  (0.12–0.20 wt%),  $\text{MnO}$  (0.02–0.03 wt%),  $\text{MgO}$  (0.04–0.15 wt%), and  $\text{P}_2\text{O}_5$  (0.04–0.07 wt%) (Table S2). They are classified in the alkalic series, and assigned to the high-K calc-alkaline igneous rocks (Figure 6a). Their A/CNK (molar  $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ ) values range from 1.08 to 1.23, indicative of weakly peraluminous granites (Figure 6b). The total rare earth elements (REEs) range from 143.96 to 156.29  $\mu\text{g/g}$  (with the exception of one datum lower than 66.45  $\mu\text{g/g}$ ). In the chondrite-normalized REE diagram (Figure 7a), the monzogranite samples have a pattern of slightly enriched LREEs but flat HREEs, with  $(\text{La}/\text{Yb})_N$  and  $\Sigma\text{LREE}/\Sigma\text{HREE}$  (total light rare-earth elements versus total heavy rare-earth elements) ratios of 3.54–19.62 and 5.29–10.06 and moderately negative Eu anomalies ( $\text{Eu}/\text{Eu}^* = 0.42\text{--}0.57$ ). In the primitive-mantle (PM) normalized trace element diagram (Figure 7b), all samples show negative Ba, Nb, Sr, P, and Ti anomalies and are all enriched in Rb, Th, K, La, Zr, and Hf.



**Figure 6.**  $\text{K}_2\text{O}$  versus  $\text{SiO}_2$  (a) and A/NK (molar/molar) versus A/CNK (molar/molar) (b) diagrams for Permian granitic rocks. Normalization values are from [50] and [51], respectively.



**Figure 7.** Chondrite-normalized REE patterns (a,c) and primitive mantle-normalized trace element spider diagrams (b,d) for these Permian granitic rocks in the Chifeng area. The values of chondrite and primitive mantle are from [52].

#### 4.2.2. Late-Middle Permian Monzogranite

All of the monzogranite samples are alkalic- and silica-rich high-K calc-alkaline igneous rocks (Figure 6a). The whole-rock analysis results yield  $\text{SiO}_2 = 73.40\text{--}74.11$  wt%,  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratios = 0.65–070, and total  $\text{Na}_2\text{O} + \text{K}_2\text{O} = 9.30\text{--}9.76$ . The samples are low in  $\text{TiO}_2 = 0.16\text{--}0.18$  wt%,  $\text{MnO} = 0.03\text{--}0.04$  wt%,  $\text{MgO} = 0.20$  wt%, and  $\text{P}_2\text{O}_5 = 0.03$  wt% (Table S2). They are classified as potassium basalt series and weakly peraluminous granites, due to their respective  $\text{A}/\text{CNK}$ ,  $\text{K}_2\text{O}$ , and  $\text{Al}_2\text{O}_3$  values of 1.07–1.11, 5.47–5.80 wt%, and 13.93–14.21 wt% (Figure 6b). The total REEs range from 272.5 to 340.64  $\mu\text{g/g}$ . The chondrite-normalized REE diagrams invariably show a relative enrichment in LREEs, with  $(\text{La}/\text{Yb})_{\text{N}}$  and  $\Sigma\text{LREE}/\Sigma\text{HREE}$  ratios of 19.58–26.88 and 18.36–20.38, and moderate to significant negative Eu anomalies with  $\text{Eu}/\text{Eu}^*$  ratios of 0.31–0.41 (Figure 7a). Furthermore, in the PM-normalized trace element diagram (Figure 7b), the rocks are enriched in large ion lithophile elements (LILEs; e.g., Rb, Th, K, La, and Ce) and depleted in high field-strength elements (HFSEs; e.g., Nb, P, and Ti). Finally, all samples show negative Ba anomalies.

#### 4.2.3. Late Permian Monzogranite and Syenogranite

The Late Permian monzogranites have  $\text{SiO}_2 = 76.29\text{--}77.30$  wt% and contain  $\text{Al}_2\text{O}_3$  of 12.75–12.93 wt%,  $\text{TiO}_2$  of 0.06–0.07 wt%,  $\text{MnO}$  of 0.01–0.08 wt%,  $\text{MgO}$  of 0.11 wt%,  $\text{P}_2\text{O}_5$  of 0.01 wt%, and total  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  of 8.40–8.79 wt%, with  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratios of 0.95–1.09 (Table S2). They are classified as the weakly peraluminous high-K calc-alkaline

series on a plot of K<sub>2</sub>O against SiO<sub>2</sub> (Figure 6a), and plot in the peraluminous field in the A/CNK vs. A/NK diagram (Figure 6b). The total REEs range from 101.75 to 128.91 µg/g. In the chondrite-normalized REE diagram, they are weakly fractionated, with (La/Yb)<sub>N</sub> and ΣLREE/ΣHREE ratios of 3.28–5.06 and 4.73–7.25 and strong negative Eu anomalies (Eu/Eu\* = 0.13–0.28) (Figure 7c). In the PM-normalized trace-element diagram (Figure 7d), they show similar patterns, albeit with notable differences in the absolute element concentrations. All samples are enriched in Rb, Th, U, K, Nd, Zr, and Hf, but depleted in Ba, Sr, P, and Ti.

The Late Permian syenogranites are high in SiO<sub>2</sub> (76.22–77.58 wt%) and K<sub>2</sub>O (4.35–5.62 wt%), but low in Al<sub>2</sub>O<sub>3</sub> (12.05–12.63 wt%), TiO<sub>2</sub> (0.09–0.16 wt%), MnO (0.01–0.05 wt%), MgO (0.20–0.56 wt%), and P<sub>2</sub>O<sub>5</sub> (0.01–0.02 wt%). They are high-K calc-alkaline, and weak peraluminous igneous rocks (Figure 6a), with total Na<sub>2</sub>O + K<sub>2</sub>O of 0.49–0.86, and A/CNK ratios ranging from 1.05 to 1.16 (Figure 6b). All but two have high total REEs, with the total REE values ranging from 107.94 to 215.80 µg/g. The chondrite-normalized REE diagram shows that they are enriched in LREEs, with (La/Yb)<sub>N</sub> and ΣLREE/ΣHREE ratios of 18.05–32.16 and 16.77–25.86, respectively (Figure 7c). The granites also have moderately negative Eu anomalies (Eu/Eu\* = 0.39–0.54). Finally, the PM-normalized trace-element diagram shows that they are enriched in LILEs (e.g., Rb, Th, K, La, and Ce) and LREEs (e.g., Nd, Zr, and Hf), and depleted in HFSEs (e.g., Ba, Nb, P, Ti, and Sr) (Figure 7d).

5. Discussion

5.1. Permian Magmatism in the Chifeng Area

Previous research on the Permian magmatism in the Chifeng area has been quite scarce, only covering the granodiorite located in the Late Permian in Mengguyingzi [15], diorite (256 ± 6 Ma) in Chaihuyingzi [53], gneissic monzogranite in the Liangjin mining area of Jinchanggou (249 ± 1 Ma) [40], Early Permian monzogranite in the Mingshan pluton, and syenite in the Jianshanzi pluton (284.4 ± 7.9 Ma, 294.7 ± 8.5 Ma) [22]. The coeval volcanic rocks include the andesite of the Permian Elitu Formation exposed in the Mingshan uplift belt in the west of Chifeng (273 Ma). Based on the available data, combined with those of this study, the Permian granitic chronology framework was established in the Chifeng area (Table 2).

Table 2. Geochronological data for the Permian granitic rocks in the Chifeng area.

| Order | Sample     | Pluton           | Lithology    | Age (Ma) | Method   | References                                                  |
|-------|------------|------------------|--------------|----------|----------|-------------------------------------------------------------|
| 1     | 14CH10     | Jianshanzi       | Monzogranite | 294 ± 2  | LA-ICPMS | [22]                                                        |
| 2     | 14CH24     | Mingshan         | Granodiorite | 284 ± 2  | LA-ICPMS | [22]                                                        |
| 3     | PM210-12-1 | Daluobogou       | Monzogranite | 269 ± 1  | LA-ICPMS | This study                                                  |
| 4     | PM105-2-2  | Aohan Banner     | Monzogranite | 268 ± 3  | LA-ICPMS | This study                                                  |
| 5     | D3038      | Daluobogou       | Monzogranite | 260 ± 4  | LA-ICPMS | This study                                                  |
| 6     | PM302-7-1  | Xiaodonghuang    | Monzogranite | 260 ± 5  | LA-ICPMS | This study                                                  |
| 7     | D5695-1    | Beizifu          | Monzogranite | 260 ± 1  | LA-ICPMS | This study                                                  |
| 8     |            | Sidaogou         | Syenogranite | 267 ± 5  | LA-ICPMS |                                                             |
| 9     |            | Jianshanzi       | Monzogranite | 263 ± 2  | LA-ICPMS | Inner Mongolia 1:250,000 Chifeng regional geological survey |
| 10    |            | Majiadi          | Granite      | 274 ± 4  | LA-ICPMS |                                                             |
| 11    |            | Zhaojiawopu      | Diorite      | 253 ± 3  | LA-ICPMS |                                                             |
| 12    | PM305-21-1 | Shangchaoyanggou | Granodiorite | 256 ± 1  | LA-ICPMS | This study                                                  |
| 13    | PM401-17-1 | Qixieyingzi      | Syenogranite | 255 ± 2  | LA-ICPMS | This study                                                  |
| 14    | T310       | Erdaohou         | Monzogranite | 254 ± 2  | LA-ICPMS | This study                                                  |
| 15    | T101       | Mengguyingzi     | Granodiorite | 251 ± 4  | LA-ICPMS | [8]                                                         |
| 16    | D2711-1    | Xiaxinjing       | Monzogranite | 250 ± 2  | LA-ICPMS | [8]                                                         |
| 17    | PM210-6-1  | Daluobogou       | Monzogranite | 248 ± 1  | LA-ICPMS | [8]                                                         |
| 18    | CH2        | Chaihulanzhi     | Diorite      | 257 ± 6  | SHRIMP   | [53]                                                        |
| 19    | DJ10-18    | Shuangjingzi     | Granite      | 278 ± 1  | LA-ICPMS | [54]                                                        |
| 20    | PM003-1    | Mengguyingzi     | Granodiorite | 253 ± 3  | LA-ICPMS | [15]                                                        |
| 21    |            | Dayingzi         | Syenogranite | 268 ± 3  | LA-ICPMS | [55]                                                        |
| 22    | XG01       | Jinchanggouliang | Monzogranite | 250 ± 1  | LA-ICPMS | [40]                                                        |



#### 5.1.1. Early Permian (294–284 Ma)

The magmatic activities are intense in the Permian in the northern margin of the NCC. However, these magmatic activities are mainly concentrated in the central region of Inner Mongolia and are rare in the Chifeng area. The Early Permian granite studied in this paper includes the syenite in the Jianshanzi pluton (294 Ma) and the monzogranite in the Mingshan pluton (284 Ma), indicating that the Early Permian granite of the Chifeng area formed during 294–284 Ma [22].

#### 5.1.2. Middle Permian (269–260 Ma)

Late Paleozoic magmatic rocks are linearly distributed in the study area and its adjacent area, among which the Middle Permian magmatic rocks are the most widely distributed. They are exposed on the northern margin of the NCC and XMOB. In the Chifeng area, rocks that have been identified include syenogranite ( $269 \pm 1$  Ma) and monzogranite ( $260 \pm 4$  Ma) in the Daluobogou pluton, fine-grained monzogranite in Aohan Banner ( $268 \pm 3$  Ma), porphyritic medium-coarse monzogranite in Xiaodonghuang ( $260 \pm 5$  Ma), and medium-grained monzogranite in Beizifu ( $260 \pm 1$  Ma). The syenogranite at the margin of the Dayingzi pluton in the northwestern Chifeng has an age of  $268 \pm 3$  Ma [55]. The geochronological results show that the Middle Permian intrusive rocks formed between 269 and 260 Ma, indicating that magmatism occurred in the Chifeng area in this period.

#### 5.1.3. Late Permian–Early Triassic (256–248 Ma)

The Late Permian–Early Triassic granitic magmatism in the study area occurred frequently in the same tectonic background, and the volcanic activity in the Early Triassic was a continuation of that in the Late Permian [13,37]. The Late Permian granitic rocks identified in the research area include the weak gneissic monzogranite of the Shangchaoyanggou pluton ( $256 \pm 1$  Ma), the medium-grained syenogranite of the Qixieyingzi pluton ( $255 \pm 2$  Ma), and medium-grained monzogranite of the Erdaogou pluton ( $253 \pm 2$  Ma). There are also many other magmatic activities, such as the diorite hosting the granulite in Chaihuyingzi ( $257 \pm 6$  Ma) [53], fine-grained granodiorite in Mengguyingzi ( $252 \pm 2$  Ma) [15], gneissic monzonite in the Liangjin mining area of Jinchanggou ( $249 \pm 1$  Ma) [40], fine-grained granodiorite in the Mengguyingzi pluton ( $251 \pm 2$  Ma), medium-grained monzogranite in the Xiaxinjing pluton ( $250 \pm 2$  Ma), and medium-grained syenogranite in the Daluobogou pluton ( $247 \pm 1$  Ma) [8]. The zircon U–Pb ages of these granitic intrusions range from 256 to 247 Ma, indicating that the most intense magmatism occurred in the Late Permian–Early Triassic.

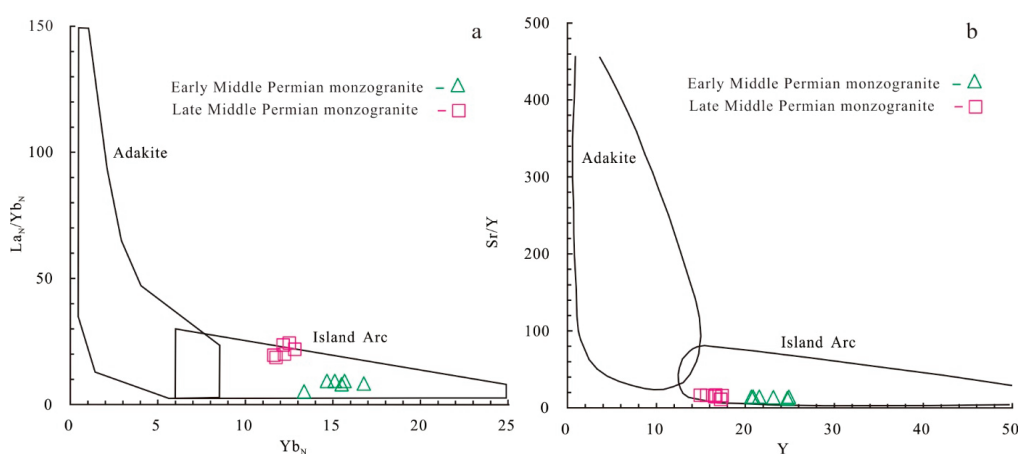
### 5.2. Genetic Types of the Middle–Late Permian Granitic Rocks in the Chifeng Area

#### 5.2.1. Middle Permian Monzogranite

The early Middle Permian monzogranite ( $269 \pm 1$  Ma) is alkali-rich and high-potassium, calc-alkaline rock, and is rich in Si and Al. The A/CNK is between 1.08 and 1.23, indicating that it is peraluminous. The fine-grained monzogranite is aluminum-saturated, high-potassium, calc-alkaline rock.  $\Sigma\text{REE}$  is low, and close to the average level of the continental crust. Europium is moderately depleted. All of these granites fall in the range of classic island arc rocks in the  $(\text{La}/\text{Yb})_{\text{N}}\text{--Yb}_{\text{N}}$  diagram and Y–Sr/Y diagram (Figure 8). By comparing the trace element ratio of fine-grained monzogranite to that of the continental crust average value and differentiated granite, it is concluded that the monzogranite of this phase is I-type granite.

The late Middle Permian monzogranite is alkali-rich, high-potassium, calcium-alkaline rock, rich in Si, with medium Al. The A/CNK value is between 1.07 and 1.11, indicating that it is slightly peraluminous. The medium-grained monzogranite is slightly aluminum-saturated, alkali-rich, high-potassium, calc-alkaline rock. The  $\Sigma\text{REE}$  content is much higher than the average level of the continental crust. Europium is moderately depleted, and these samples fall in the range of classic island arc rocks in the  $(\text{La}/\text{Yb})_{\text{N}}\text{--Yb}_{\text{N}}$  and Y–Sr/Y diagrams (Figure 8). By comparing the trace-element ratio of medium-grained

monzogranite to that of the continental crust average value and differentiated granite, it is concluded that this monzogranite in the Daluobogou pluton is I-type granite.

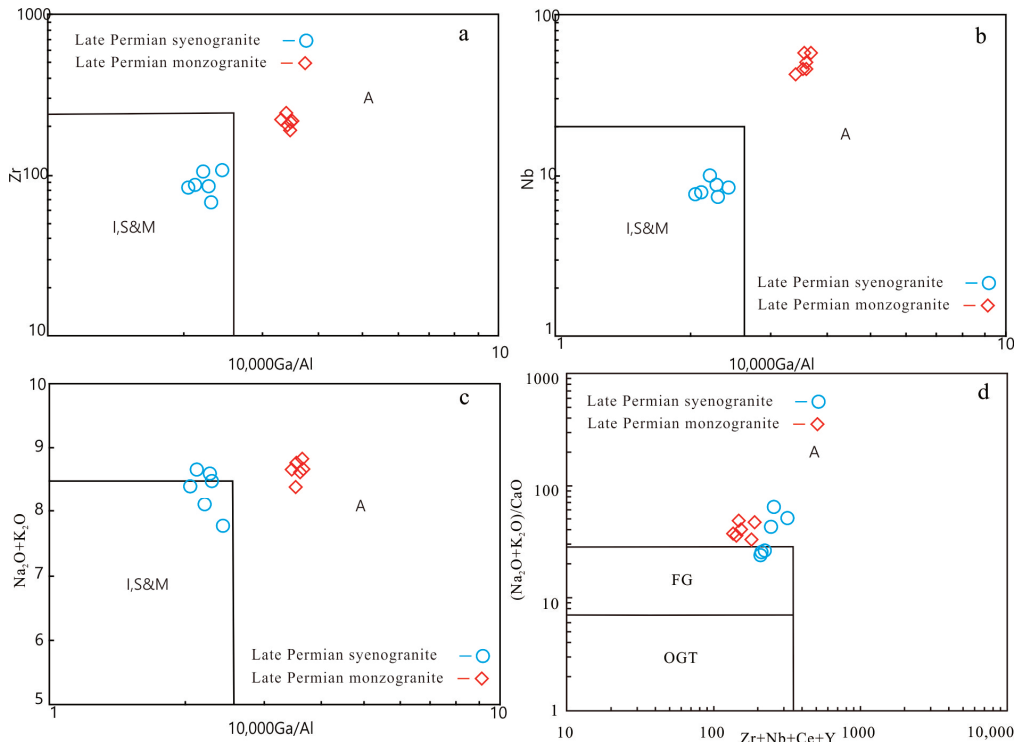


**Figure 8.** (a)  $La_N/Yb_N$  versus  $Yb_N$ ; (b)  $Sr/Y$  versus  $Y$  diagram of the Middle Permian granites in Aohan area, modified after [56].

### 5.2.2. Genesis of the Late Permian Granite

The geochemistry characteristics show that the Late Permian monzogranite is alkali-rich, high-potassium, calc-alkaline rock, rich in Si and poor in Al. The A/CNK value is in the range of 0.95–1.05, indicating moderately peraluminous rock. The monzogranite belongs to alkali-rich, medium-Al, high-potassium, calc-alkaline rock.  $\Sigma REE$  is close to the average level of the continental crust. The trace elements have similar characteristics to those of A-type granite [57]. The light and heavy rare-earth elements are obviously fractionated, with strongly negative Eu anomalies. The rare-earth element distribution pattern forms a “V” shape. A-type granite has high heavy rare-earth elements and Zr, Nb, Ce, and Y content levels due to their rich alkalinity [57]. The observed enrichment of heavy rare-earth elements show high contents of high field-strength elements such as Nb, Zr, and Hf, yet low Sr and Ba contents (Figure 7), showing the characteristics of A-type granite. In the 10,000 Ga/Al-Zr, 10,000 Ga/Al-Nb, and 10,000 Ga/Al-Na<sub>2</sub>O + K<sub>2</sub>O diagrams (Figure 9a, Figure 9b, and Figure 9c, respectively) of the Late Permian intrusive rocks, the monzogranite falls in the range of A-type granite. The (Zr + Nb + Ce + Y) content of the monzogranite is low (288.49–354.33  $\mu\text{g/g}$ , less than 350  $\mu\text{g/g}$  [57]), being slightly lower than the (Zr + Nb + Ce + Y) value of A-type granite (usually greater than 350  $\mu\text{g/g}$ ); however, there were some exceptions [58]. This puts the rock in the range of A-type granite in the (Zr + Nb + Ce + Y)–(K<sub>2</sub>O + Na<sub>2</sub>O)/CaO diagram (Figure 9d). Zhang et al. (2012) suggested that A-type granite should be distinguished based on the comprehensive analyses of the (Zr + Nb + Ce + Y), rare-earth-element and trace-element diagrams rather than the (Zr + Nb + Ce + Y) diagram alone [57]. The most important geochemical characteristics of A-type granite are rich in SiO<sub>2</sub> (usually >70%, mostly >75%); rich in K<sub>2</sub>O (4–6% or higher); depleted in Al<sub>2</sub>O<sub>3</sub> (content of 12–13%), Sr, Ba, Eu, Ti, and P; and a “V”-shaped REE pattern with an obviously negative Eu anomaly [57]. The monzogranite has a SiO<sub>2</sub> content of 76.32–77.20%, a K<sub>2</sub>O content of 4.15–4.47%, and an Al<sub>2</sub>O<sub>3</sub> content of 12.77–12.93%, showing negative anomalies of Sr, Ba, Ti, and P. The monzogranite has a rare-earth element distribution pattern of a “V” shape with an obviously negative Eu anomaly, which is the same as the A-type granite distributed in northeastern China [6]. A-type granite is generally formed in high-temperature environments [57]. With the Zr saturation temperature of 807–828 °C, the monzogranite in the EDG pluton is not high-temperature granite. However, experimental petrology shows that when the pressure is less than 0.5 GPa and the water

content is 1–6%, then the partial melting temperature of A-type granite can be reduced to 800–830 °C [59], or even lower [60–62]. In summary, it is concluded that the Late Permian monzonitic granite can be classified as A-type granite.



**Figure 9.** Diagram of  $10,000 \text{ Ga/Al}$  vs.  $\text{Zr}$ ,  $\text{Nb}$ ,  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  (a–c), and  $(\text{Zr} + \text{Nb} + \text{Ce} + \text{Y})$  vs.  $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{CaO}$  (d) for the Late Permian granitic intrusions [56]. A, A-type granite; FG, highly fractionated I-type granite; I, S, & M, OGT, unfractionated I, S, and M-type granite.

The syenogranite is high-potassium, calc-alkaline rock, rich in Si, and depleted in Al. The A/CNK value is in the range of 1.05–1.16, indicating slight peraluminous. The content of the  $\Sigma\text{REE}$  is close to the crust average level and the existing Eu moderately negative anomaly. The syenogranite does not fall in the range of A-type granite in the  $10,000 \text{ Ga/Al}$ – $\text{Zr}$  and  $10,000 \text{ Ga/Al}$ – $\text{Nb}$  diagrams (Figure 9). The syenogranite presented here shows the characteristics of A-type granite, with  $\text{SiO}_2$  content of 76.22–77.58%,  $\text{K}_2\text{O}$  content of 4.35–4.87%,  $\text{Al}_2\text{O}_3$  content of 12.05–12.56%, and negative anomalies of Sr, Ba, Eu, Ti, and P [57]. The samples fall in the transitional range of I-, S-, and A-type granite in the  $10,000 \text{ Ga/Al}$ – $\text{Na}_2\text{O} + \text{K}_2\text{O}$  diagram (Figure 9a–c), but in the range of A-type granite in the  $(\text{Zr} + \text{Nb} + \text{Ce} + \text{Y})$ – $(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{CaO}$  diagram (Figure 9d). In the standardized diagram of chondrite-normalized REE patterns (Figure 7c), the syenogranite does not show the “V”-shaped pattern or obviously negative Eu anomaly, which is inconsistent with the characteristics of A-type granite [6]. Combined with its relatively low content of  $(\text{Zr} + \text{Nb} + \text{Ce} + \text{Y})$  (132.44–185.68  $\mu\text{g/g}$ ), it is considered that the syenogranite belongs to I-type rather than A-type granite.

### 5.2.3. Petrogenesis of High-K, I-Type Granitic Rocks of the Permian

As discussed above, both the Middle Permian monzogranite and Late Permian syenogranite in the Chifeng area are high-K calc-alkaline I-type granite, and the origins of such granite are still under debate [63,64]. Some geologists uphold the model of fractional

crystallization and crustal assimilation of mantle-derived basaltic magma [65,66], while some insist on the model of mixing of crust-derived and mantle-derived magmas [67–70], and still others attribute the model of partial melting of hydrous medium- to high-K andesitic to basaltic meta-igneous rocks under crustal conditions [63,71,72].

The Permian granitic rocks are classic high-K, I-type granite. They have high silica and alkali contents, low MgO,  $\text{TFe}_2\text{O}_3$ , CaO, and transition-element contents, positive Th, Zr, and Hf anomalies, and negative Ba, Nb, Ta, P, and Ti anomalies in a primitive mantle-normalized diagram. These different characteristics indicate that the primary magma of these rocks originated from the partial melting of the continental crust, and may have been produced by the chemical differentiation of arc-derived magma [73,74]. The low CaO,  $\text{Fe}_2\text{O}_3$ , and MgO contents suggest that the source rock with this granitic component was likely formed under partial melting low-pressure conditions and that its source depths were relatively shallow. The negative anomalies of Nb were caused by the residual of rutile in the melt, since rutile is the main carrier mineral of Nb [75]. Therefore, the obvious depletions of Nb indicate residual rutile in the magma source of the Middle Permian monzogranite. Plagioclase, as the main carrier mineral of Ba, Sr, and Eu, becomes a residual mineral in the magma source in the event of negative anomalies in these elements. The negative Ba, Sr, and Eu anomalies of the granite sample indicate that plagioclase was retained in the residue of the source, or fractionated during magma evolution [76]. In conclusion, these Permian-age high-K, I-type granites were formed by partial melting of a lower crustal source under relatively low-pressure conditions.

### 5.3. Tectonic Implications and Geological Significance

#### 5.3.1. Tectonic Setting

##### Tectonic Setting of the Middle Permian Monzogranite

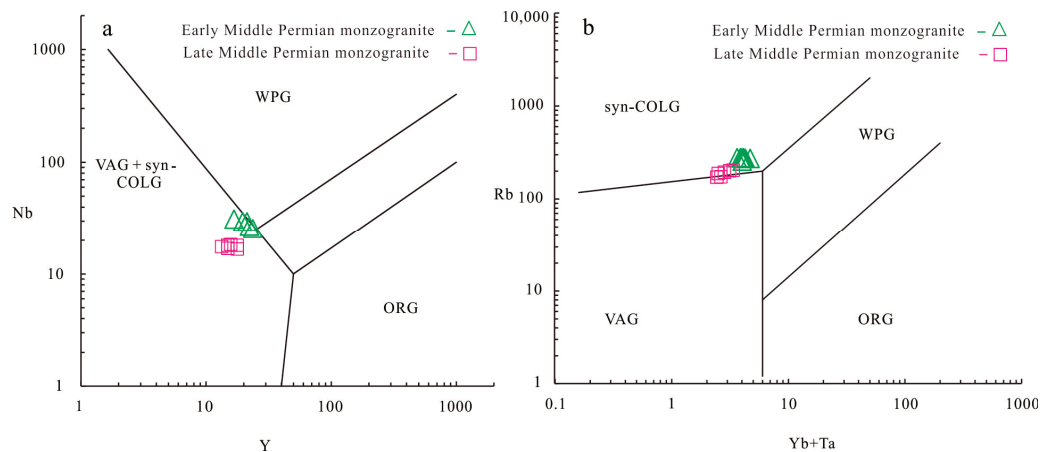
In recent models, some scholars hold that the PAO closed in the Early Permian based on a late Early Permian–Middle Permian alkaline-peralkaline intrusion (276–259 Ma) distributed on the northern margin of the NCC, which indicates a post-collision environment in the Middle Permian [10,21,31]. All these intrusions studied by scholars are in the Jinjing area in the west section of the NCC's northern margin. However, the characteristics of the rock assemblages in the Middle Permian in the Changchun-Yanji area of the eastern section of the northern margin of the NCC show an active continental margin [74], while the widespread diorite, tonalite, and granodiorite indicate that the active continental marginal environment lasted until the Late Permian [38,77]. Therefore, the eastern section of the NCC's northern margin was still under the subduction background of the PAO in the Middle Permian [77]. In this case, then, what is the tectonic background of the Chifeng area in the central of the north margin of the NCC during the Middle Permian?

The Middle Permian granitic magma covers a large area in the Chifeng and is mainly dominated by monzogranite. Geochemical characteristics show that the monzogranite is the I-type granite originating from the lower crust. In the Y-Nb diagram, all samples fall into the volcanic arc and syn-collision area (Figure 10a). However, they fall into the transitional range between the volcanic arc and syn-collision and deviate to the syn-collision area in the  $\text{Yb} + \text{Ta}$  vs.  $\text{Rb}$  diagram (Figure 10b). In the R1-R2 structural environment discrimination diagram, they are in the group of syn-collision granite (Figure 11). Compared to the tectonic environment discriminant ratio of the orogenic granite proposed by Maniar and Piccoli (1989) [51], the monzogranite has characteristics like continental collision granite (CCG). Therefore, the Middle Permian monzogranite in the Chifeng area formed in a syn-collision environment.

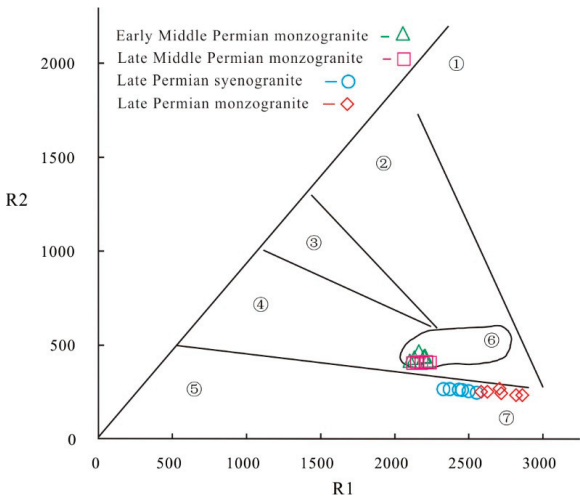
##### Tectonic Setting of Late Permian Granite

Previous studies have shown that the Late Permian–Triassic magmatic rocks on the northern margin of the NCC exhibit post-collision/post-orogeny magmatism in terms of rock assemblage, mineral composition, high-potassium and calc-alkaline-based geochemical characteristics, magmatic evolution and isotope composition [8,28,29,37,53]. In the

R1-R2 diagram (Figure 11), all the Late Permian granites fall within the range of post-orogenic area, suggesting that the granite in the study area is related to the post-orogenic extension environment.



**Figure 10.** (a) Y versus Nb; (b) Yb + Ta versus Rb diagrams of the Middle Permian granites in Chifeng area (after [78]). The fields are ORG—oceanic ridge granites; syn-COLG—syn-collisional granites; VAG—volcanic arc granites; WPG—within-plate granites.



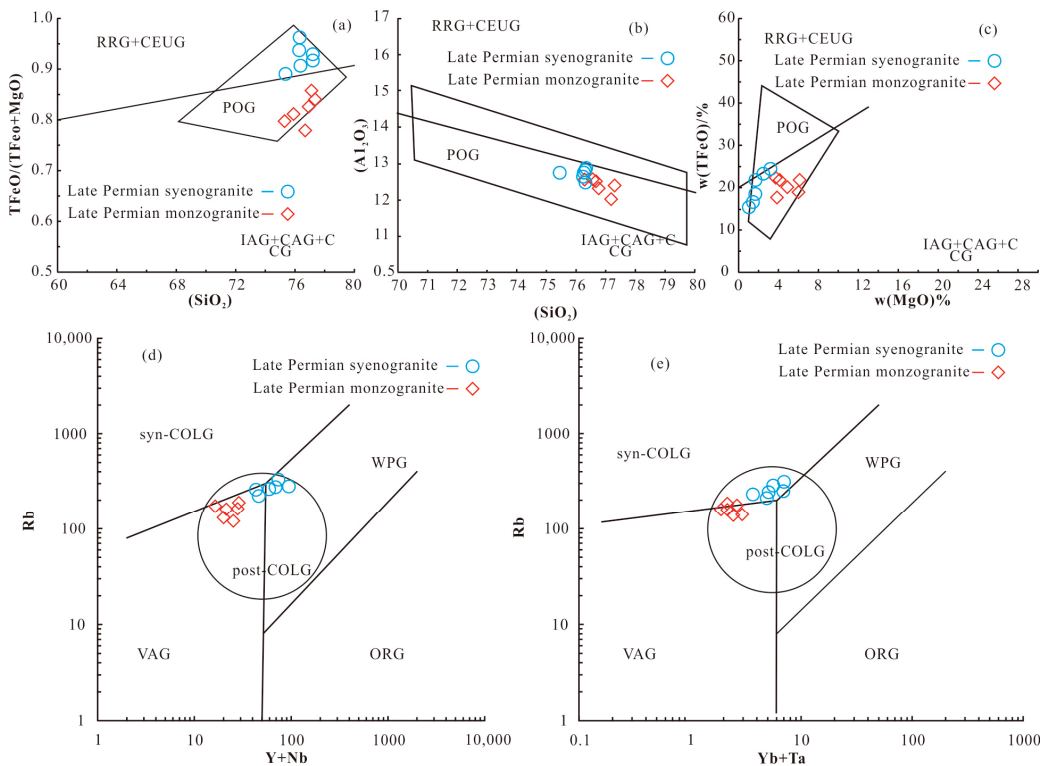
**Figure 11.** Diagram of R2 versus R1 for the Middle-Late Permian granites in the Chifeng area. ①—plagiogranite; ②—active continental margin granite; ③—collisional-orogenic granite; ④—late orogenic granite; ⑤—unorogenic A-type granite; ⑥—collisional granite (S-type); ⑦—post-orogenic granite (after [79]).

The granites that formed in the Chifeng area in the Late Permian and Early Triassic were of I- and A-type. Combined with the available data [8,15,40,53], these granites represent the acidic unit (256–248 Ma). The ophiolite formed from 256 to 246 Ma represents coeval basic members [7,33,35,36]. “Bimodal volcanic rocks” appeared between the northern margin of the NCC and XMOB in the Late Permian–Early Triassic. Previous studies have shown that bimodal volcanic rocks can be formed under the following extensional environments: continental rift, oceanic island extensional, plate margin extensional, post-orogenic extensional, oceanic island arc, mature island arc, and initial back-arc



basin [80,81]. The Late Permian granitic rocks in the Chifeng area are dominated by middle-high potassium calc-alkaline I- and A-type granite, indicating a post-orogenic extensional environment [57,82–86].

The Late Permian granite is characterized by the enrichment of light rare-earth elements and large ion lithophile elements (LILEs), and depletion of high field-strength elements (HFSEs) and elements such as Nb, Ti, and P, showing the characteristics of the granite in the post-collision evolutionary stage of continental orogenic belts. The tectonic environment discriminant map (Figure 12a–c) shows that all granites fall in the range of post-collision granite. In the Y + Nb–Rb and Yb + Ta–Rb diagrams, all the samples fall in the post-collision range, too (Figure 12d,e).



**Figure 12.** Identification diagram of tectonic setting for the Late Permian granites in the Chifeng area. (a)  $\text{SiO}_2$  (wt%) versus  $\text{TFeO}/(\text{TFeO} + \text{MgO})$ ; (b)  $\text{SiO}_2$  (wt%) versus  $\text{Al}_2\text{O}_3$  (wt%); (c)  $\text{MgO}$  (wt%) versus  $\text{TFeO}$  (wt%), IAG— island arc granite; CAG—continental arc granite; CCG—continental collision granite; POG—post-orogenic granite; RRG—rift related granite; CEUG—continental epeirogenic uplift granite (after [51]). (d) Yb + Nb versus Rb, (e) Yb + Ta versus Rb (after [78]), VAG—volcanic arc granites; syn-COLG—syn-collisional granites; WPG—within-plate granites; ORG—oceanic ridge granites; post-COLG—post-collisional granites.

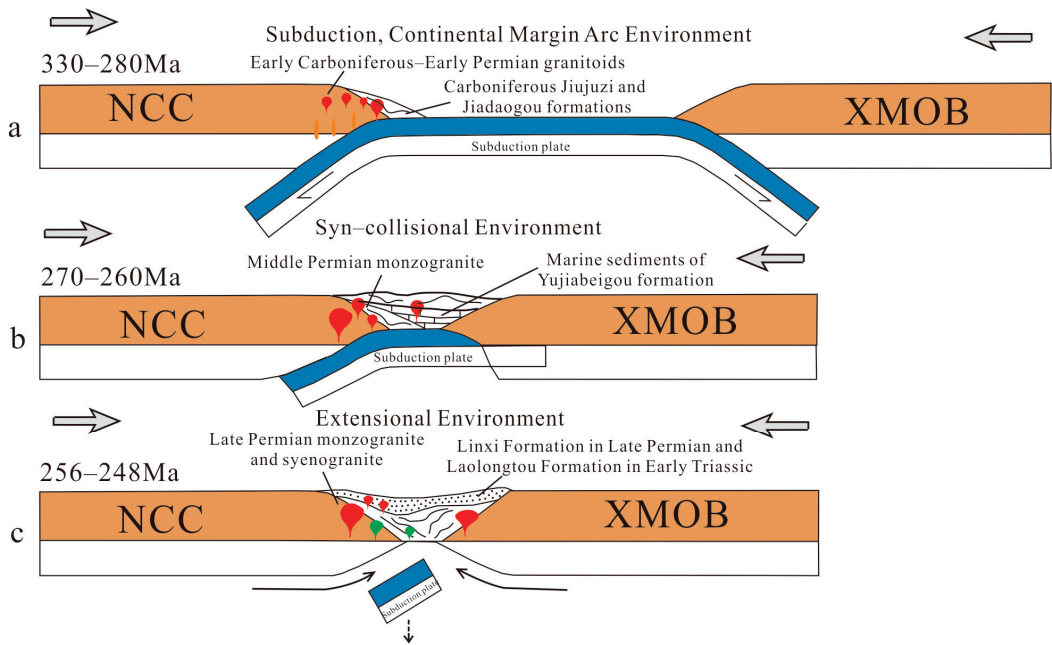
The post-collisional, which is usually considered to begin after the closure of the main ocean, is a complex period when large-scale horizontal block movement still occurred along the giant shear zone [64]. Most post-collision granites in orogenic belts are dominated by medium-high potassium calc-alkaline I-type granite, along with some S-type and A-type granites [87]. The appearance of various types of rock assemblages shows the complexity and diversity of post-collision magmatism [37,87]. In a post collision environment, the pressure decreases under the action of extension, which facilitates rock melting. The extensional environment leads to lithospheric crust thinning and mantle-derived magma

underplating. Sufficient heat then further drives the crust’s partial melting, leading to the formation of many acidic rocks. Consequently, the appearance of these post-collision intermediate-acid igneous rocks may represent a transition environment from continental convergence to extension [64,88].

The following dynamic mechanisms may result in post-collision or post-orogenic magmatism: mantle convective thinning, gravity collapse, slab fragmentation, and delamination. As previously mentioned, the Late Permian–Early Triassic intrusive rocks with post-orogenic characteristics constitute a long and narrow magmatic rock belt, which spreads along both sides of the deep fault zone in the middle section of the northern margin of the NCC. The distribution pattern of Late Permian granites in the study area indicates that they were emplaced in an extensional environment caused by the slab breaking off after final closure of the PAO between the XMOB and NCC [8,89].

5.3.2. Permian Tectonic-Magmatic Evolution in the Chifeng Area

The chronological results show three phases of tectonic-magmatism in the Chifeng area during the Permian. The rock assemblage, geochemical characteristics, genesis, and tectonic setting of the granite from each phase are discussed here. Then, combined with previous research results, the Permian tectonic-magmatic evolution model is constructed (Figure 13), the specific dynamic process of which is as follows.



**Figure 13.** A tectonic evolution model from Carboniferous to Permian in the north margin of the NCC in the Chifeng-Aohan area. NCC, North China Craton; XMOB, Xing’an-Mongolian Orogenic Belt. (a): Subduction, Continental Margin Arc Environment; (b): Syn-collisional Environment; (c): Extensional Environment.

Early Permian–Active Continental Marginal Environment

The Early Permian granite in the Chifeng area formed in an active continental margin environment against the background of the PAO’s southward subduction. The coeval volcanic rocks of the Permian Elitu Formation are also products of the subduction environment [22].

Regionally, the PAO began to subduct southward from the late Early Carboniferous, and magmatic rocks from the late Early Carboniferous to Middle Permian showed charac-

teristics of active continental margins in terms of distribution, rock assemblages, mineral compositions, geochemical characteristics, and isotopes, also known as an Andean active continental marginal arc [12,21,25]. The results of the SHRIMP U-Pb ages and geochemistry of several granite intrusive rocks in the northern margin of the NCC show that the granite has the characteristics of calc-alkaline and subduction-related I-type granite, with an emplacement age of 300–320 Ma. This indicates that there was an Andean continental arc in the NCC's northern margin, and that the PAO still existed in the Late Carboniferous–Early Permian, then eventually closed after 290 Ma [25]. Continuous Late Carboniferous–Early Permian (324–274 Ma) rock assemblages were identified on the northern margin of the NCC, including hornblende gabbro, diorite, quartz diorite, granodiorite, and granite. According to the geochemical characteristics of this group of intrusions, it is believed that the continental arc in the northern margin of the NCC lasted at least 50 Ma [90]. By studying the Early Permian granite in Xilinhot, Li et al. (2018) also confirmed that the northern margin of the NCC was in a continental marginal arc environment from the Late Carboniferous to the end of the Early Permian [22]. By studying the granite in Siziwang Banner, Wang (2014) proposed that the Early Permian quartz diorite formed in a continental marginal arc environment [10]. Li et al. (2018) also held that the Early Permian monzogranite and syenogranite in the western Chifeng area formed in a continental marginal arc environment [22].

From the above studies, the middle section of the northern margin of the NCC was under the tectonic environment of the active continental margin, due to southward subduction of the PAO during the Early Carboniferous–Early Permian (Figure 13a). As a result, Andean-type active continental margin calc-alkaline rock assemblages of west-east trending formed along the northern margin of the NCC. Based on previous data, the existence of the Early Carboniferous–Early Permian intrusive rocks (330–280 Ma) with high-potassium and calc-alkaline characteristics related to subduction implies that the subduction of the PAO lasted for at least 50 Ma [10,13,19,22,54].

The evidence of magmatic events indicates a magmatic arc lasting about 80 Ma in the Jining-Chifeng area in the middle section of the northern margin of the NCC during the Early Carboniferous–Early Permian (330–280 Ma) (Figure 13a). The entire northern margin of the NCC was likely in an active continental margin environment under the subduction, indicating that the PAO was not closed at this time.

#### Middle Permian-Continent-Continent Collision Environment

Geochemical characteristics show that the Middle Permian granite in the study area is monzogranite formed in a syn-collisional environment, indicating that the XMOB collided with the NCC at this time (Figure 13b). Collisional granite with an age of 230–250 Ma was identified in Sonid Left Banner, thus indicating that the PAO closed between 310 and 230 Ma [9,41]; thus, the collision between the XMOB and the NCC lasted from the Middle Permian to the Middle-Late Triassic. Li et al. (2007) discovered granite with SHRIMP U-Pb ages of 229 and 237 Ma and considered it to be S-type granite formed by the crystallization of younger remelted crust. The geochemical characteristics show that the Shuangjingzi intrusions were like syn-collisional granite, implying they likely emplaced in the late-collisional orogenic period. It was thus concluded that the XMOB and NCC collided along the Xar Moron suture zone beginning at about 270 Ma, and ending at 230 Ma [31].

During the early Middle Permian, the plant fossils in the Yujiabeigou Formation (the zircon age of crystalline tuff of which was 270 Ma) all belong to Cathaysian flora, and there was no mixing growth phenomenon, indicating the study area was a Cathaysian flora distribution area. At that time, the Solonker-Xar Moron-Changchun-Yanji suture zone was not yet closed [91], and the PAO developed into an intercontinental residual ocean basin. Subsequently, the oceanic crust was subducted, and continent-continent collision occurred, in turn forming multiple Middle Permian syn-collisional granitic intrusions. The gray-black slate and shale of the Linxi Formation from the Late Permian distributed in the southern margin of Inner Mongolia are rich in freshwater bivalves, leaf limbs, and plant fossils [39].

The Linxi Formation, which has marine sediments at the bottom and delta-lacustrine-delta continental deposits in the middle-upper part, indicates that two large plates had collided and collided together, then jointly assimilated the deposition during the Late Permian [14]. The above evidence shows that the northern margin of the NCC was in a co-collisional environment, and that the monzogranite formed in the Chifeng area.

During the Middle Permian, the Jining area in the western section of the northern margin of the NCC was in a post-collisional environment [10,21,31], yet the Yanbian area in the eastern section was in an active continental margin environment [14,74]. The study area covered in this paper was between these two areas; thus, in the Middle Permian, it was also in a co-collisional environment. This proves that the PAO closed in a “scissor closure” mode from west to east.

#### Late Permian-Early Triassic-PAO Final Closure and Subduction Slab Break-off

The granite of the Late Permian-Early Triassic consisted of A- and I-type granite, and it formed in a post-collisional extensional environment in response to slab fragmentation after the collisional orogeny between the XMOB and the NCC (Figure 13c).

Today, there is much evidence to support the conclusion that the PAO was closed from the Late Permian to the Early Triassic. The build-up types, biota, and tectonic activities on both sides of the Xar Moron fault were obviously different during the Carboniferous-Permian. The paleobiogeographical flora were in disarray until the Middle or Late Permian [92]. Moreover, the Linxi Formation from the Late Permian and the Xingfuzhilu Formation from the Early Triassic were in conformity contact, indicating that the study area was in the same tectonic environment from the Late Permian to the Early Triassic [39]. There were continental deposits and terrestrial flora and fauna fossils in the Late Permian [39], thus indicating that the two major plates had collided and assimilated sedimentation together, resulting in the formation of the Linxi Formation [14]. According to the age of the radiolarian in the siliceous rocks of the Xar Moron, the final mixed accumulation time of the ophiolite belt was proposed to be the Middle-Late Permian [10]. Both the biological extinction event and paleomagnetic evidence indicated that the PAO closed at the end of the Late Permian [24].

There were large quantities of intrusive rocks with continental margin arc magmatic character on the northern margin of the NCC, and the emplacement age ranged from 358 to 260 Ma [21,37,42,93]. The appearance of the post-collisional A-type granite and the bimodal volcanic rocks and the emplacement of the coeval ophiolite also indicated that the PAO completely disappeared during the Permian-Early Triassic, and finally closed along the Xar Moron Suture Zone [7,8,25,28,29,94].

In summary, immediately after the Middle Permian continental collisional orogeny, the subducted slabs remaining in the lithospheric mantle experienced eclogite facies metamorphism and fragmented under the influence of gravity from the Late Permian to Early Triassic (Figure 13c). After the collision between the XMOB and the NCC, the Chifeng area was in an extensional environment. The crust underwent partial melting in response to the underplating of mantle-derived magma, the upwelling of deep asthenospheric mantle materials, increasing heat, and decreasing pressure. As a result, the post-collisional A-type granite of west-east trending, bimodal volcanic rock, and ophiolite formed during the Late Permian-Early Triassic. The lacustrine Linxi Formation had abundant freshwater bivalves and gray-black slate and shale containing leaf limbs and plant fossils [14]. In addition, the paleobiogeographical divisions disappeared. All of these indicate that the PAO finally closed along the Solonker-Xar Moron-Changchun-Yanji Suture (SXCYS) during the Late Permian-Early Triassic, at which time the ocean basin completely disappeared [8,28,29].

## 6. Conclusions

In this study, on the Permian granitic rocks of the northern margin of the NCC, the following conclusions were obtained:

- (1) According to the zircon U-Pb dating results, three events of Permian granitic magmatism were identified in the Chifeng area: (1) a suite of syenogranites and monzogranites dated at ca. 294–284 Ma (Cisuralian); (2) a suite of monzogranites dated at ca. 269–260 Ma (Guadalupian); and (3) a suite of monzogranites and syenogranites dated at ca. 256–254 Ma (Lopingian).
- (2) The two events related to the Middle Permian monzogranite represent I-type granite with Al-saturated, Si- and K-rich, negative Eu anomaly; enrichment of LILEs (Rb, Th, K, and La); and negative Sr, P, and Ti anomalies. The Late Permian syenogranite is rich in Si and K and poor in Al, classified as I-type granite with moderately negative Eu anomalies; enrichment of LILEs (Rb, Th, K, La, and Ce); minor enrichment in HFSEs (Nd, Zr, and Hf); and negative anomalies of Ba, P, Ti, and Sr. These Permian high-K I-type granites were formed by partial melting of the lower crustal source under relatively low-pressure conditions. The Late Permian monzogranite is A-type granite, displaying a “V” shape of rare-earth elements, with strongly negative Eu anomalies; enrichment of LILEs (Rb, Th, U, and K); negative anomalies of Ba, P, and Ti; and obvious Sr negative anomalies, formed in a low-pressure environment caused by tension.
- (3) The Permian tectono-magmatic evolution of the PAO can be divided into three events: (1) Early Permian granite formed in the setting of the PAO subducting to the NCC; (2) Middle Permian granite formed during the collision of the XMOB and the NCC; and (3) Late Permian-Early Triassic granite formed in an extensional setting induced by the slab breaking off after the collision between the XMOB and the NCC, responsible for the closing of the PAO.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/min13121554/s1>, Table S1. LA-ICP-MS zircon U-Pb data for the Permian granites in the Chifeng area; Table S2. Major (wt%) and trace (ppm) element data of Permian granites in the Chifeng area.

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## Article

# In Situ Trace Element and Sulfur Isotope Composition of Pyrite from the Beiwagou Pb-Zn Deposit, Liaodong Peninsula, Northeast China: Implications for Ore Genesis

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**Abstract:** The Beiwagou Pb-Zn deposit, located in the western part of the Liaodong Peninsula, is a carbonate-hosted stratiform deposit with a Pb + Zn reserve of 0.08 Mt @ 4.14% (Pb + Zn). The orebodies occur as conformable layers and lenses and are strictly controlled by strata (the Paleoproterozoic Gaojiayu and Dashiqiao Formations) and lithology (plagioclase amphibolite and dolomitic marble). Given that previous studies have focused only on the mineralization features and mineralogy of deposits, herein, we report in situ trace element analyses of pyrite using LA-ICP-MS, together with in situ sulfur isotopes of pyrite, to constrain the composition, substitution mechanisms, source of sulfur, and sulfate reduction pathways of pyrite in the Beiwagou deposit. Based on pyrite morphology, texture, and chemistry, four pyrite types were identified: subhedral, porous-to-massive pyrite (Py1) related to chalcopyrite; subhedral, porous crushed pyrite (Py2) associated with fine-grained sphalerite; rounded and porous pyrite (Py3) related to the Zn-rich part of the laminated ore; and anhedral, porous-to-massive pyrite (Py4) associated with pyrrhotite, arsenopyrite, sphalerite, and galena. Py1 is characterized by high As, Ag, Cd, In, Au, Cu, and Zn concentrations and low Te, Bi, and Mo concentrations, whereas Py2 has high concentrations of Co and Ni and low concentrations of other trace elements, such as Cu, Zn, Bi, and Te. Py3 is characterized by elevated As concentrations, low Co, Ni, In, W, Te, and Tl concentrations, and varying Pb concentrations, whereas Py4 has low Ag, Cd, In, Zn, Cu, and Mn concentrations and varying W, Co, Ni, Pb, Sb, and As concentrations. Significant correlations between some elements in each pyrite type suggest substitution mechanisms, such as  $(Zn^{2+} + Cu^{2+} + Mn^{2+} + Cd^{2+}) \leftrightarrow 2Fe^{2+}$ ,  $Ag^{+} + (Sb)^{3+} \leftrightarrow 2Fe^{2+}$ , and  $(Te^{+} + Ag^{+}) + Sb^{3+} \leftrightarrow 2Fe^{2+}$ , and the existence of a negative correlation between Co and Ni implies competition between both elements. The strongly positive  $\delta^{34}S$  values (12.11‰–23.54‰) are similar to that of seawater sulfates and likely result from thermochemical sulfate reduction (TSR). In conclusion, the Beiwagou Pb-Zn deposit is a typical SEDEX deposit and mineralization likely occurred during diagenesis.

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**Keywords:** Paleoproterozoic; SEDEX deposit; trace elements; sulfur isotope

## 1. Introduction

The Liaodong Peninsula is located in the southern part of Liaoning Province in Northeast China and hosts numerous medium- and large-scale lead-zinc, gold, and silver deposits. These deposits can be divided into Paleoproterozoic strata-bound Pb-Zn mineralization (e.g., Zhenzigou, Dongsheng, and Beiwagou Pb-Zn deposits [1,2]) and Mesozoic magmatism-related vein-type Pb-Zn-Au-Ag mineralization (e.g., Baiyun and Wulong Au and Gaojiapuzi Ag deposits [3–5]). Previous studies have shown that later magmatism-related Pb-Zn veins were spatially superimposed onto the former stratiform Pb-Zn orebodies (e.g., the Zhenzigou Pb-Zn deposit [2,6]), which is also documented in many ore districts worldwide, e.g., the Yenefrito Pb-Zn mine in the Pyrenees, Spain [7],



the Macmillan Pass Pb-Zn ± Ba deposit in Yukou, Canada [8], and the Red Dog Zn-Pb-Ag district, Northern Alaska [9]. Due to essential base metal elements, studies on the mineralization process of lead-zinc deposits have been pursued by scholars around the globe, and the type of genesis can be classified into SEDEX [2], skarn [10,11], Mississippi Valley-type (MVT) [12], and hydrothermal vein-type deposits [13]. In this context, the ore genesis and metal sources of the Pb-Zn deposits in the Liaodong Peninsula are still debated, as indicated by the Proterozoic seafloor exhalation model [2,14] and the sedimentation metamorphism-hydrothermal reworking model [15,16]. In addition, hypotheses about these strata-bound sedimentary-dominated Pb-Zn deposits formed by either true exhalative processes or subseafloor replacement during sedimentation or early diagenesis are contentious [17–19].

As a ubiquitous mineral in various ore systems, pyrite incorporates numerous trace elements (e.g., Ag, As, Au, Bi, Co, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, and Zn), which are either substituted within the crystal lattice or exist as nanoparticles or micro-inclusions [20,21]. Previous studies have shown that variations in pyrite textures and compositions can reflect changes in the fluid signatures and/or precipitation conditions during the evolution of the hydrothermal system [22–24]. For instance, pyrite has a homogeneous distribution of trace elements in sub-seafloor replacement processes but this is not the case in exhalation processes that involve a significant loss of metals through dispersion on the seafloor [25,26]. Detailed pyrite studies (e.g., those implementing laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)) can detect these subtle variations during ore precipitation and have been commonly applied to porphyry [23], skarn [27], VMS [28,29], and SEDEX [19,30] deposits.

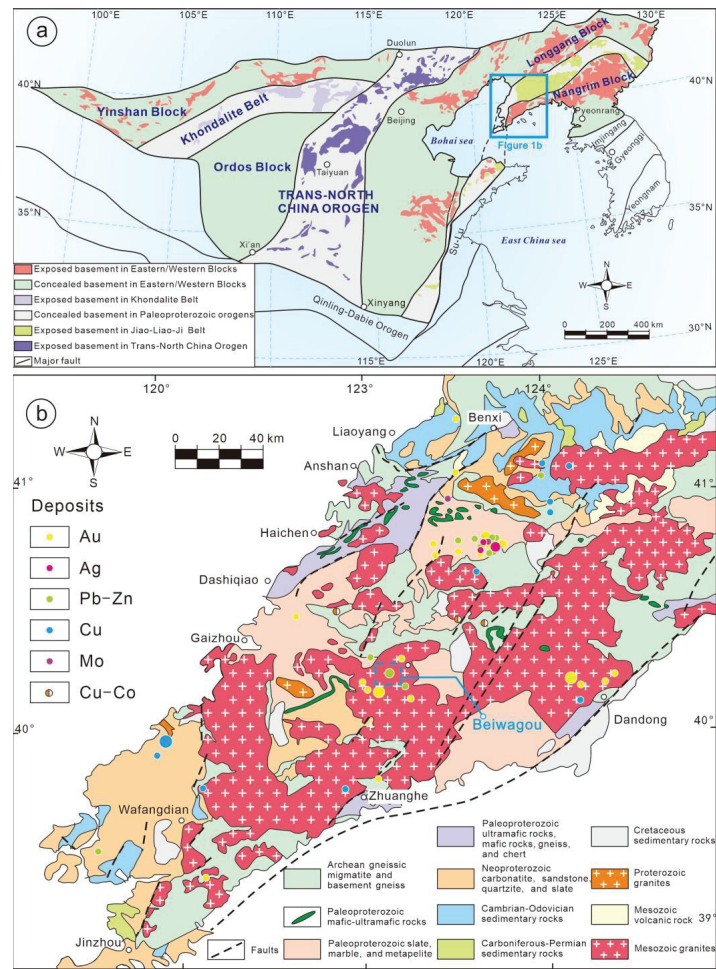
Previous sulfur isotope analyses of sulfide separates have some obvious limitations, especially when considering fine-grained sulfide minerals (e.g., pyrite) with complex textures and multiple sources in superimposing deposits. In situ sulfur isotope analysis using high-spatial-resolution ion microprobe instruments (e.g., those used in secondary ion mass spectrometry (SIMS)) can measure the variability in the sulfur isotope composition of fine-grained intergrown sulfide minerals [31,32]. This method is useful for distinguishing between syngenetic, diagenetic, and epigenetic pyrite in strata-bound sedimentary-dominated Pb-Zn deposits [33,34].

The Beiwagou deposit, a typical strata-bound Pb-Zn deposit in the Liaodong Peninsula, was formed in the Paleoproterozoic Gaojiayu and Dashiqiao Formations and has a Pb + Zn reserve of 0.08 Mt @ 4.14% (Pb + Zn) [35]. Previous studies have focused only on the mineralization features [35] and mineralogy [36] of deposits. The Beiwagou Pb-Zn deposit was proposed to be a sedimentary metamorphic deposit that was modified by later hydrothermal fluids [35]. Nevertheless, there is no convincing evidence on the mineralization process. Here, we present detailed in situ pyrite trace element and sulfur isotope composition measurements that can provide critical information about the pyrite's growth history and conditions and processes of ore formation and can distinguish origins. These results are useful for investigating the relationship between pyrite formation and base metal sulfide mineralization as well as for developing a robust deposit model for the formation of the Beiwagou deposit.

## 2. Geological Setting

The Liaodong Peninsula (the Liaodong Rift Zone, ca. 700 km in the NNE) is bordered by the Tanlu fault in the west and the Japan Sea in the east and records the main geological evolution of the North China Craton (NCC) from the Archean to the Cenozoic (Figure 1). Regionally exposed strata comprise (i) the Archean metamorphic Anshan Group, comprising mainly amphibolite, magnetite quartzite, plagiogneiss, and granulite [37], and (ii) the Paleoproterozoic metamorphic Liaohe Group (including Langzishan, Lieryu, Gaojiayu, Dashiqiao, and Gaixian Formations) comprising a suite of greenschist-epidote-amphibolite-facies metamorphosed clastic and volcano-sedimentary rocks [38], and (iii) Paleozoic-to-Mesozoic clastic and volcanic sequences, for example, Cambrian,

Ordovician, Carboniferous, and Permian-to-Cretaceous rocks [39]. The Anshan Group, a product of the recycling of ancient crustal material, is an Anshan-type BIF iron-ore host that includes the Waitoushan, Qidashan, Xi'anshan, Baoguolao, Xiaolaihe, and Yanglin iron deposits [37,40]. The Liaohe Group hosts strata-bound sedimentary-dominated deposits (including Pb-Zn, Cu-Co, boron, talc, and magnesite deposits) such as the Zhenzigou Pb-Zn [2], Dahenglu Cu-Co [41], Houxianyu boron [42], Yangjiadian talc [43], and Qing-shanhuai magnesite [44] deposits. The protoliths of the metavolcanic rocks from the Liaohe Group were formed at ca. 2.19 Ga and were modified by a metamorphic event around 1.90 Ga. The evolutionary mechanism may be related to arc-continent collision [38,45]. These Paleoproterozoic strata and deposits are partly hosted in the core and limbs of the NWW/NEE-trending anticlines/synclines (e.g., Dashiqiao-Caohekou, Hupiyu-Kuandian, and Gaixian-Xiuyan). Paleozoic-to-Mesozoic volcano-sedimentary units are generally bounded by regional EW/NE-trending faults and their secondary structures (e.g., Fuzhou-Daziyang, Yalvjiang, and Xiongyue-Anshan).



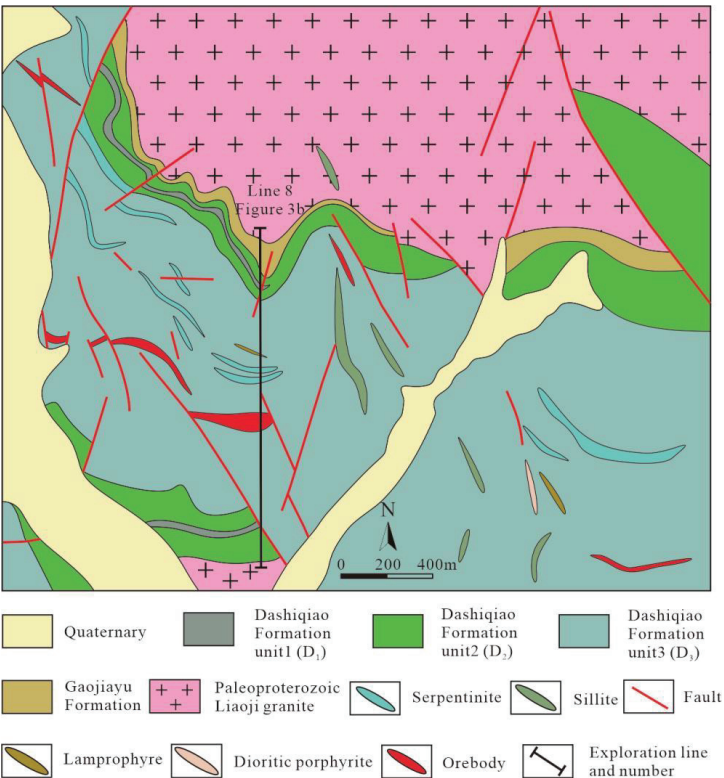
**Figure 1.** (a) Geologic map of the NCC (after [46]). (b) Geological map of the Liaodong Peninsula (after [3]).

Magmatism in the Liaodong Peninsula occurred during four episodes: (1) the Paleoproterozoic (ca. 2332–1756 Ma), (2) the Triassic (ca. 243–210 Ma), (3) the Jurassic (ca. 196–144 Ma), and (4) the Early Cretaceous (ca. 130–120 Ma) [2]. The Paleoproterozoic intrusive rocks comprise mainly gneissic granite, monzogranite, syenogranite, and granitic pegmatite [45,47], and their formation ages are concentrated at approximately 2332–2132 Ma and 1904–1756 Ma, respectively, which are related to collisions and extensions of the Liaonan block to the south and the Longgang block to the north [1,43,45]. Magmatism corresponds to three major orogenic/mobile belts during Mesozoic, namely the Central Asian orogenic belt on its northern margin, the Dabie–Sulu orogenic belt on its southern segment, and the subduction of the Pacific Plate on its eastern margin [2]. The Mesozoic plutons, including monzogranite, granodiorite, biotite granite, quartz diorite, etc. [39,47–51], show a close spatial-temporal-genetic link with the Au–Ag and local vein-type Pb–Zn mineralization (e.g., the Wulong Au, Baiyun Au, and Gaojiapuzi Ag deposits and the Xinling Ag–Pb–Zn deposits [2,52,53]).

### 3. Ore Deposit Geology

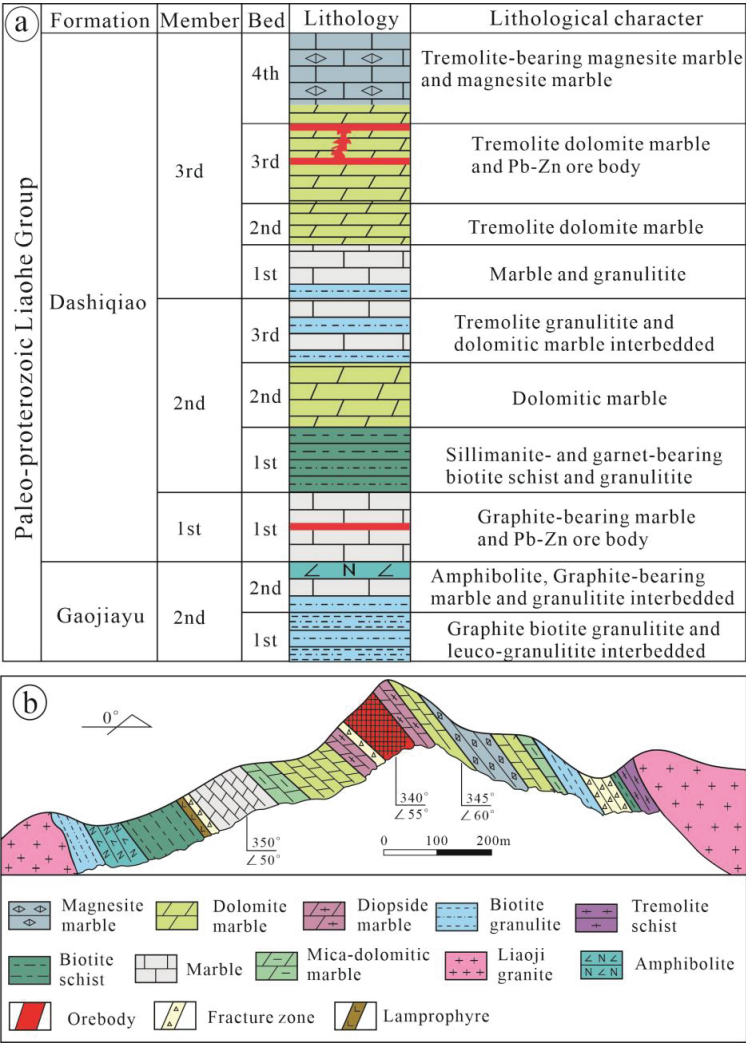
The Beiwagou Pb–Zn deposit (40°27′02″ N, 123°02′08″ E) is located in the western part of the Liaodong Peninsula (Figure 1b). Local strata mainly include the Gaojiayu and Dashiqiao Formations of the Paleoproterozoic Liaohe Group and Quaternary sediments (Figure 2). The Gaojiayu Formation (strike: 290–310°, NE dipping at 50–60°) is mainly distributed in the northern part of the ore district and is comprised of plagioclase hornblende, graphite-bearing marble, and biotite-tremolite-graphite granulite. The Dashiqiao Formation, the chief ore-bearing strata in the ore district, conformably overlies the Gaojiayu Formation and is distributed in the central part of the ore district. It can be divided into three units (e.g., D<sub>1</sub>, D<sub>2</sub>, and D<sub>3</sub>) based on different lithological assemblages. Unit D<sub>1</sub> consists primarily of graphite-bearing marble, whereas unit D<sub>2</sub> comprises garnet/sillimanite-mica schist and dolomitic marble. Unit D<sub>3</sub> contains banded dolomitic and tremolite-bearing marble. Local structures include mainly NW/NE-trending faults and secondary EW-trending faults (Figure 2) and were formed after lead-zinc mineralization, which cut some stratiform orebodies but were limited in scale. Magmatic rocks are mainly discovered in the northern and southern parts of the ore district (Figure 2) and belong to the Paleoproterozoic Liaoji granite that was intruded upon by late Mesozoic magmatism (ca. 157.4–156.3 Ma [54]).

The orebodies of the Beiwagou deposit occur as conformable layers and lenses and are strictly controlled by strata (Paleoproterozoic Gaojiayu and Dashiqiao Formations) and lithology (plagioclase amphibolite and dolomitic marble) (Figure 3). Twelve NW-trending Pb–Zn orebodies (e.g., No. I, I-1, II, III, III-1, and V) have been delineated in the ore district, striking at 280–310° and dipping 35–60° NE. These orebodies are 46–305 m long and 0.61–13.03 m thick, with ore grades of 0.3%–0.79% Pb and 2.58%–9.74% Zn. Beiwagou Pb–Zn mineralization occurs mostly as layers, lenses, and veins and minorly as breccias and dissemination (Figure 4). The late Mesozoic intrusive bodies or dikes and vein-type Pb–Zn mineralization are significantly governed by the EW-trending and NW-trending faults, implying a close connection among them. The scales of vein-type orebodies are finite despite the grades achieving industrial requirements. The ore minerals of the Beiwagou Pb–Zn deposit are predominantly sphalerite, galena, and pyrite, along with minor chalcopyrite, arsenopyrite, marcasite, and pyrrhotite (Figure 5). The gangue minerals include dolomite, tremolite, diopside, talc, taxonite, and quartz. Wallrock alterations are predominantly serpentinization, dolomitization, and silicification, which are closely related to Pb–Zn mineralization.



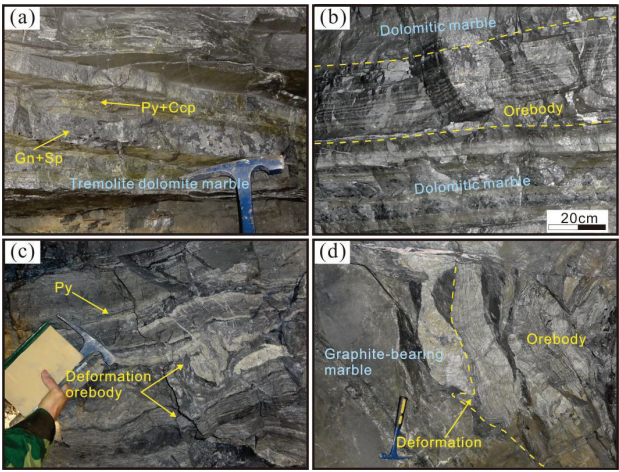
**Figure 2.** Geologic map of the Beiwagou Pb-Zn deposit (modified from [35]).

The delicately laminated nature of the Pb-Zn mineralization at Beiwagou and the surrounding carbonaceous host rocks (e.g., dolomitic marble) of the Gaojiayu and Dashiqiao Formations indicate that deposition occurred in a relatively static tectonic setting (Figures 3 and 4). Localized laminated orebodies show soft-sediment deformation features, such as slumping, folding, and dewatering pipes (Figure 4c,d). These soft-sediment deformation features may be related to the late Paleoproterozoic compressional tectonism (e.g., ca. 1800 Ma, during the “Lvliang Movement”) [53,55,56].

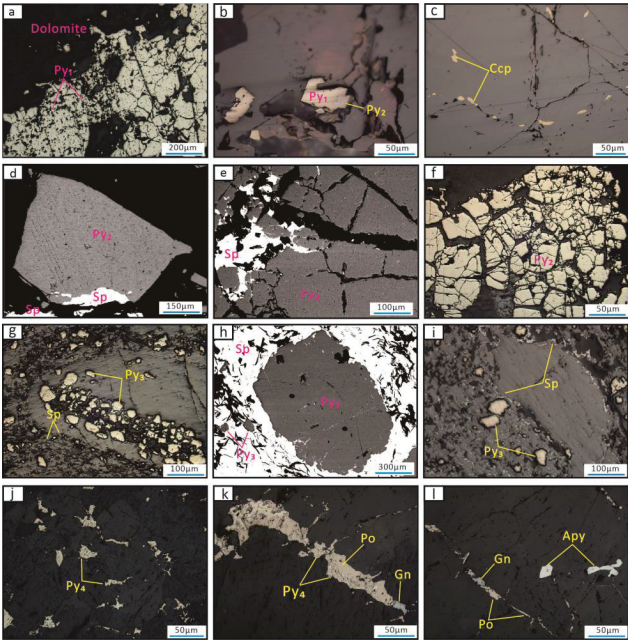


**Figure 3.** (a) Stratigraphic column of the Beiwagou Pb-Zn deposit; (b) The No. 8 exploration section map in the Beiwagou Pb-Zn deposit (modified from [35]).





**Figure 4.** Photographs of strata-bound mineralization in tremolite dolomite marble (a) and dolomitic marble (b) of the Dashiqiao Formation; (c,d) Deformation orebodies in the Beiwagou deposit.



**Figure 5.** Photomicrographs of the Beiwagou Pb-Zn ore textures: (a) Subhedral, porous-to-massive pyrite (Py1); (b) Subhedral, porous-to-massive pyrite (Py1) and subhedral, porous crushed pyrite (Py2) developed in dolomitic marble; (c) Fine-grain chalcopyrite in the Py1; (d,e) Py2 replaced with sphalerite (BSE image); (f) Subhedral, porous crushed pyrite (Py2); (g) Clusters of rounded and porous pyrite (Py3); (h) Py3 replaced with sphalerite (BSE image); (i) Py3 replaced with sphalerite; (j) Anhedral, porous-to-massive pyrite (Py4); (k) Py4 replaced with pyrrhotite and galena; (l) Py4 replaced with pyrrhotite, galena, and arsenopyrite. Abbreviations: Apy = Arsenopyrite; Ccp = Chalcopyrite; Gn = Galena; Po = Pyrrhotite; Py = Pyrite; Sp = Sphalerite.

#### 4. Sampling and Analytical Methods

##### 4.1. Sampling Strategy

The samples were collected from underground mine working sites (e.g., PD3, 5, and 330) and drill cores (e.g., ZK8604, ZK8605, ZK8611, and ZK9006) from the Beiwagou deposit. Based on microscopic observations under transmitted and reflected light, a representative suite of samples were selected for trace element and sulfur isotopic analyses.

##### 4.2. In Situ LA-ICP-MS Analyses

In situ LA-ICP-MS analyses were performed using an Analytik Jena PlasmaQuant MS Elite ICP-MS with a RESOLUTION SE 193 nm excimer laser denudation system at Beijing Createch Testing Technology Co., Ltd. (Beijing, China) [57]. Quantitative pyrite analyses were conducted by ablating a series of trenches in a high-purity He atmosphere to minimize beam attenuation and obtain an even ablation profile. The laser denudation was performed with a beam diameter of 30  $\mu\text{m}$ , a laser frequency of 6 Hz, and an energy density of about 6 J/cm<sup>2</sup>. The analysis time for each sample was 85 s, including a 40 s background with the laser off and 45 s analysis with the laser on. External standards, including synthetic glass standards NIST 611 and 612, as well as MASS-3, BHVO-2G, BCR-2G, and BIR-1G, were used at intervals of one every 10 denudation points for quantitative analyses [58]. Sample and blank signal selection, instrument sensitivity drift correction, and elemental content calculation were performed using ICPMSData Cal (v7.8) software.

##### 4.3. In Situ Sulfur Isotope Analyses

In situ sulfur isotope analysis was performed on the same samples analyzed via LA-ICP-MS at Beijing Createch Testing Technology Co., Ltd (Beijing, China). The analysis was performed using a RESOLUTION SE 193 nm LA system coupled with a Neptune Plus Multi-Collector (MC)-ICP-MS. Pyrite and reference material samples were analyzed using 20 to 30  $\mu\text{m}$  spot sizes at a frequency of 5 Hz with an energy density of 3 J/cm<sup>2</sup>. High-purity helium was used as a carrier gas at a flow rate of 320 mL/min. <sup>32</sup>S and <sup>34</sup>S were statically received simultaneously with a Faraday cup detector array, and the integration time was 0.131 s. Each analysis took approximately 27 s to collect 200 sets of data. Standard WS-1 was utilized as external standard for sulfur isotope fractionation correction. Results are reported as  $\delta^{34}\text{S}$  relative to Vienna Canyon Diablo Troilite (V-CDT) with a precision of  $\pm 0.2\text{‰}$ .

#### 5. Results

##### 5.1. Pyrite Types

Based on pyrite morphology, texture, and chemistry, four pyrite types were identified in the Beiwagou Pb-Zn deposit, including subhedral, porous-to-massive pyrite (Py1) (Figure 5a–c), subhedral, porous crushed pyrite (Py2) (Figure 5d–f), rounded and porous pyrite (Py3) (Figure 5g–i), and anhedral, porous-to-massive pyrite (Py4) (Figure 5j–l). In accordance with the formation sequence of the minerals and the associations of pyrite with the mineral assemblages, the four pyrite species were generated in the order of formation from Py1 to Py4. The detailed characteristics of each type of pyrite are described below.

Py1 was composed of subhedral-to-euhedral pyrite related to the Cu-rich part of the ore. The pyrite crystallites had a narrow range of diameters (40–100  $\mu\text{m}$ , 65  $\mu\text{m}$  on average) and locally occurred with chalcopyrite, commonly <10  $\mu\text{m}$  in diameter.

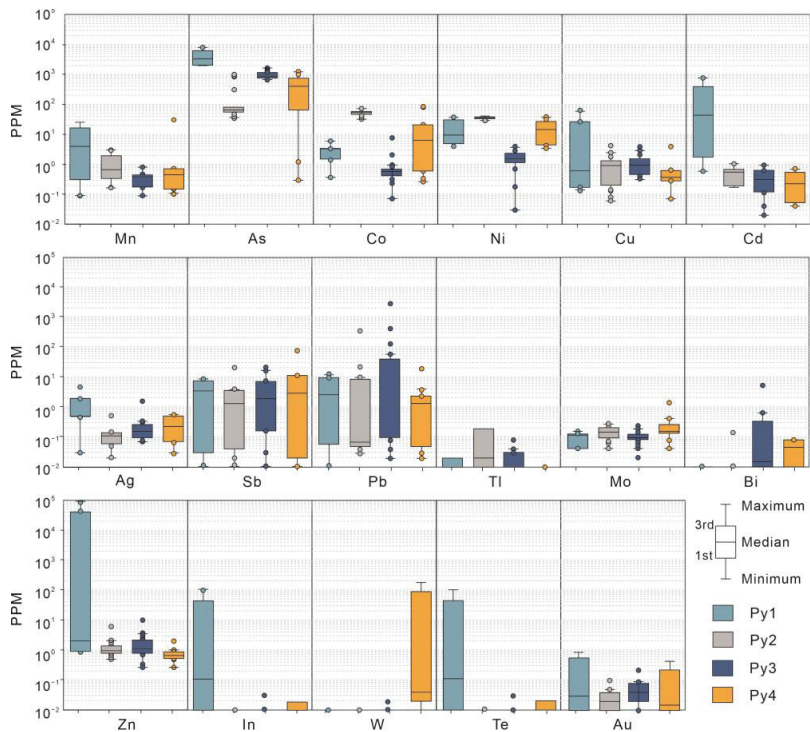
Py2 was identified by its subhedral and crushed crystals, probably due to deformation from late Paleoproterozoic compressional tectonism. The grains were generally coarser (100–1100  $\mu\text{m}$ , average of 400  $\mu\text{m}$ ) than in any other part of the deposit and locally filled with sphalerite (<10  $\mu\text{m}$ ) in the fracture space.

Py3 consisted of irregular and rounded pyrite crystallites related to the Zn-rich part of the laminated ore. These pyrite layers followed the bedding in the dolomitic marble independently or in groups. The grains had a wide range of diameters (<10–800  $\mu\text{m}$ , 40  $\mu\text{m}$  on average) and occurred with sphalerite crystallites, commonly 5 to 20  $\mu\text{m}$  in diameter.

Py4 was defined by its association with pyrrhotite, arsenopyrite, sphalerite, and galena. Numerous macroscopic and petrographic observations have shown that pyrrhotite and sphalerite locally replace anhedral pyrite. The pyrite crystallites also had a wide range of diameters (20–500 µm, with an average of 150 µm).

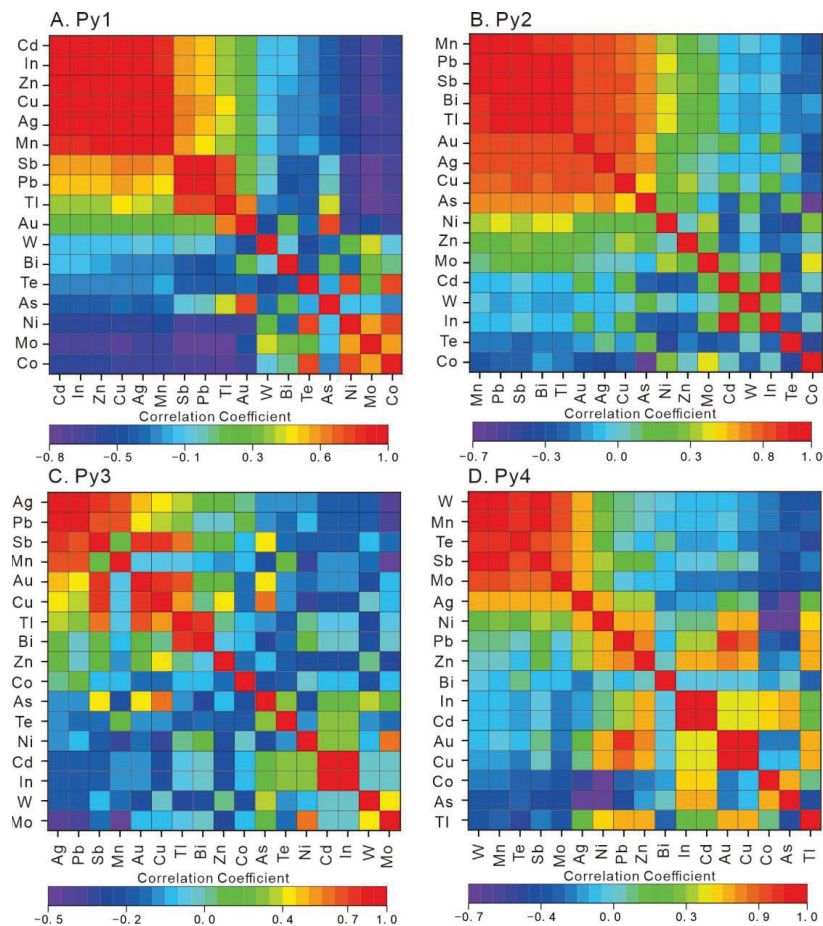
5.2. Trace Element Characteristics of Pyrite

Seventeen trace elements were measured in all the pyrite varieties by LA-ICP-MS analysis (Table S1). Elements such as Mn, As, Co, Ni, Cu, Cd, Zn, In, W, Te, and Au show distinct trace element characteristics for each of the four pyrite types, as illustrated in Figure 6.



**Figure 6.** Simple box and whisker plots of trace element contents of each pyrite type (including Py1, Py2, Py3, Py4).

**Py1:** The trace element composition of the pyrite-chalcopyrite assemblage (Py1) is distinct in that it is characterized by elevated As (1980.75–8044.62 ppm), Ag (0.03–4.75 ppm), Cd (0.59–776.26 ppm), In (0.01–109.93 ppm), Au (0.01–0.88 ppm), Cu (0.14–59.60 ppm), and Zn (0.88–93,853.23 ppm) and low Te (<0.54 ppm), Bi (<0.01 ppm), and Mo (0.03–0.15 ppm) concentrations (Figure 6; Table S1). The data for Py1 formed the largest cluster in the box and whisker plots of trace element content when compared to the other pyrite types (Figure 6). The enriched Zn concentrations of Py1 were scattered within single grains and showed a strong association with Cd, In, Cu, Ag, and Mn and a minor association with Sb and Pb (Figure 7A).



**Figure 7.** Correlation matrices showing element compositions of each pyrite type (including Py1, Py2, Py3, Py4).

Py2: Eighteen spots in four samples containing recrystallized and overgrown pyrite were analyzed. Py2 has higher Co (31.90–72.27 ppm) and Ni (29.52–41.14 ppm) concentrations than the other pyrite types (average = 1.64 ppm (Py3), 15.12 ppm (Py4), and 13.92 ppm (Py1)) (Figure 6; Table S1). But contents of some trace elements are low in Py2 grains, such as Cu (0.06–4.21 ppm), Zn (0.49–6.03 ppm), Bi (0.01–0.14 ppm), and Te (0.11–0.17 ppm). For Py2, positive correlations were observed between Pb and elements including Mn, Sb, Bi, Tl, Au, Ag, Cu, and As, together with the In vs. Cd correlation (Figure 7B).

Py3: Seventeen spots in three samples were observed on the rounded and porous pyrite. The result indicates very little chemical spread that is characterized by elevated As (665.86–1647.51 ppm), low Co (0.07–7.58 ppm), Ni (0.03–3.76 ppm), In (0.01–0.03 ppm), W (0.01–0.02 ppm), Te (0.01–0.89 ppm), and Tl (0.01–0.08 ppm), and varying Pb (0.02–2955.15 ppm) concentrations (Figure 6; Table S1). The scatter of Pb concentrations may be due to small inclusions in the porous pyrite. Positive correlations were observed between Pb and Ag, Sb, Mn, and Au, together with Au and Cu, Au and Tl, Au and Sb, In and Cd, and Bi and Tl (Figure 7C).

Py4: Chemically, the pyrite related to the pyrite-pyrrhotite-arsenopyrite assemblage (Py4) is clearly identified by low Ag (0.03–0.56 ppm), Cd (0.04–0.69 ppm), In (0.01–0.02 ppm), Zn (0.26–1.98 ppm), Cu (0.07–3.92 ppm), and Mn (0.11–25.45 ppm) and varying W (0.03–



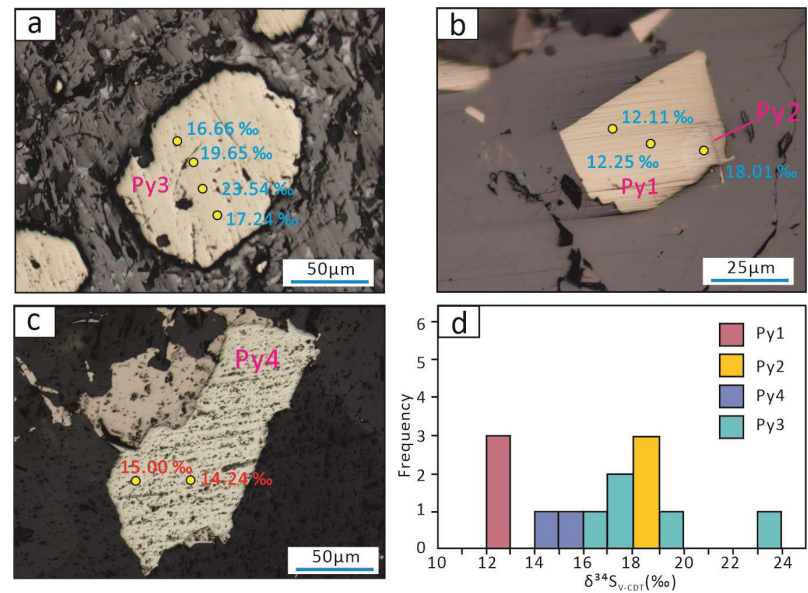
180.75 ppm), Co (0.26–83.87 ppm), Ni (3.47–37.53 ppm), Pb (0.02–19.88 ppm), Sb (0.01–73.94 ppm), and As (0.29–1223.66 ppm) concentrations (Figure 6; Table S1). Py4 displays a broad positive correlation between W and elements such as Mn, Te, Sb, and Mo, together with Au vs. Cu and Cd vs. In (Figure 7D).

5.3. Sulfur Isotope Compositions

The sulfur isotope compositions of Py1, Py2, Py3, and Py4 had slightly narrow and highly positive ranges of  $\delta^{34}\text{S}$  values (Table 1; Figure 8). The sulfide  $\delta^{34}\text{S}_{\text{V-CDT}}$  values are 12.11‰–12.33‰ (mean: 12.23‰; Py1), 18.01‰–18.50‰ (mean: 18.25‰; Py2), 16.66‰–23.54‰ (mean: 18.89‰; Py3), and 14.24‰–15.00‰ (mean: 14.62‰; Py4).

**Table 1.** LA-MC-ICP-MS in situ S isotope compositions of each pyrite type from the Beiwagou Pb-Zn deposit.

| Sample No. | $\delta^{34}\text{S}_{\text{V-CDT}}$ (‰) | Generations |
|------------|------------------------------------------|-------------|
| BWG-4-1    | 12.33                                    | Py1         |
| BWG-4-2    | 12.11                                    | Py1         |
| BWG-4-3    | 12.25                                    | Py1         |
| BWG-4-4    | 18.01                                    | Py2         |
| BWG-7-1    | 18.23                                    | Py2         |
| BWG-7-2    | 18.50                                    | Py2         |
| BWG-3-1    | 14.24                                    | Py4         |
| BWG-3-2    | 15.00                                    | Py4         |
| BWG-6-1    | 16.66                                    | Py3         |
| BWG-6-2    | 17.38                                    | Py3         |
| BWG-6-3    | 19.65                                    | Py3         |
| BWG-6-4    | 23.54                                    | Py3         |
| BWG-6-5    | 17.24                                    | Py3         |



**Figure 8.**  $\delta^{34}\text{S}$  values of representative pyrites: (a–c) Positive  $\delta^{34}\text{S}$  values (TSR signature) in each pyrite type (including Py1, Py2, Py3, Py4); (d) Sulfur isotopic composition of pyrites in Beiwagou deposit.



## 6. Discussion

### 6.1. Partitioning of Trace Elements

Previous studies have demonstrated that many elements (e.g., Ag, Co, Ni, Sn, Zn, Au, Cu, As, Bi, Mn, Te, and Mo) have similar ionic radii to that of  $\text{Fe}^{2+}$  and are easily incorporated into the pyrite lattice via isomorphous substitution [59,60]. Huston et al. [20] suggested that these elements occur as either nonstoichiometric lattice substitutions (e.g., Cu, Mo, and Bi) or stoichiometric lattice substitutions (e.g., Co and Ni) within pyrite crystals. Therefore, the preferential concentration in pyrite can record not only changes in the physicochemical parameters of the parental fluid but also the subsequent deformation, dissolution-remobilization, and recrystallization processes.

The box and whisker plots of the trace element contents show that Py3 is more depleted in Co and Ni than Py4, Py1, and Py2 (Figure 6). This suggests that the fluids are barren in Co and Ni in nature or that little Co and Ni are partitioned to the pyrite via the isomorphous replacement of Fe. In addition, average Co and Ni ratios (1.38) are commonly accepted to indicate pyrite of sedimentary origin, as pyrite related to hydrothermal fluids has Co/Ni ratios of  $\gg 1$  [61,62]. The abundance of As in all pyrite types may be associated with the significant substitution of As for S in the pyrite lattice. The Cd and In contents of all pyrite types showed a positive correlation (Figure 7), indicating that Cd and In entered the pyrite lattice via isomorphism. The low Mo content in the Beiwagou pyrite (up to 1.35 ppm) may reflect widespread oxidizing seawater conditions [63].

Py1 has higher Mn, Cd, As, In, and Te contents than other pyrite types, which is likely caused by surface defects in the pyrite lattice that facilitate elemental residence [64]. Metals with ionic sizes close to that of  $\text{Fe}^{2+}$ , such as  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Cd}^{2+}$ , are generally incorporated into pyrite structures in the form  $(\text{Zn}^{2+} + \text{Cu}^{2+} + \text{Mn}^{2+} + \text{Cd}^{2+}) \leftrightarrow 2\text{Fe}^{2+}$ . The median values of As, Cd, In, and Te in Py1 were higher than those in the other pyrite types (Figure 6), indicating that the bulk replacement of S by As can promote a higher uptake of Cd, In, and Te in a more reduced environment. Py2 has higher Co (31.90–72.27 ppm) and Ni (29.52–41.14 ppm) concentrations than the other pyrite types (average = 13.92 ppm (Py1), 1.64 ppm (Py3), and 15.12 ppm (Py4)) (Figure 6; Table S1). However, a low correlation between Co and Ni was observed for each pyrite type, suggesting that Co and Ni are not direct substitutes for Fe in the pyrite lattice, forming Co- and Ni-bearing sulfides such as Co-pentlandite and pentlandite  $((\text{Fe}, \text{Ni})_9\text{S}_8)$ . In addition, Sb shows positive correlations with Pb, Cu, and As in Py2 (Figure 7), which likely implies that some Sb may present in the pyrite lattice in the form of tetrahedrite  $((\text{Cu}, \text{Fe})_{12}\text{Sb}_4\text{S}_{13})$  and freieslebenite  $(\text{AgPbSbS}_3)$  inclusions and behaves similarly to As when incorporated into the pyrite structure. The high correlation of the Ag, Pb, and Sb contents in Py3 suggests that Sb is incorporated into pyrite as a trivalent cation through the coupled substitution of  $\text{Ag}^+ + (\text{Sb})^{3+} \leftrightarrow 2\text{Fe}^{2+}$ . However, due to its large ionic size, Pb barely enters the pyrite lattice. Most Pb occurs as a solid solution in pyrite and as a minor direct substitution of  $\text{Fe}^{2+} \leftrightarrow \text{Pb}^{2+}$  in the pyrite structure [65]. Py4 and Py1 mostly have Co/Ni ratios  $< 1$ , which indicates that  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  directly substitute for  $\text{Fe}^{2+}$  in pyrite [66,67]. The strong correlation between W, Mn, and Mo in Py4 may be attributed to the incorporation of them into the pyrite structure via the simple substitution equation:  $\text{M}^{2+} \leftrightarrow \text{Fe}^{2+}$ , while the strong correlation between monovalent and trivalent cations, such as Te, Ag, and Sb, may likely be caused by coupled substitutions in the pyrite lattice:  $(\text{Te}^+ + \text{Ag}^+) + \text{Sb}^{3+} \leftrightarrow 2\text{Fe}^{2+}$ .

### 6.2. Source of Sulfur

The  $\delta^{34}\text{S}$  values for each pyrite type are strongly positive (12.11‰–23.54‰; Figure 8; Table 1) and similar to those of seawater sulfates (20‰ [68]), which is the predominant source of sulfur in stratiform, sediment-hosted Zn-Pb polymetallic deposits in most cases (e.g., [34,69]). Owing to the interference of the physicochemical properties of the ore fluid, such as the oxygen fugacity ( $f_{\text{O}_2}$ ), temperature, pH, and ionic strength [70], the sulfur isotopic composition ( $\delta^{34}\text{S}_i$ ) of sulfides generally does not represent the sulfur content ( $\delta^{34}\text{S}_{\text{SS}}$ ) of the ore fluids. In order to reliably estimate the sulfur content of the ore fluids

from the pyrite data, it is necessary to know the temperature at which the pyrite was deposited. However, we could not obtain the formation temperature of the Beiwagou deposit because of a lack of microthermometric data for fluid inclusions and geothermal data for suitable mineral pairs. In most cases, the SEDEX-type Pb–Zn deposits were formed in a medium-low-temperature environment (e.g., 150–270 °C [71]). For this temperature range, the  $\delta^{34}\text{S}$  value of pyrite corresponding to that of  $\text{H}_2\text{S}$  is 2‰ at 150 °C and 1‰ at 270 °C. Thus, we calculated that the  $\delta^{34}\text{S}$  value of  $\text{H}_2\text{S}$  in the ore-forming fluid was 21‰–22‰ of the maximum  $\delta^{34}\text{S}$  value analyzed for pyrite (~23‰) at Beiwagou and the above fractionation between pyrite and  $\text{H}_2\text{S}$ . Obviously, this is consistent with the  $\delta^{34}\text{S}$  value of seawater for the Paleoproterozoic (~20‰ [72–74]). Therefore, we believe that the sulfur in the Beiwagou Pb–Zn deposit was sourced from coeval seawater sulfate.

### 6.3. Sulfate Reduction Pathways

There are several possible mechanisms for generating reduced sulfur (e.g., bacterial sulfate reduction (BSR) and thermochemical sulfate reduction (TSR)); the pathways by which sulfate is reduced to sulfide are still debated and remain contentious. BSR leads to the reduction of sulfate through bacterial respiration in an anaerobic environment, triggering a reaction of  $2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S}$  [75]. TSR, which is an abiogenic process, reduces sulfate to sulfide by oxidizing labile organic carbon during diagenesis [76]. Although these two sulfate reduction pathways occur in different environments and processes, the end products of BSR and TSR are similar. Machel [75] suggested that the sulfur isotope composition of sulfide minerals could be effectively used to distinguish these processes. The presence of non-framboidal pyrite and high positive  $\delta^{34}\text{S}$  values for each pyrite type from the Beiwagou deposit imply that the contribution of BSR sulfur to stratiform sediment-hosted Zn–Pb mineralization is not significant. This is because BSR can shrink the sulfate reservoir and subsequently increase the  $\delta^{34}\text{S}$  value of sulfide as a sulfate-limited closed system in the ambient water column, which requires lower temperatures (<100 °C) to sustain microbial life [77]. BSR commonly leads to very negative  $\delta^{34}\text{S}$  values and synsedimentary framboidal pyrite, which are shown in some SEDEX-type deposits elsewhere, such as the Howard’s Pass SEDEX-type Zn–Pb deposit, Canada (−26 to −4.6‰ [33]), the Dajiangping pyrite deposit, China (−30 to −16‰ [34]), and the Navan Zn–Pb deposit, Ireland (−25 to −5‰ [78]).

As an important role in the formation of either vent-proximal or vent-distal SEDEX deposits, TSR by hydrothermal fluids generally occurs in higher-temperature environments (>100–140 °C) and significantly increase the  $\delta^{34}\text{S}$  value of sulfide (TSR of seawater: 18‰–19‰ [79]). This is consistent with the highly positive  $\delta^{34}\text{S}$  value of each pyrite type at Beiwagou from 12.11 to 23.54‰. Previous studies have experimentally determined that the kinetic fractionation between parent sulfate and daughter sulfide, expressed as  $\Delta^{34}\text{S}_{\text{SO}_4\text{--H}_2\text{S}}$ , is 20, 15, and 10‰ at 100, 150, and 200 °C, respectively [80]. Assuming that the initial  $\delta^{34}\text{S}$  sulfate value was approximately 30‰, the  $\delta^{34}\text{S}$  values (12.11‰–23.54‰) of each pyrite type at Beiwagou are consistent with TSR at 150 to 200 °C ( $\Delta^{34}\text{S}_{\text{SO}_4\text{--H}_2\text{S}} = 10\text{‰}$ –15‰). The temperature at which TSR occurs is consistent with the formation temperature of the SEDEX-type Pb–Zn deposit mentioned above.

### 6.4. Integrated Model for the Genesis of the Beiwagou Deposit

The stratiform nature of the orebodies and sulfide lamination are essential features of the Beiwagou deposit and are generally considered evidence of the SEDEX origin of deposits of this type (e.g., [19,34,81]). Recent studies on the genesis of stratiform sediment-hosted Pb–Zn deposits have shown that the diagenetic model is superior to the original synsedimentary-exhalative model. For instance, Gadd et al. [33] concluded that most of the mineralizing events in the Howard’s Pass SEDEX Zn–Pb district took place in the pores of sediments during diagenesis, as is also the case for the HYC Zn–Pb–Ag and Tom–Jason Pb–Zn–Ba deposits [82,83]. Pyrite is a moderately refractory mineral that can retain its texture and trace composition during low-grade metamorphism but undergoes extensive

recrystallization and trace composition changes in the presence of hydrothermal fluids [84]. Therefore, the texture and compositional changes of pyrite in different generations can effectively reflect the genesis of stratiform sediment-hosted Pb–Zn mineralization in Beiwagou.

As mentioned above, much of the Py3 in the stratified ores of the Beiwagou deposit occurs as rounded and anhedral crystals with a wide range of diameters (<10–800 µm, 40 µm on average), suggesting the replacement of the dolomitic marble during diagenesis. This is an important process in the formation of laminated sulfide ores in SEDEX deposits, such as the McArthur River (HYC), Mount Isa, and Hilton deposits [85,86]. Py4 crystals with anhedral shapes mostly occur in microfractures within the sediment layers (e.g., dolomitic marble), indicating the compaction during diagenesis. In contrast to Py3 and Py4, Py1, on the basis of its euhedral-to-subhedral pyrite cubes, clearly rules out the replacement model and likely precipitated from a mixture of vent fluid and seawater [87]. Owing to the subhedral and crushed crystals in Py2, the deformation from the late Paleoproterozoic compressional tectonism may have occurred within the Beiwagou deposit. Significantly, the trace element and sulfur isotope compositions in each pyrite type in the Beiwagou deposit suggest that Pb–Zn mineralization likely occurred within the sediments during diagenesis rather than only within the water column.

Mixing the exhalative metalliferous fluids with anoxic seawater caused the crystallization of sulfide particles in the water column along the interface between these two fluids. Sulfide aggregates gravitationally settle at the bottom of the basin, forming typical laminated sulfide textures and euhedral-to-subhedral pyrite cubes (e.g., Py1 and Py2) [88]. After deposition, the compaction and lithification during diagenesis could have induced the precipitated SEDEX-forming fluid to enter the unconsolidated carbonaceous sediments by displacing the less dense sediment pore water, as experimentally modeled by Sangster [89]. Hydrothermal chemical deposition near the sediment–water interface caused sulfate to undergo thermochemical sulfate reduction (TSR), thus turning it into sulfide and producing particulate pyrite and sphalerite. Continued compaction and lithification promoted the loss of permeability and vertical dewatering. Diagenetic fluid transport below the sediment–water interface may have deposited galena, sphalerite, and anhedral pyrite by replacing dolomitic marble during diagenesis.

The Liaodong Peninsula experienced an integrated introversion tectonic process that was initiated at ca. 2.2–2.0 Ga during an intra-continental rifting event and transitioned to an active continental margin at ca. 2.0–1.9 Ga, followed by an arc-continent collision at ca. 1.9 Ga and post-collisional extension at ca. 1.9–1.8 Ga [90]. LA-ICP-MS zircon U–Pb chronology data suggest that the Dashiqiao Formation was formed at 2.17–2.13 Ga while, at ca. 1866 ± 9 Ma, it underwent regional metamorphism [91], indicating that the stratiform Pb–Zn mineralization (SEDEX mineralization) in the Beiwagou ore district occurred during the tectonic setting of intra-continental rifting. The Dashiqiao Formation, as the chief ore-bearing stratum in the Beiwagou Pb–Zn district, is characterized by clastic deposition in the lower section, interbedded clastic deposition and carbonate in the middle section, and carbonate in the upper section, implying a mineralization environment of a transgression sedimentary cycle [35].

## 7. Conclusions

The Beiwagou sediment-hosted Pb–Zn deposit comprises stratiform orebodies hosted by carbonaceous rocks (e.g., dolomitic marble) of the Paleoproterozoic Gaojiayu and Dashiqiao Formations, similar to those of many SEDEX deposits. Based on the textural and compositional features of pyrite in the Beiwagou deposit, four pyrite generations (Py1, Py2, Py3, and Py4) were identified. Py1 is characterized by high As, Ag, Cd, In, Au, Cu, and Zn concentrations and low Te, Bi, and Mo concentrations, whereas Py2 is characterized by high concentrations of Co and Ni and low concentrations of other trace elements, such as Cu, Zn, Bi, and Te. Py3 was characterized by elevated As, low Co, Ni, In, W, Te, and Tl, and varying Pb concentrations, whereas Py4 was chemically identified by low Ag, Cd, In, Zn, Cu, and Mn and varying W, Co, Ni, Pb, Sb, and As concentrations. Significant correlations

between some elements in each pyrite type suggest substitution mechanisms, such as  $(\text{Zn}^{2+} + \text{Cu}^{2+} + \text{Mn}^{2+} + \text{Cd}^{2+}) \leftrightarrow 2\text{Fe}^{2+}$ ,  $\text{Ag}^+ + (\text{Sb})^{3+} \leftrightarrow 2\text{Fe}^{2+}$ , and  $(\text{Te}^+ + \text{Ag}^+) + \text{Sb}^{3+} \leftrightarrow 2\text{Fe}^{2+}$ , and the existence of a negative correlation between Co and Ni implies competition between both elements. The average Co and Ni ratios of 1.38 may indicate pyrite of sedimentary origin, whereas the low Mo content (up to 1.35 ppm) may reflect seawater conditions as widespread oxidizing conditions. Therefore, each pyrite type in the Beiwagou deposit demonstrates the contribution of Paleoproterozoic seawater sulfate to mineralization. The ores have strongly positive  $\delta^{34}\text{S}$  values, reflecting thermochemical sulfate reduction at 150 to 200 °C by hydrothermal fluids during diagenesis. Our data suggest that most mineralization events occurred due to the compaction and lithification during diagenesis, which induced sulfate to undergo TSR, loss of permeability, and vertical dewatering.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13091176/s1>, Table S1. Trace element compositions of each pyrite type in the Beiwagou Pb–Zn deposit.xls.

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**Data Availability Statement:** The experimental data used to support the conclusions of this study are included within the article and supplementary materials.

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## Article

# Late Triassic Tectonic Setting in Northeastern Margin of North China Craton: Insight into Sedimentary and Apatite Fission Tracks

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**Abstract:** The closure timing of the Paleo-Asian Ocean and the terminal stage of the Central Asian Orogenic Belt have been widely debated in the geological community. It's known that the gradual scissor-like closure of the Paleo-Asian Ocean occurred from west to east during the Paleozoic period. However, it was not until the Triassic period that the complete closure of the ocean occurred at the northeastern margin of the North China Craton. Nevertheless, there is still much uncertainty regarding the Late Triassic tectonic setting in Northeast China. In this study, we focused on the Upper Triassic Dajianggang Formation, located in the Shuangyang area of central Jilin Province, which is situated on the northeastern margin of the North China Plate. Our aim was to determine the formation age of the Dajianggang Formation by analyzing the detrital particle composition, petrogeochemistry, detrital zircon U-Pb isotope dating, and apatite fission track thermochronology. Our results indicated that the primary sandstone provenance area of the Dajianggang Formation in the Shuangyang area is the island arc orogenic belt. The tectonic background of the sandstone provenance area is mainly a continental island arc environment. The provenance area is mostly composed of felsic rocks with sedimentary tendencies, and some of its material may have originated from the northern margin of the North China Craton or the eroded recycle orogenic belt. LA-ICP-MS U-Pb dating of detrital zircons shows that the Dajianggang Formation formed after  $226.8 \pm 5$  Ma. Moreover, analysis of the thermal evolution history modelling shows that the Dajianggang Formation in the Shuangyang area continued to be deposited and heated in the early stage, and then experienced rapid exhumation around 30 Ma. This suggests that the study area underwent an orogenic process during the early stage of formation, but then transitioned into a post-orogenic extension period, which constrained the final closure of the Paleo-Asian Ocean prior to the Late Triassic period. In addition, our study indicates that the remote effect of the Pacific subduction did not reach the study area until 30 Ma. The central age of the detrital apatite fission track of sample 19DJ-1 is  $94.2 \pm 8.3$  Ma, which is younger than its corresponding stratigraphic age. The two peak ages of the fission track analysis are  $62.9 \pm 5.4$  Ma and  $126 \pm 11$  Ma. These findings provide new evidence for the tectonic evolution of Northeast China and shed light on the Late Triassic tectonic setting, as well as the influence time of subsequent tectonic domains in the southern part of Northeast China.

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**Keywords:** northern margin of North China Craton; Dajianggang Formation; sediment provenance; zircon U-Pb dating; thermochronology

## 1. Introduction

Northeast China is situated at the convergence of the Siberian Plate and the North China Plate, characterized by the superposition of the tectonic domains of the Paleo-Asian, Mongolia–Okhotsk, and Pacific Oceans [1,2]. Its complex tectonic evolution is marked

by the early subduction of the Paleo-Asian Ocean, the intercontinental accretion of the Siberian and North China plates, and the final collage in the Middle Triassic period [3–6]. Furthermore, the geological history of Northeast China has been shaped by the convergence and subduction of two major tectonic plates, the Mongolia–Okhotsk plate and the Paleo-Pacific plate, towards the Eurasian continent since the Late Jurassic period. These geological events have played a crucial role in the formation and evolution of the region, leading to the development of complex geological structures and the sediment of diverse rock types [7–14]. Northeast China has a long and complex tectonic evolution, and thus plays a key role in studying the history of the three tectonic domains present in the region. However, the Late Triassic tectonic setting connecting the two periods has been debatable. This period is particularly significant, as it marks the final closure of the Paleo-Asian Ocean. The precise timing of the Paleo-Asian and Pacific tectonic domain influences on Northeast China remains unclear. Therefore, further geological investigations are necessary in order to shed light on this issue. There is still ongoing debate among geologists regarding the tectonic setting of Northeast China during the Late Triassic period. Some scholars argue that the subduction of the Paleo-Pacific plate to the eastern margin of the northeast Asian continent began during this time, due to the presence of a high-pressure metamorphic belt in the region [15–17]. On the other hand, other researchers propose that the northeastern region experienced an extensional tectonic background in the Late Triassic period, which was related to the extension of the lithosphere after the closure of the Paleo-Asian Ocean, rather than to the subduction of the Paleo-Pacific plate. This view is supported by the presence of alkaline rocks and bimodal volcanic rocks in the area [9,18,19]. Despite the ongoing debate, it is widely acknowledged that the Late Triassic is a crucial period for understanding the tectonic evolution of Northeast China. This period witnesses the final closure of the Paleo-Asian Ocean and marks an important transition in the region's tectonic history. However, while much research has focused on Late Triassic magmatic activity, there is a scarcity of information regarding the tectonic setting reflected by sedimentary events during this time.

Considering the ongoing debate surrounding the Late Triassic tectonic setting in Northeast China, this study focuses on the Upper Triassic Dajianggang Formation, located in the northeastern margin of the North China Craton. Through the utilization of detrital zircon U–Pb isotope dating, major and trace element analysis, detrital particle composition analysis, apatite fission track thermochronology, and other techniques, the goal of this research is to elucidate the Late Triassic tectonic setting and the timing of subsequent tectonic domains in the southern part of Northeast China. By doing so, this paper aims to provide new insights into the overall tectonic evolution of this region.

## 2. Geological Setting and Sample Description

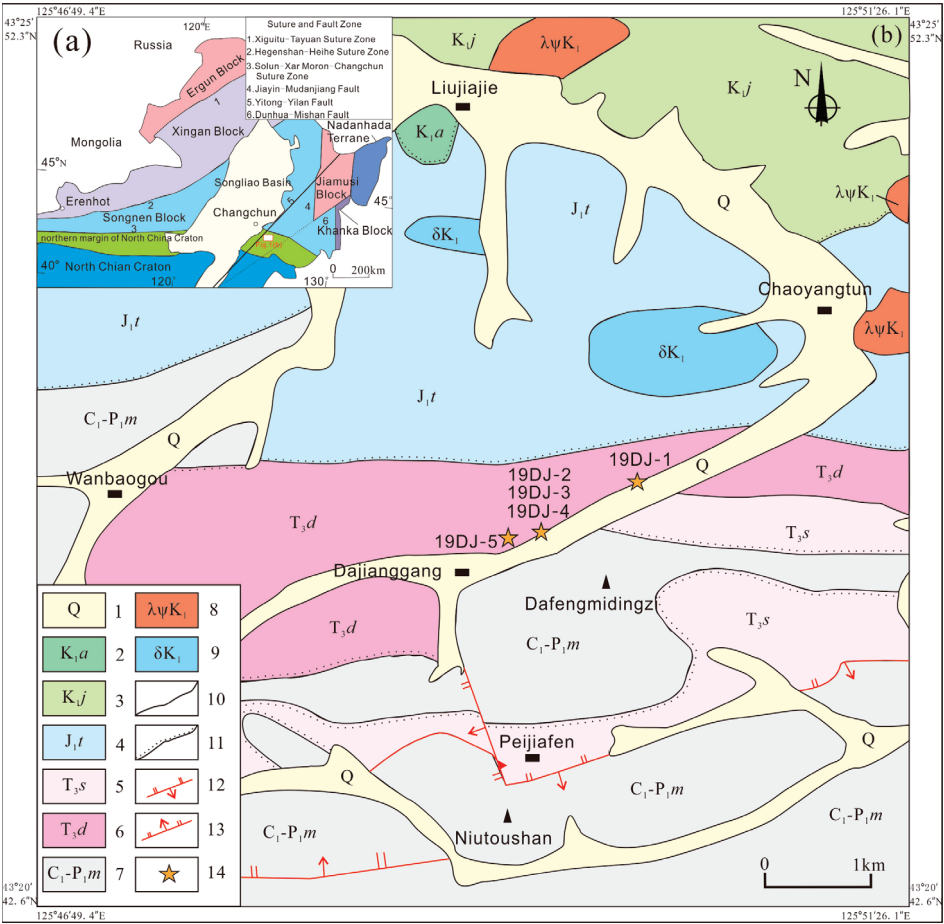
The study area is situated in the central part of Jilin Province, which is geotectonically located in the eastern portion of the accretionary belt on the northern margin of the North China Craton (as depicted in Figure 1a). It is bounded by the Songnen Block and Jiamusi–Xingkai block to the north, the Songliao Basin to the west, and the North China Plate to the south. In the north of the study area lies the Solon–Xar Moron–Changchun–Yanji suture zone, while the Yitong–Yilan fault can be found to the west. Furthermore, the Dunhua–Mishan fault, trending in the northeast direction, cuts through the area to the south.

The geological characteristics of the study area are dominated by Carboniferous, Triassic, Jurassic, and Quaternary strata (Figure 1b). The Dajianggang Formation, which is the focus of this study, is mainly distributed along the northeast fault basin in the syncline axis of Jiangjunling–Dajianggang village, on the southern margin of the Mesozoic basin in the Shuangyang area of central Jilin Province [20]. The Dajianggang Formation is unconformably overlain by the basal conglomerate of the Lower Jurassic Taiyangling Formation, and it unconformably overlies the Permian–Carboniferous Mopanshan Formation and the Upper Triassic Sihetun Formation (Figure 1b) [21]. The Dajianggang Formation is a set of clastic rocks with a positive sequence of fluvial, lake, and marsh



sedimentary facies. The lithological assemblage consists of yellow-green conglomerate, yellow-green sandstone, siltstone, clayslate, and coal-bearing strata, with a total thickness of approximately 1439 m [21,22]. The study area is characterized by the presence of coarse terrigenous clastic rocks with molasse characteristics, which are located at the base of the Changchun–Yanji suture zone complex [16,23,24]. The accumulated thickness of these rocks is over 400 m, with the upper part consisting of coal-bearing sedimentary strata. Fossil evidence suggests that the Late Triassic *Drepanozamites*–*Glossoptillum* assemblage of terrestrial plants existed within these strata [21,24], including species such as *Drepanozamites*, *Neocalamites carrerei*, *N. hoerensis*, *Todites williamsoni*, *Taeniopteris* sp., cf. *Glossophyllum florin*, and *Pityophyllum* sp. [21,22,25]. A strata column section is shown in Supplementary Figure S1.

For the purpose of laboratory research, five representative samples were collected (19DJ-1, 19DJ-2, 19DJ-3, 19DJ-4, and 19DJ-5; sample location shown as Figure 1b). Petrographic observations were carried out on all five samples, while three samples (19DJ-1, 19DJ-4, and 19DJ-5) were subjected to bulk rock geochemical analysis. Additionally, sample 19DJ-1 was chosen for detrital zircon U–Pb dating and apatite fission track testing.



**Figure 1.** (a) Geological sketch map (modified after [23]). (b) Sampling location of study area. 1. Quaternary flood plain: alluvial sand and gravel; 2. Lower Cretaceous Anmin Formation: basalt, andesite, rhyolite, rhyolite containing agglomerate breccia, tuff breccia; 3. Lower Cretaceous Jiuda

Formation: grayish yellow pebbled coarse sandstone and fine sandstone; 4. Lower Jurassic Taiyangling Formation: grayish yellow conglomerate, medium fine and grained sandstone with coarse sandstone, thin conglomerate, upper black-gray siltstone, fine sandstone, mudstone, and coal seam; 5. Upper Triassic Sihetun Formation: Andesite, Andesitic litho-crystalline tuff, dacite, rhyolite litho-crystalline tuff, Dacitic breccia-bearing litho-crystalline tuff; 6. Upper Triassic Dajianggang Formation: black slate, sandstone, conglomerate mixed with acid, volcanic rock, and recoverable coal seam; 7. Permian–Carboniferous Mopanshan Formation: micrite limestone, micrite bioclastic limestone, chert-nodule and chert-banded limestone, dolomitic limestone, dolomite, off-white marble, siliceous rock; 8. Early Cretaceous quartz albite porphyry; 9. Early Cretaceous diorite; 10. Geological boundary; 11. Angular unconformity boundary; 12. Thrust fault; 13. Normal fault; 14. Sampling location.

### 3. Methodology

#### 3.1. Analysis of Geochemical Characteristics

After observation under a microscope, the weathered and altered samples were removed, and three samples from the Dajianggang group were selected for research and analysis. Geochemical analysis of the major, minor, and rare earth elements of the samples was carried out at the Key Laboratory of Mineral Resources Evaluation in Northeast Asia, Jilin University. The fresh sample was pulverized to a particle size of <200 mesh (0.174 mm) using an agate ball mill. The major elements were determined using XRF spectroscopy, and the firing loss (LOI) was determined after the sample powder was ignited at 1000 °C for 1 h. The calcined sample (0.9 g) was added to 9.0 g lithium borate reagent ( $\text{Li}_2\text{B}_4\text{O}_7\text{-LiBO}_2$ ), thoroughly mixed, and fused in a fusion machine between 1050 and 1100 °C. Glass melt samples were prepared from the obtained melt and measured using an X-ray fluorescence spectrometer (XRF). The determination of trace elements, including rare earth elements, was conducted using the inductively coupled plasma mass spectrometry (ICP-MS) method after the melting sample bomb mixed with high purity HF and  $\text{HNO}_3$  was baked in a closed oven for 2 days. The detection limits of some key elements (integration time, 3 s) are as follows ( $\times 10^{-6}$ ): Th (0.05), Nb (0.2), Hf (0.2), Zr (2), La (0.5), and Ce (0.5). Repeated analyses based on the analysis results and international standard reference materials (SRMS) show that the precision and accuracy of the data are better than 5% for major elements and better than 10% for trace elements.

#### 3.2. Zircon U-Pb Isotope Dating

In this paper, sandstone sample 19DJ-1, from the Dajianggang Formation in the Shuangyang area, was chosen for LA-ICP-MS zircon analysis. The zircon dating was carried out at the Key Laboratory of Mineral Resources Evaluation in Northeast Asia, Ministry of Land and Resources, Jilin University, Changchun, China. The use of helium as a carrier gas provided efficient aerosol transport to the ICP and minimized aerosol deposition around the ablation site and within the transport tube [26,27]. Argon was used as the make-up gas and was mixed with the carrier gas via a T-connector before entering the ICP. The analysis spots were 32  $\mu\text{m}$  in diameter, and U, Th, and Pb concentrations were calibrated using  $^{29}\text{Si}$  as an internal standard. The standard zircon 91500 was used as an external standard in order to normalize isotopic fractionation during analysis. The analytical procedures used follow those described by Yuan, Gao [28]. The raw data were processed using the GLITTER program, and uncertainties of individual analyses were reported with  $1\sigma$  error. Weighted mean ages were calculated at  $1\sigma$ , and the data were processed using the IsoplotR program [29]. The zircon Plešovice was dated as an unknown sample and yielded a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $337.5 \pm 2.4$  Ma ( $n = 8, 2\sigma$ ), which is in good agreement with the suggested age of  $337.13 \pm 0.37$  Ma [30]. These methods and procedures ensured the accuracy and reliability of the zircon dating results.

#### 3.3. Apatite Fission Track

Apatite fission track thermochronology is a method that utilizes the damage caused by the spontaneous fission of radioactive  $^{238}\text{U}$  in a mineral lattice [31]. Many previous studies

have been conducted on the annealing of apatite and the characteristics of partial annealing zones. The fission tracks in apatite provide information on the exhumation time, amplitude, rate, and mode of orogenic belts, as well as on the low-temperature domain of the thermal history of mountain exhumation [32,33]. The partial annealing zone of apatite is situated at a temperature range of 60–120 °C, which means that apatite fission track (AFT) data can indicate paleotemperature information of up to 120 °C, and fission tracks above 120 °C cannot be preserved on geological time scales. The accumulation of apatite tracks occurs with time at the temperature of the partial annealing zone or lower, and the age of a fission track can be determined by measuring its density and uranium content [34,35].

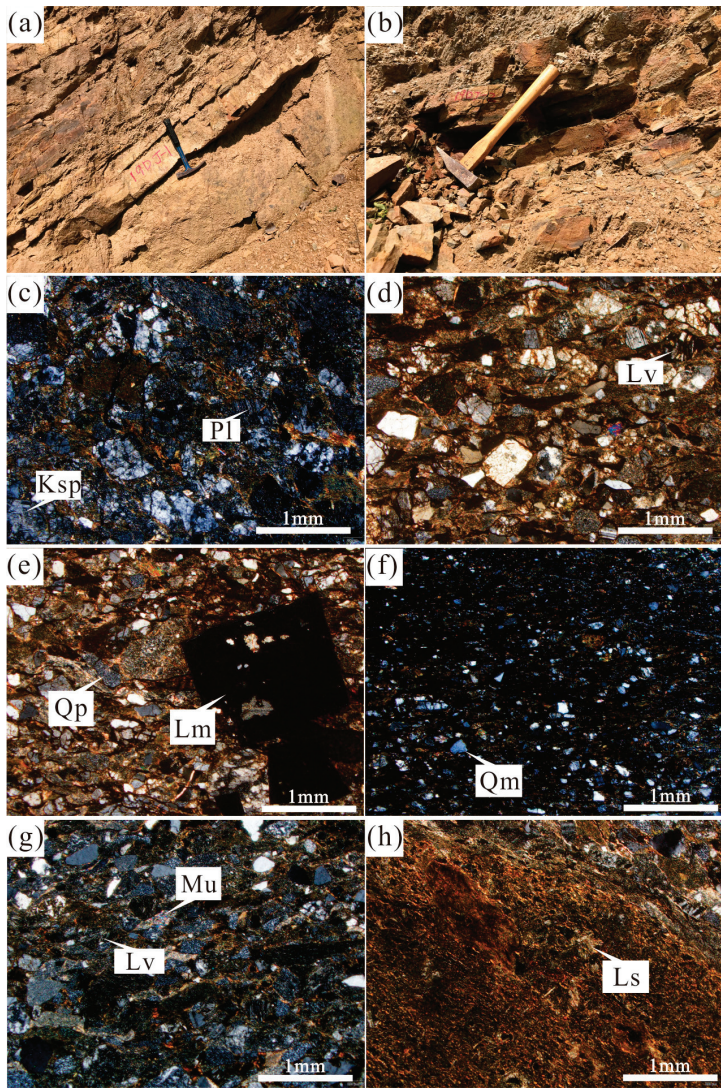
This study employed apatite fission track thermochronology in order to investigate the thermal history of the Dajianggang Formation in the Shuangyang area. The first step in the analysis was the collection of pure apatite grains in sandstone sample 19DJ-1. The sample was subjected to various preparatory procedures, including fragmentation, screening, magnetic separation, and heavy liquid separation in order to obtain pure apatite grains. Following this, apatite mounts in epoxy resin were ground and polished to expose maximum grain internal surfaces, which were then etched with 5.5 N HNO<sub>3</sub> at 20 °C for 20 s to reveal the spontaneous tracks. Low-uranium muscovite was then used as the external detector, while standard uranium glass IRRM540 was used as the dosimeter with which to detect irradiation neutron fluence. Subsequently, the pure apatite grains were irradiated with thermal neutrons at the Radiation Center in Oregon State University, USA. The fission track age of detrital apatite was then measured and analyzed in order to infer the thermal history of the Dajianggang Formation.

Fission track analysis was performed at the Fission Track Dating Laboratory, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, using an automatic fission track counting system, consisting of a Zeiss AxioImager Z2m microscope, ES16 platform, and Fission Track Studio software. Generally, about 80 particles per sample are analyzed to produce reliable statistical results. The fission track's age was determined by the  $\xi$  calibration method [36], and the personal  $\xi$  value was  $257.56 \pm 17.67$ . The  $\chi^2$  test was used to quantify age homogeneity. The value of  $P(\chi^2) > 5\%$  represents a homogeneous age population [37]. The ability to retain fission tracks depends on the mineral and its composition, with apatite being a well-investigated mineral in this regard [34,38–41]. There was no obvious failure in the analyses. Moreover, the variation in Dpar is small and less likely to cause dispersion of the grain ages. For samples with a  $P(\chi^2)$  value less than 5%, reflecting a wide distribution of individual grain ages, the distribution of the observed grain age should be decomposed to correspond to different grain age components of different clastic sources [42]. Track length distributions, combined with track density for a known uranium content, offer valuable insights into the thermal history of geological processes.

#### 4. Petrographic Characteristics and Analysis of Detrital Particle Composition

In this study, the Dajianggang Formation in the Shuangyang area of central Jilin Province was systematically sampled to investigate the petrographic characteristics of the rock. In order to achieve this, five representative samples, namely 19DJ-1, 19DJ-2, 19DJ-3, 19DJ-4, and 19DJ-5, were selected for thin-section analysis. The Dajianggang Formation sandstones exhibit a medium–fine clastic texture and massive structure. They primarily consist of heterogenous matrix support, basement cement, and floating contacts between particles. The detrital particles are predominantly angular to subangular, with a wide range of particle sizes, varying from 0.1 to 2 mm, and the average content of heterogenous matrix is about 46%. Iron cement is the primary cementing agent in the sandstones. The clastic composition is dominated by feldspar, quartz, and lithic fragments, with an average content of feldspar at 29%, quartz at 30%, and lithic fragments at 41%. The rock type can be classified as feldspar lithic sandstone. The feldspar type includes plagioclase and alkaline feldspar, with plagioclase showing obvious polysynthetic twinning (Figure 2c). The alkaline feldspar type comprises potassium feldspar and microcline, with potassium feldspar showing Carlsbad twinning and microcline exhibiting grid twinning. The content

of both types of alkaline feldspar is minimal. Monocrystalline quartz grains are small, irregular, and granular, with wavy extinction and no secondary enlarging. Polycrystalline quartz grains are large and often appear as aggregates or even gravel (Figure 2e,f). The lithic fragments vary in size, shape, and distribution and are dominated by volcanic and sedimentary lithic fragments, with rare metamorphic lithic fragments. Some volcanic lithic fragments show an obvious lattice made up of plagioclase (Figure 2d,g). Euhedral limonite is also observed (Figure 2e). The detritus exhibits poor sorting and roundness, uneven particle size, and a low component maturity, indicating that it originates from a nearby provenance area and has not been transported for a long distance or time.



**Figure 2.** (a,b) Field photos of sandstone in the Dajianggang Formation; (c) microscopic photos of 19DJ-1; (d,e) microscopic photos of 19DJ-2; (f) microscopic photos of 19DJ-3; (g) microscopic photos of 19DJ-4; and (h) microscopic photos of 19DJ-5. Pl—Plagioclase; Ksp—K-feldspar; Qp—Polycrystalline quartz; Qm—Monocrystalline quartz; Ls—Lithic fragment of sedimentary rock; Lv—Lithic fragment of volcanic rock; Mu—Muscovite; Lm—Limonite.



The Gazzi–Dickinson point method was used to perform microscopic thin section analysis and Dickinson sandstone model analysis. The compositional analysis of the samples revealed the presence of monocrystalline quartz, polycrystalline quartz, total quartz, plagioclase, potassium feldspar, sedimentary rock debris, volcanic rock debris, total debris, muscovite, biotite, cement, or matrix. Such detailed petrographic analysis of the rock can provide valuable insights into the sedimentary environment and provenance of the rock [43,44]. The Gazzi–Dickinson point-counting method was used to conduct microscopic analysis of thin sections of five samples (19DJ-1, 19DJ-2, 19DJ-3, 19DJ-4, and 19DJ-5) selected from the Dajianggang Formation in the Shuangyang area of central Jilin Province. Each component’s node count, obtained from pattern analysis, was converted into a percentage in order to determine its content in the sample. The statistical results of both the point-counting method and pattern analysis are presented in Table 1 and Figure 3, respectively. It should be noted that the section of sandstone sample 19DJ-5 contains gravels with diameters ranging from 3 to 12 mm and a content of 40%–50%; therefore, fewer than 300 particles met the statistical requirements.

Table 1. Analysis results of sandstone clastic particles in the Dajianggang Formation.

| Group                 | Sample | Qm | Qp | Pl | Ksp | F   | Ls | Lv | Lm | Mu | Bt | M   | Total | Qt  | L  | Lt  |
|-----------------------|--------|----|----|----|-----|-----|----|----|----|----|----|-----|-------|-----|----|-----|
| Dajianggang Formation | 19DJ-1 | 39 | 14 | 70 | 15  | 85  | 33 | 21 | 0  | 0  | 11 | 192 | 395   | 53  | 54 | 68  |
|                       | 19DJ-2 | 54 | 28 | 82 | 20  | 102 | 45 | 44 | 0  | 7  | 0  | 141 | 421   | 82  | 89 | 117 |
|                       | 19DJ-3 | 23 | 11 | 32 | 11  | 43  | 9  | 47 | 0  | 0  | 0  | 235 | 368   | 34  | 56 | 67  |
|                       | 19DJ-4 | 65 | 54 | 43 | 15  | 58  | 18 | 29 | 0  | 6  | 0  | 183 | 413   | 119 | 47 | 101 |
|                       | 19DJ-5 | 11 | 27 | 11 | 8   | 19  | 27 | 25 | 0  | 0  | 0  | 59  | 168   | 38  | 52 | 79  |

The values in the table are the numbers of various mineral particles counted using the Dickinson point method, the number of skeleton mineral components counted using Total, and the percentage of cement or matrix calculated using percentage. Qm—monocrystalline quartz; Qp—polycrystalline quartz; Qt—total quartz (Qt = Qm + Qp); F—feldspar (F = Pl + Ksp; Pl—plagioclase; Ksp—potassium feldspar); Ls—lithic fragment of sedimentary rock; Lv—lithic fragment of volcanic rock; Lm—lithic fragment of metamorphic rock; L—lithic fragments (L = Ls + Lv + Lm); Lt—total lithic fragments (Lt = L + Qp); Mu—Muscovite; Bt—biotite; M—cement or matrix.

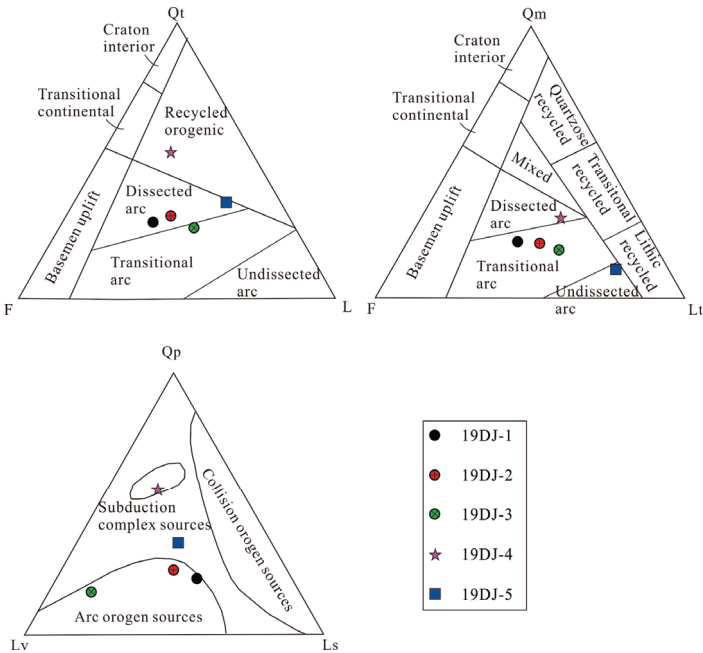


Figure 3. Structural diagram of sandstone skeleton triangle of the Dajianggang Formation (modified after [43]).



According to the statistical results of the detrital composition of sandstone and the Dickinson sandstone model analysis theory, Qt-F-L, Qm-F-Lt and Qp-Lv-Ls triangular diagrams were illustrated (Figure 3).

As shown in Figure 3, the diagrams reveal that some of the samples of the Dajianggang Formation belong to the side close to the dissected arc region within the recycled orogenic belt in the Qt-F-L diagram, while others fall on the dissected arc region, and the rest fall on the side close to the dissected arc region within the transitional arc region. In the Qm-F-Lt diagram, some samples are situated in the dissected arc area close to the transitional arc region, while most of them fall in the transitional arc area, and the remaining samples are located in the undissected arc area close to the transitional arc side. Regarding the Qp-Lv-Ls diagram, most of the Dajianggang Formation samples are distributed in and around the provenance area of the island arc orogenic belt, and some of them are found in the subduction complex belt. Based on the above analysis, it can be inferred that the sandstone provenance area of the Dajianggang Formation in the Shuangyang area is complex, mainly consisting of the provenance of the island arc orogenic belt.

5. Analysis of Geochemical Characteristics

The geochemical characteristics of clastic sedimentary rocks play a crucial role in understanding their origins, tectonic settings, and evolutionary processes. The composition of sedimentary rocks is closely linked to their provenance, tectonic environment, and depositional history. Studies have demonstrated that the texture of sandstones and their major element geochemistry can provide valuable information for evaluating provenance and tectonic settings. However, inactive trace elements and rare earth elements are even more effective in providing information on provenance. Hence, this study aims to examine the provenance of sandstones through the analysis of major elements and trace elements.

5.1. Geochemical Characteristics of Major Elements

The geochemical analysis results of the major elements of three sandstone samples from the Dajianggang Formation are shown in Table 2. The SiO<sub>2</sub> content of the sandstone is high, ranging from 63.01% to 72.92%, with an average of 66.97%. Meanwhile, the Al<sub>2</sub>O<sub>3</sub> content is between 13.67% and 16.79%, with a mean of 15.69%, and the TFe<sub>2</sub>O<sub>3</sub> content is between 3.82% and 8.37%, with a mean of 6.14%. The contents of CaO and MgO, which are indicators of carbonate rocks, are relatively low, ranging from 0.36% to 0.63% and 0.92% to 2.26%, respectively (the average contents are 0.49% and 1.38%, respectively). These results suggest that the proportion of carbonate rocks in the sample is minimal. The K<sub>2</sub>O and Na<sub>2</sub>O contents are average, ranging from 1.69% to 1.75% and 2.68% to 4.30% (average contents are 1.75% and 2.68%, respectively). The TiO<sub>2</sub> content ranges from 0.67 to 0.89, with an average content of 0.78%. The sample contains small amounts of P<sub>2</sub>O<sub>5</sub> and MnO (ranging from 0.13% to 0.26% and 0.07% to 0.11%, with average contents of 0.20% and 0.09%, respectively), suggesting the presence of accessory minerals, such as apatite and epidote.

Table 2. Major elements of the Dajianggang Formation sandstone in the Shuangyang area (wt%).

| Sample | Lithology               | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | TFe <sub>2</sub> O <sub>3</sub> | CaO  | MgO  | K <sub>2</sub> O | Na <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | MnO  | LOI  | Total | CIA   | CIW   | ICV  |
|--------|-------------------------|------------------|--------------------------------|---------------------------------|------|------|------------------|-------------------|------------------|-------------------------------|------|------|-------|-------|-------|------|
| 19DJ-1 | conglomeratic sandstone | 64.98            | 16.6                           | 6.23                            | 0.63 | 0.96 | 1.71             | 4.3               | 0.89             | 0.26                          | 0.07 | 3.19 | 99.82 | 62.23 | 66.88 | 0.89 |
| 19DJ-4 | sandstone               | 63.01            | 16.79                          | 8.37                            | 0.36 | 2.26 | 1.69             | 3.04              | 0.77             | 0.13                          | 0.11 | 3.12 | 99.66 | 69.15 | 74.8  | 0.99 |
| 19DJ-5 | greywacke               | 72.92            | 13.67                          | 3.82                            | 0.48 | 0.92 | 1.75             | 2.68              | 0.67             | 0.22                          | 0.08 | 2.53 | 99.73 | 65.56 | 72.12 | 0.76 |

In order to evaluate the intensity and nature of weathering of the source rock in the provenance area, the difference in stability of major element oxides can be utilized. The chemical index of alteration (CIA) and chemical index of weathering (CIW) have been proposed for this purpose, allowing for the quantitative analysis of weathering intensity.

The chemical index of alteration (CIA), first introduced by Nesbitt and Young [45], is calculated based on the mole number of oxides CaO, Na<sub>2</sub>O, K<sub>2</sub>O, and Al<sub>2</sub>O<sub>3</sub>. Its formula is

widely used in geochemical studies and can provide insight into the degree of chemical alteration of the source rock. The specific formula is as follows:

$$\text{CIA} = [(\text{Al}_2\text{O}_3)/(\text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Al}_2\text{O}_3)] \times 100$$

Under natural conditions, the CIA value of rocks is usually greater than 50. The mole number of CaO, Na<sub>2</sub>O, and K<sub>2</sub>O in rocks decreases gradually with increasing weathering intensity, while the proportion of stable oxide Al<sub>2</sub>O<sub>3</sub> increases accordingly, resulting in an increase in the CIA value. A range of 50–60 in the CIA value indicates initial weathering, a range of 60–80 indicates moderate weathering, and a CIA value greater than 80 indicates intense weathering [46]. The formula for the CIA calculation involves the mole number of each oxide, with CaO\* representing the mole number of CaO in silicate minerals, excluding phosphate and carbonate minerals. Nesbitt and Young [45] first introduced the CIA as a quantitative parameter for evaluating the intensity of weathering of source rocks in the provenance area, allowing for the determination of the intensity and nature of weathering.

In evaluating weathering intensity using the chemical index of alteration (CIA), it is important to consider the potential influence of potassium metasomatism, which can cause the illitization of kaolinite and result in a lower calculated CIA value than the actual weathering intensity. In order to address this issue, Harnois [47] introduced the chemical index of weathering (CIW) by removing K<sub>2</sub>O from the CIA formula. The CIW formula is as follows:

$$\text{CIW} = [(\text{Al}_2\text{O}_3)/(\text{CaO}^* + \text{Na}_2\text{O} + \text{Al}_2\text{O}_3)] \times 100$$

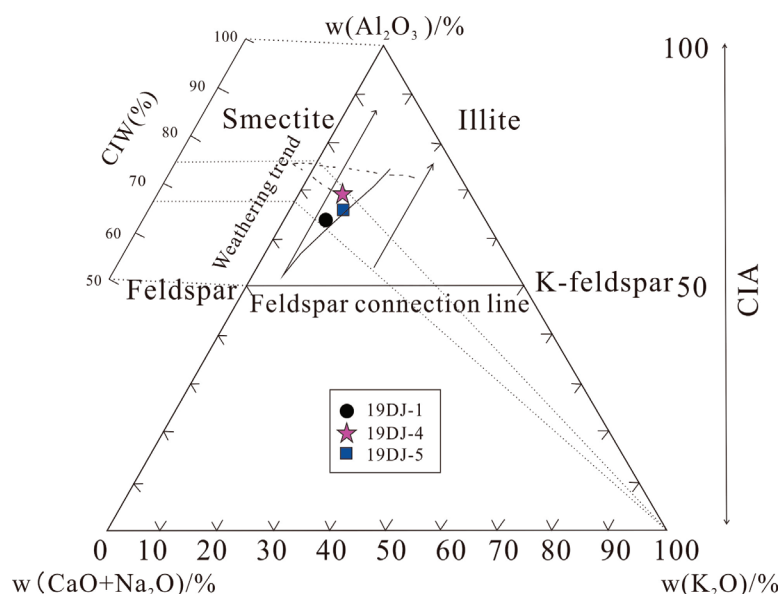
On the A-CN-K weathering triangle diagram, the CIW value of a rock can be determined by projecting the line connecting the K endpoint and the sample point onto the edge of A-CN. This diagram is widely used in the field of geochemistry to assess the degree of weathering and chemical alteration of rocks, particularly in the study of soils and sediments. The A-CN-K diagram plots the percentage of Al<sub>2</sub>O<sub>3</sub> (A), CaO + Na<sub>2</sub>O (CN), and K<sub>2</sub>O (K) on a ternary plot, which enables geochemists to assess the extent of weathering and alteration based on the position of a given sample in the plot. The CIW value calculated from the A-CN-K diagram provides a more accurate estimate of weathering intensity than does the CIA, as it eliminates the potential bias introduced by potassium metasomatism.

The above methods for evaluating weathering intensity were applied to the sandstone of the Dajianggang Formation in the Shuangyang area, yielding an average CIA value of 65.65, which indicates a moderate level of weathering intensity (as shown in Table 2). In the A-CN-K diagram (Figure 4), in order to correct for potassium metasomatism, the average CIW was obtained by projecting a line connecting the K endpoint and the sample point, resulting in a value of 71.27, which is approximately 6 higher than the CIA value. Taken together, both the CIA and CIW values suggest that the sandstone of the Dajianggang Formation underwent moderate weathering during diagenesis. Additionally, the ICV, which is the indicator of compositional variation introduced by Cox, Lowe [48], can also be utilized to estimate the composition of clastic sandstone, with the following calculation formula:

$$\text{ICV} = (\text{Fe}_2\text{O}_3 + \text{Na}_2\text{O} + \text{CaO} + \text{K}_2\text{O} + \text{MgO} + \text{MnO} + \text{TiO}_2)/\text{Al}_2\text{O}_3$$

The ICV value is a useful indicator for estimating the composition of clastic sandstone, and it varies depending on the mineralogical composition. Clastic source rocks composed mainly of non-clay minerals typically have higher ICV values than those composed mainly of clay minerals. Sandstones composed primarily of biotite, amphibolite, or pyroxene, with low clay mineral content, usually have ICV values greater than 1 and are often associated with sediments from the first cycle in tectonically active areas [48]. In contrast, first-cycle terrigenous sediments that have undergone intense weathering and have been in the clay for a long time may have ICV values less than 1 due to further weathering. The ICV value of the sandstone from the Dajianggang Formation ranges from 0.76 to 0.99, with an average value of 0.88, which is less than 1, indicating that it may be the result of recycled sediments or sediments that have undergone intense weathering. Therefore, it can be concluded

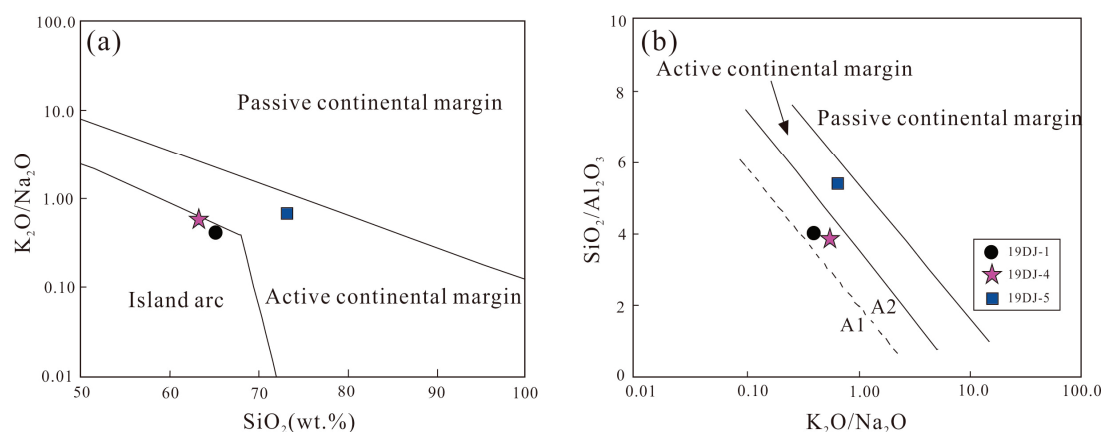
that the sandstone debris of the Dajianggang Formation has undergone the process of terrigenous recycling.



**Figure 4.** Weathering diagram of the major element A-CN-K of Dajianggang Formation sandstone in the Shuangyang area (Modified after [45]).

The geochemical characteristics of clastic sedimentary rocks are influenced by the composition of their source rocks. These characteristics not only reflect the type of source rock from a geochemical perspective, but also provide information about the tectonic setting of the formation. This is because plate tectonic activities are crucial in controlling the composition of source rocks, the sedimentary topography of provenance areas, the diagenesis of sedimentary rocks, the deposition rate, and the weathering intensity. The changes in geochemical characteristics can thus reflect the different tectonic settings of the sedimentary rocks. While it can be challenging to determine the relationship between geochemical characteristics and the tectonic setting of detrital sedimentary rocks throughout their long sedimentary history, researchers have established the relationship between them by analyzing the geochemical characteristics of sedimentary rocks with similar tectonic settings and studying their mechanisms from the perspective of diagenesis. Therefore, based on previous studies, we can discuss the tectonic background of the sandstone formation in the Dajianggang Formation in the Shuangyang area.

Roser and Korsch [49] developed a bivariate diagram based on the geochemical characteristics of sandstones and mudstones from modern tectonic settings to determine the tectonic background of sedimentary provenance. The diagram is based on the  $\text{SiO}_2\text{-K}_2\text{O}/\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}/\text{Na}_2\text{O-SiO}_2/\text{Al}_2\text{O}_3$  ratios, containing three categories of tectonic settings: active continental margin, passive continental margin, and island arc provenance. By projecting the geochemical data of sandstones from the Dajianggang Formation in the Shuangyang area onto this diagram (Figure 5), except for the graywacke sample 19DJ-5, the other two samples form in the island arc tectonic background. These results suggest that the provenance area of the Dajianggang Formation in the Shuangyang area was an island arc provenance area undergoing feldspar intrusive rock evolution. These findings are consistent with previous studies on the tectonic setting of the study area and provide further support for the geological evolution of the region.



**Figure 5.** (a)  $SiO_2$ - $K_2O/Na_2O$  and (b)  $K_2O/Na_2O$ - $SiO_2/Al_2O_3$  (Cited in [49]). A1—basaltic and andesitic island arc sources; A2—felsic intrusive rock evolution island arc source.

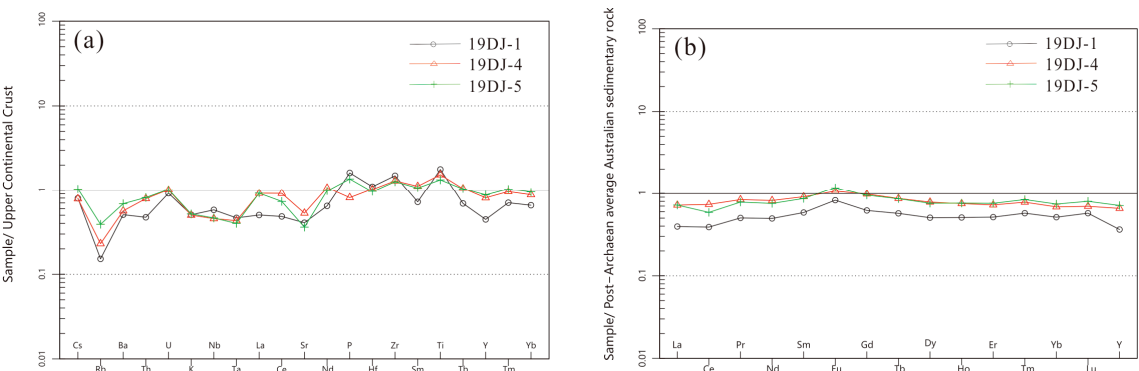
## 5.2. Geochemical Characteristics of Trace Elements

The results of trace and REE geochemical analysis of sandstone samples from the Dajianggang Formation are shown in Table 3. The large ion lithophile elements Rb, Sr, Ba, and Cs have concentrations ranging from  $17.06$  to  $43.76 \times 10^{-6}$ ,  $126.60$  to  $185.60 \times 10^{-6}$ ,  $279.40$  to  $377.40 \times 10^{-6}$ , and  $2.90$  to  $3.83 \times 10^{-6}$ , respectively. Notably, Rb, Sr, and Ba are found to be deficient relative to the upper continental crust component. Similarly, the high field intensity elements Nb, Ta, Th, and Ce exhibit deficits, with concentrations ranging from  $11.61$  to  $14.49 \times 10^{-6}$  (average of  $12.51 \times 10^{-6}$ ) for Nb,  $0.88$  to  $1.02 \times 10^{-6}$  (average of  $0.95 \times 10^{-6}$ ) for Ta,  $5.06$  to  $8.69 \times 10^{-6}$  (average of  $7.40 \times 10^{-6}$ ) for Th, and  $30.99$  to  $58.42 \times 10^{-6}$  for Ce. On the other hand, the sandstone samples from the Dajianggang Formation in the study area exhibit slight enrichment of Ti and Zr, with Ti content ranging from  $4016$  to  $5335 \times 10^{-6}$ , with an average of  $4655.33 \times 10^{-6}$ , and Zr content ranging from  $241.70$  to  $284.70 \times 10^{-6}$ , with an average of  $258.00 \times 10^{-6}$ . Meanwhile, other elements, such as U and Hf, show comparable contents to the average values of the upper continental crust. The U content ranges from  $2.56$  to  $2.85 \times 10^{-6}$ , with an average of  $2.74 \times 10^{-6}$ , while the Hf content ranges from  $5.60$  to  $6.44 \times 10^{-6}$ , with an average of  $6.00 \times 10^{-6}$ . The trace element distribution pattern of the sandstone samples in the study area is similar to the average component distribution of the upper crust, with a gentle curve on the spider diagram (Figure 6a). Floyd and Leveridge [50] introduced the Hf-La/Th discrimination diagram (Figure 7a) in order to investigate the relationship between different provenance components. The diagram suggests that the content of Hf elements in sandstones would increase due to the decomposition of zircons, as a result of the gradual erosion of island arcs or continental basement. Based on this diagram, the sandstone samples from the Dajianggang Formation in the study area are mainly characterized by a felsic provenance. In addition, the Ni-TiO<sub>2</sub> discrimination diagram (Figure 7b) shows that the samples are mainly distributed in the sandstone area with a sedimentary tendency. This result is consistent with the two-dimensional bivariate diagram of  $SiO_2$ - $K_2O/Na_2O$  and  $K_2O/Na_2O$ - $SiO_2/Al_2O_3$ , which further validates the conclusion. In summary, the provenance of the sandstones from the Dajianggang Formation in the study area can be attributed to felsic rocks with sedimentary tendency, and there might be a small amount of mixed source.

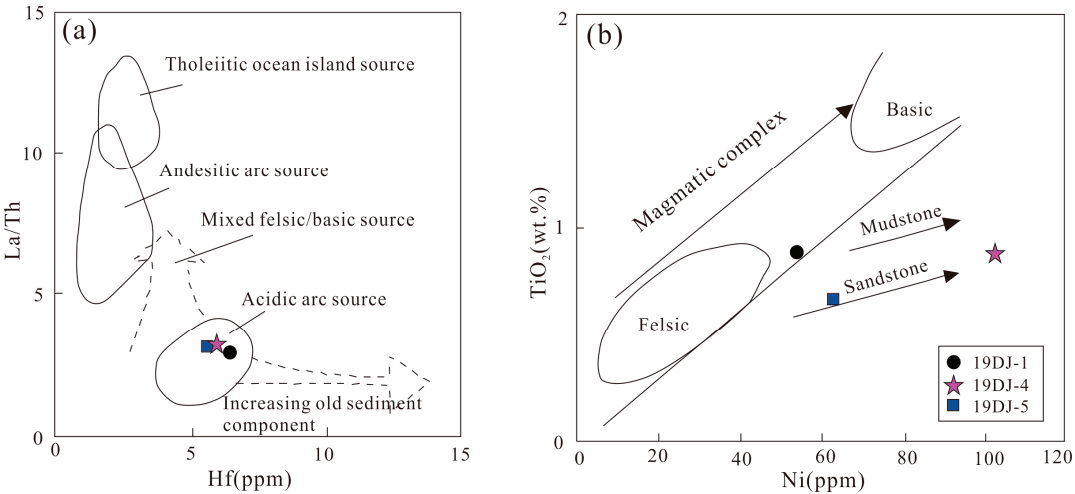
Table 3. Trace elements of the Dajianggang Formation sandstone in the Shuangyang area ( $\times 10^{-6}$ ).

| Sample                              | 19DJ-1                  | 19DJ-4    | 19DJ-5    |
|-------------------------------------|-------------------------|-----------|-----------|
| Lithology                           | Conglomeratic Sandstone | Sandstone | Greywacke |
| trace elements ( $\times 10^{-6}$ ) |                         |           |           |
| Li                                  | 26.66                   | 36.37     | 14.15     |
| Be                                  | 1.74                    | 1.79      | 1.75      |
| B                                   | 14.94                   | 13.53     | 16.66     |
| Sc                                  | 5.76                    | 7.77      | 6.85      |
| V                                   | 104.3                   | 104.4     | 77.27     |
| Cr                                  | 74.4                    | 227       | 157.9     |
| Co                                  | 8.75                    | 17.45     | 10.46     |
| Ni                                  | 53.73                   | 105.2     | 62.63     |
| Cu                                  | 20.49                   | 22.16     | 19.58     |
| Zn                                  | 83.64                   | 113.4     | 60.55     |
| Ga                                  | 19.95                   | 21.02     | 18.22     |
| Ge                                  | 6.94                    | 9.54      | 7.83      |
| As                                  | 22.85                   | 7.63      | 7.42      |
| Se                                  | 1.37                    | 1.98      | 1.35      |
| Rb                                  | 17.06                   | 25.82     | 43.76     |
| Sr                                  | 142.7                   | 185.6     | 126.6     |
| Y                                   | 9.83                    | 17.73     | 19.22     |
| Zr                                  | 284.7                   | 247.6     | 241.7     |
| Nb                                  | 14.49                   | 11.42     | 11.61     |
| Mo                                  | 10.89                   | 10.57     | 11.74     |
| Ag                                  | 0.42                    | 0.42      | 0.36      |
| Cd                                  | 2.5                     | 2.17      | 2.23      |
| Sn                                  | 1.63                    | 2.05      | 1.95      |
| Sb                                  | 3.12                    | 2.79      | 3.18      |
| Cs                                  | 2.95                    | 2.9       | 3.83      |
| Ba                                  | 279.4                   | 310.1     | 377.4     |
| La                                  | 15.11                   | 27.49     | 27.51     |
| Ce                                  | 30.99                   | 58.42     | 46.72     |
| Pr                                  | 4.438                   | 7.412     | 6.91      |
| Nd                                  | 16.8                    | 27.77     | 25.57     |
| Sm                                  | 3.25                    | 5.06      | 4.81      |
| Eu                                  | 0.89                    | 1.16      | 1.28      |
| Gd                                  | 2.89                    | 4.59      | 4.44      |
| Tb                                  | 0.44                    | 0.67      | 0.67      |
| Dy                                  | 2.37                    | 3.67      | 3.55      |
| Ho                                  | 0.5                     | 0.74      | 0.75      |
| Er                                  | 1.47                    | 2.06      | 2.16      |
| Tm                                  | 0.23                    | 0.32      | 0.34      |
| Yb                                  | 1.45                    | 1.93      | 2.09      |
| Lu                                  | 0.25                    | 0.3       | 0.35      |
| Hf                                  | 6.44                    | 5.96      | 5.6       |
| Ta                                  | 1.02                    | 0.95      | 0.88      |
| W                                   | 1.95                    | 2.48      | 2.1       |
| Au                                  | 0.09                    | 0.08      | 0.09      |
| Tl                                  | 0.4                     | 0.54      | 0.47      |
| Pb                                  | 18.93                   | 19.59     | 14.69     |
| Bi                                  | 0.15                    | 0.29      | 0.19      |
| Th                                  | 5.06                    | 8.44      | 8.69      |
| U                                   | 2.56                    | 2.82      | 2.85      |
| ΣREE                                | 81.07                   | 141.58    | 127.14    |
| ΣLREE                               | 71.48                   | 127.3     | 112.8     |
| ΣHREE                               | 9.6                     | 14.28     | 14.34     |
| (La/Yb) <sub>N</sub>                | 0.77                    | 1.05      | 0.97      |
| (La/Sm) <sub>N</sub>                | 0.68                    | 0.79      | 0.83      |
| (Eu/Yb) <sub>N</sub>                | 1.61                    | 1.56      | 1.6       |





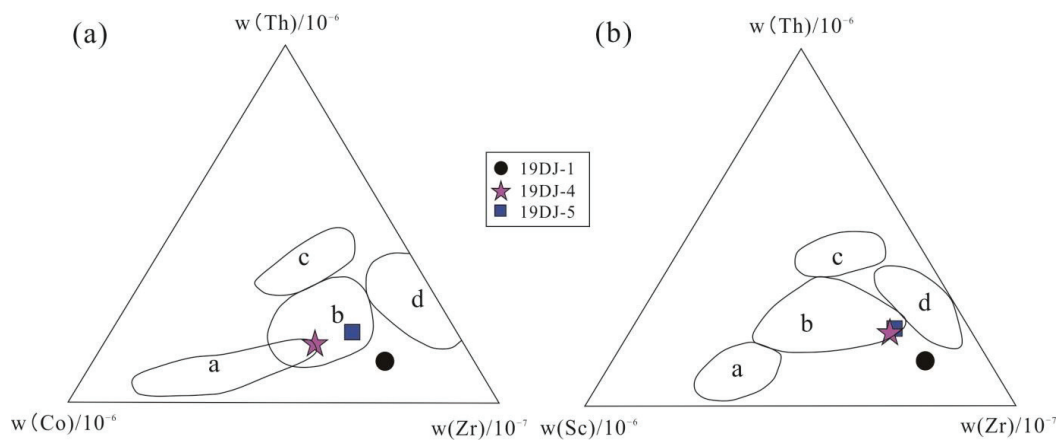
**Figure 6.** (a) A standardized spider diagram of trace elements in the upper crust of sandstone in the Dajianggang Formation (Modified after [51]) and (b) standard distribution model of rare earth elements in sandstone of the Dajianggang Formation (Modified after [52]).



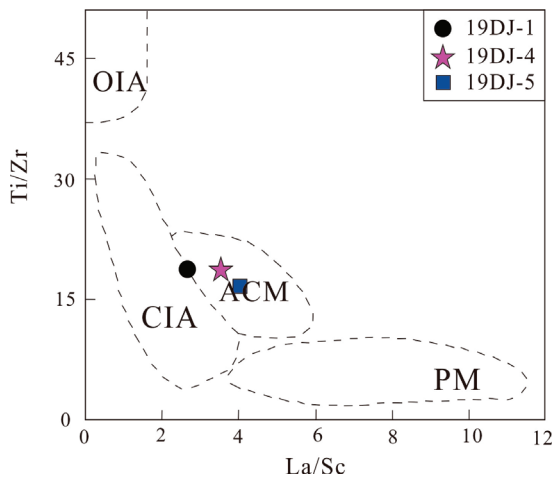
**Figure 7.** (a) Hf-La/Th source discrimination diagram (Modified after [50]); (b) Ni-TiO<sub>2</sub> diagram (Modified after [53]).

Trace elements, such as La, Ce, Y, Th, Zr, Nd, Hf, and Sc, are highly useful in identifying the provenance tectonic background of sedimentary rocks, due to their low mobility during the sedimentary process and high stability in seawater. These elements are abundant in clastic sedimentary rocks and are not prone to weathering and erosion, making them an ideal tool for understanding the characteristics of source rocks. Based on this premise, Bhatia and Crook [54] conducted a study on the tectonic significance of trace elements in provenance analysis, and categorized active continental margins (ACM), passive continental margins (PCM), oceanic island arcs (OIA), and continental island arcs (CIA) as the four major geotectonic source locations. In order to further understand the tectonic setting and provenance of the sandstones in the study area, several structure diagrams have been used. The Th-Co-Zr and Th-Sc-Zr triangle diagrams (Figure 8) were employed in order to analyze the compositional characteristics of the sandstones. The majority of the samples were found to fall within the continental island arc region. However, in the La/Sc-Ti/Zr diagram (Figure 9), they were mainly classified as active continental margin in source, with only one sample (19DJ-1) located at the boundary between the continental island arc and active continental margin, indicating that the tectonic setting of the Dajianggang Formation

in the Shuangyang area is relatively complex. These findings provide valuable insights into the provenance and tectonic history of the study area. The sandstones of the Dajianggang Formation in the Shuangyang area were found to have a slightly scattered distribution of total rare earth elements ( $\Sigma\text{REE}$ ), with values ranging from  $81.07$  to  $141.58 \times 10^{-6}$ , and an average value of  $116.60 \times 10^{-6}$ . The content of light rare earth elements ( $\Sigma\text{LREE}$ ) ranges from  $71.48$  to  $127.30 \times 10^{-6}$ , with an average value of  $103.86 \times 10^{-6}$ . The ratio of  $(\text{La}/\text{Sm})_{\text{N}}$  is between  $0.68$  and  $0.83$ . The content of heavy rare earth elements ( $\Sigma\text{HREE}$ ) ranges from  $9.60$  to  $14.34 \times 10^{-6}$ , with a mean value of  $12.74 \times 10^{-6}$ . The  $(\text{Eu}/\text{Yb})_{\text{N}}$  ratio is between  $1.56$  and  $1.61$ . The ratio of light rare earth to heavy rare earth elements ( $\Sigma\text{LREE}/\Sigma\text{HREE}$ ) ranges from  $7.45$  to  $8.91$ , with an average of  $8.08$ . The  $(\text{La}/\text{Yb})_{\text{N}}$  ratio ranges from  $0.77$  to  $1.05$ , with an average value of  $0.93$ . Overall, the standard distribution pattern of rare earth elements in the sandstone samples of the Dajianggang Formation is very similar to that of post-Archaean Australia sedimentary rocks (Figure 6b), indicating a gentle trend.



**Figure 8.** (a) Th-Co-Zr diagram of sandstone triangle structure of the Dajianggang Formation in the Shuangyang area and (b) Th-Sc-Zr diagram of sandstone triangle structure of the Dajianggang Formation in the Shuangyang area (Modified after [53]). a—oceanic island arc; b—continental island arc; c—active continental margin; d—passive continental margin.

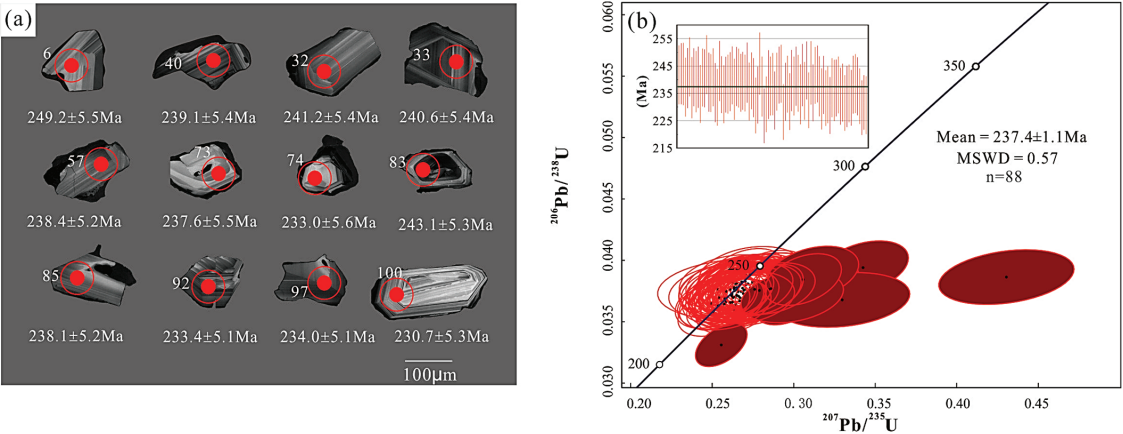


**Figure 9.** La/Sc-Ti/Zr tectonic diagram. PM—passive continental margin; ACM—active continental margin; CIA—continental island arc; OIA—oceanic island arc.

To summarize, the application of various structural background discrimination diagrams indicates that the sandstone of the Dajianggang Formation has been derived from the continental island arc environment, although there may be some contributions from mixed sources. By considering the geological time scale, this suggests that the tectonic activity in the source area was relatively unstable during the Late Triassic period, characterized by a geological setting with active tectonic movement.

6. Analysis of LA-ICP-MS Zircon Dating Results

In this study, LA-ICP-MS detrital zircon U-Pb dating was utilized in order to determine the age of sandstone sample 19DJ-1 from the Late Triassic Dajianggang Formation in the Shuangyang area, located in central Jilin Province. Detailed observations of the crystal morphology using CL images revealed that the majority of the detrital zircons are semi-euhedral and heteromorphic crystals with typical magmatic oscillating growth zones (Figure 10a). The presence of high Th/U values (0.31–1.61) further indicates their magmatic origin, which is in accordance with the geological context [55]. The age distribution of detrital zircons and the U-Pb Concordia diagram, as shown in the Figure 10, were used to analyze the provenance and geological history of the Dajianggang Formation in the Shuangyang area.



**Figure 10.** (a) Cathodoluminescence (CL) images of selected zircons from samples 19DJ-1. Solid circles show positions of LA-ICP-MS analytical sites with their ages in Ma. (b) Concordia diagram of conglomeratic sandstone in the Dajianggang Formation. Filled ellipses are discordant data.

The  $^{206}\text{Pb}/^{238}\text{U}$  age range of the 100 analyzed zircons ranges from 210 to 363 Ma (Table 4), the majority of the 88 concordant zircons falling within the range of 226.8 to 246.5 Ma. The weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of these zircons is  $237.4 \pm 1.1$  Ma (MSWD = 0.57), indicating that they were likely crystallized around the Middle to Late Triassic boundary (Figure 10b). The CL images of the detrital zircons show that most zircons are semi-euhedral and heteromorphic crystals, further supporting their magmatic origin.

Table 4. LA-ICP-MS Zircon U-Pb dating data of conglomeratic sandstone of the Dajianggang Formation.

| Point Number | Content (×10 <sup>−6</sup> ) |      |        |  | Th/U | 207Pb/235U |         |  | 206Pb/238U |        |  | 207Pb/235U |      |  | 206Pb/238U |      |  | Concordance (%) |
|--------------|------------------------------|------|--------|--|------|------------|---------|--|------------|--------|--|------------|------|--|------------|------|--|-----------------|
|              | U                            | Th   | Pb     |  |      | Ratio      | 1σ      |  | Ratio      | 1σ     |  | Age (Ma)   | 1σ   |  | Age (Ma)   | 1σ   |  |                 |
| 1 *          | 386                          | 997  | 40.379 |  | 2.58 | 799.2065   | 20.6331 |  | 6.8468     | 0.1741 |  | 6787.7     | 26.2 |  | ****       | 143  |  | ****            |
| 2 *          | 564                          | 713  | 31     |  | 1.26 | 0.3146     | 0.0098  |  | 0.0371     | 0.0008 |  | 277.8      | 7.6  |  | 234.9      | 5.2  |  | 83              |
| 3            | 399                          | 421  | 21     |  | 1.06 | 0.2979     | 0.0103  |  | 0.0382     | 0.0009 |  | 264.8      | 8.1  |  | 241.8      | 5.4  |  | 91              |
| 4            | 200                          | 97   | 9      |  | 0.49 | 0.2702     | 0.0123  |  | 0.0383     | 0.0009 |  | 242.8      | 9.8  |  | 242.2      | 5.6  |  | 100             |
| 5 *          | 400                          | 350  | 21     |  | 0.88 | 0.3424     | 0.0114  |  | 0.0394     | 0.0009 |  | 299        | 8.6  |  | 249.2      | 5.5  |  | 82              |
| 6            | 162                          | 103  | 8      |  | 0.64 | 0.2746     | 0.0137  |  | 0.0383     | 0.0009 |  | 246.4      | 11   |  | 242.1      | 5.7  |  | 98              |
| 7            | 272                          | 326  | 15     |  | 1.2  | 0.2757     | 0.0111  |  | 0.0375     | 0.0009 |  | 247.3      | 8.9  |  | 237.3      | 5.4  |  | 96              |
| 8            | 240                          | 125  | 11     |  | 0.52 | 0.2706     | 0.0114  |  | 0.038      | 0.0009 |  | 243.2      | 9.1  |  | 240.6      | 5.5  |  | 99              |
| 9            | 378                          | 325  | 20     |  | 0.86 | 0.2845     | 0.0101  |  | 0.0387     | 0.0009 |  | 254.2      | 8    |  | 244.7      | 5.4  |  | 96              |
| 10           | 162                          | 144  | 8      |  | 0.89 | 0.255      | 0.013   |  | 0.0375     | 0.0009 |  | 230.6      | 10.5 |  | 237.1      | 5.6  |  | 97              |
| 11           | 594                          | 440  | 29     |  | 0.74 | 0.2715     | 0.0086  |  | 0.0381     | 0.0009 |  | 243.9      | 6.9  |  | 240.9      | 5.3  |  | 99              |
| 12           | 174                          | 141  | 9      |  | 0.81 | 0.2798     | 0.0133  |  | 0.0378     | 0.0009 |  | 250.5      | 10.5 |  | 239.3      | 5.6  |  | 95              |
| 13           | 184                          | 114  | 9      |  | 0.62 | 0.2642     | 0.0125  |  | 0.0381     | 0.0009 |  | 238        | 10   |  | 240.9      | 5.6  |  | 99              |
| 14           | 301                          | 254  | 15     |  | 0.84 | 0.279      | 0.0108  |  | 0.0371     | 0.0009 |  | 249.9      | 8.5  |  | 234.8      | 5.3  |  | 94              |
| 15           | 489                          | 358  | 24     |  | 0.73 | 0.2846     | 0.0096  |  | 0.0381     | 0.0009 |  | 254.3      | 7.6  |  | 240.8      | 5.3  |  | 95              |
| 16           | 526                          | 518  | 28     |  | 0.98 | 0.267      | 0.0087  |  | 0.038      | 0.0009 |  | 240.3      | 7    |  | 240.5      | 5.3  |  | 100             |
| 17           | 388                          | 475  | 22     |  | 1.23 | 0.2704     | 0.0097  |  | 0.0388     | 0.0009 |  | 243        | 7.8  |  | 245.5      | 5.4  |  | 99              |
| 18           | 309                          | 196  | 15     |  | 0.63 | 0.2648     | 0.0103  |  | 0.0378     | 0.0009 |  | 238.6      | 8.3  |  | 239.1      | 5.4  |  | 100             |
| 19           | 469                          | 217  | 21     |  | 0.46 | 0.2655     | 0.009   |  | 0.0377     | 0.0009 |  | 239.1      | 7.3  |  | 238.8      | 5.3  |  | 100             |
| 20           | 539                          | 561  | 29     |  | 1.04 | 0.2719     | 0.0088  |  | 0.0381     | 0.0009 |  | 244.2      | 7.1  |  | 240.9      | 5.3  |  | 99              |
| 21           | 232                          | 154  | 11     |  | 0.66 | 0.2761     | 0.0118  |  | 0.0372     | 0.0009 |  | 247.6      | 9.4  |  | 235.3      | 5.4  |  | 95              |
| 22           | 332                          | 280  | 17     |  | 0.84 | 0.2747     | 0.0104  |  | 0.0369     | 0.0008 |  | 246.4      | 8.3  |  | 233.6      | 5.2  |  | 95              |
| 23           | 298                          | 164  | 14     |  | 0.55 | 0.2842     | 0.0109  |  | 0.0385     | 0.0009 |  | 254        | 8.6  |  | 243.2      | 5.5  |  | 96              |
| 24 *         | 1382                         | 2794 | 699    |  | 2.02 | 11.4984    | 0.3994  |  | 0.1275     | 0.004  |  | 2564.4     | 32.5 |  | 773.8      | 22.6 |  | 7               |
| 25           | 457                          | 409  | 23     |  | 0.89 | 0.2703     | 0.0091  |  | 0.0376     | 0.0008 |  | 242.9      | 7.3  |  | 238.2      | 5.2  |  | 98              |
| 26           | 319                          | 351  | 17     |  | 1.1  | 0.2719     | 0.0102  |  | 0.0371     | 0.0008 |  | 244.2      | 8.1  |  | 234.7      | 5.3  |  | 96              |
| 27           | 1000                         | 864  | 51     |  | 0.86 | 0.2608     | 0.0073  |  | 0.0376     | 0.0008 |  | 235.3      | 5.9  |  | 238.2      | 5.1  |  | 99              |
| 28           | 283                          | 149  | 13     |  | 0.55 | 0.2605     | 0.0105  |  | 0.0377     | 0.0009 |  | 235.1      | 8.5  |  | 238.4      | 5.4  |  | 99              |
| 29           | 288                          | 275  | 15     |  | 0.96 | 0.2632     | 0.0103  |  | 0.0378     | 0.0009 |  | 237.2      | 8.3  |  | 239.3      | 5.4  |  | 99              |
| 30           | 667                          | 569  | 34     |  | 0.85 | 0.2785     | 0.0085  |  | 0.0382     | 0.0009 |  | 249.4      | 6.7  |  | 241.6      | 5.3  |  | 97              |
| 31           | 150                          | 116  | 7      |  | 0.77 | 0.2757     | 0.0141  |  | 0.0374     | 0.0009 |  | 247.3      | 11.2 |  | 236.5      | 5.6  |  | 96              |
| 32           | 310                          | 254  | 16     |  | 0.82 | 0.2673     | 0.0103  |  | 0.0381     | 0.0009 |  | 240.6      | 8.2  |  | 241.2      | 5.4  |  | 100             |
| 33           | 314                          | 265  | 16     |  | 0.85 | 0.2669     | 0.0101  |  | 0.038      | 0.0009 |  | 240.2      | 8.1  |  | 240.6      | 5.4  |  | 100             |
| 34           | 416                          | 298  | 20     |  | 0.72 | 0.2807     | 0.0097  |  | 0.0378     | 0.0009 |  | 251.2      | 7.7  |  | 238.9      | 5.3  |  | 95              |
| 35           | 394                          | 558  | 23     |  | 1.42 | 0.2806     | 0.0098  |  | 0.0379     | 0.0009 |  | 251.2      | 7.8  |  | 239.6      | 5.3  |  | 95              |

Table 4. Cont.

| Point Number | Content ( $\times 10^{-6}$ ) |      |    |  | Th/U | $^{207}\text{Pb}/^{235}\text{U}$ |            | $^{206}\text{Pb}/^{238}\text{U}$ |            | $^{207}\text{Pb}/^{235}\text{U}$ |            | $^{206}\text{Pb}/^{238}\text{U}$ |            | Concordance (%) |
|--------------|------------------------------|------|----|--|------|----------------------------------|------------|----------------------------------|------------|----------------------------------|------------|----------------------------------|------------|-----------------|
|              | U                            | Th   | Pb |  |      | Ratio                            | 1 $\sigma$ | Ratio                            | 1 $\sigma$ | Age (Ma)                         | 1 $\sigma$ | Age (Ma)                         | 1 $\sigma$ |                 |
| 36           | 531                          | 488  | 27 |  | 0.92 | 0.2685                           | 0.0087     | 0.0377                           | 0.0008     | 241.5                            | 7          | 238.8                            | 5.2        | 99              |
| 37           | 252                          | 196  | 13 |  | 0.78 | 0.2757                           | 0.0113     | 0.0384                           | 0.0009     | 247.3                            | 9          | 242.6                            | 5.5        | 98              |
| 38           | 368                          | 328  | 19 |  | 0.89 | 0.2803                           | 0.0102     | 0.0372                           | 0.0008     | 250.9                            | 8.1        | 235.7                            | 5.3        | 94              |
| 39           | 1095                         | 960  | 56 |  | 0.88 | 0.275                            | 0.0076     | 0.0379                           | 0.0008     | 246.7                            | 6          | 239.6                            | 5.2        | 97              |
| 40           | 276                          | 178  | 13 |  | 0.65 | 0.2675                           | 0.0108     | 0.0375                           | 0.0009     | 240.7                            | 8.7        | 237.1                            | 5.4        | 98              |
| 41           | 366                          | 380  | 19 |  | 1.04 | 0.2527                           | 0.0094     | 0.0364                           | 0.0008     | 228.8                            | 7.6        | 230.6                            | 5.1        | 99              |
| 42           | 339                          | 217  | 16 |  | 0.64 | 0.2716                           | 0.0102     | 0.037                            | 0.0008     | 244                              | 8.2        | 234.4                            | 5.2        | 96              |
| 43           | 170                          | 108  | 8  |  | 0.63 | 0.2734                           | 0.0131     | 0.0389                           | 0.0009     | 245.4                            | 10.5       | 245.9                            | 5.7        | 100             |
| 44           | 198                          | 157  | 10 |  | 0.79 | 0.2637                           | 0.0123     | 0.0375                           | 0.0009     | 237.6                            | 9.9        | 237.5                            | 5.5        | 100             |
| 45           | 435                          | 444  | 22 |  | 1.02 | 0.2507                           | 0.009      | 0.0358                           | 0.0008     | 227.2                            | 7.3        | 226.8                            | 5          | 100             |
| 46 *         | 560                          | 262  | 27 |  | 0.47 | 0.3162                           | 0.0097     | 0.0379                           | 0.0008     | 279                              | 7.5        | 239.9                            | 5.3        | 85              |
| 47           | 408                          | 537  | 22 |  | 1.32 | 0.2494                           | 0.0091     | 0.0365                           | 0.0008     | 226.1                            | 7.4        | 231                              | 5.1        | 98              |
| 48           | 69                           | 47   | 3  |  | 0.69 | 0.265                            | 0.0199     | 0.0376                           | 0.001      | 238.7                            | 16         | 238.2                            | 6.3        | 100             |
| 49           | 254                          | 153  | 12 |  | 0.6  | 0.2787                           | 0.0116     | 0.0376                           | 0.0009     | 249.6                            | 9.2        | 237.7                            | 5.4        | 95              |
| 50           | 146                          | 102  | 7  |  | 0.7  | 0.2633                           | 0.0139     | 0.0377                           | 0.0009     | 237.3                            | 11.1       | 238.4                            | 5.7        | 100             |
| 51           | 245                          | 143  | 11 |  | 0.58 | 0.2667                           | 0.0113     | 0.0367                           | 0.0009     | 240                              | 9          | 232.4                            | 5.3        | 97              |
| 52           | 511                          | 557  | 28 |  | 1.09 | 0.2768                           | 0.009      | 0.0378                           | 0.0009     | 248.1                            | 7.2        | 239.3                            | 5.3        | 96              |
| 53           | 757                          | 693  | 40 |  | 0.92 | 0.2746                           | 0.0081     | 0.0382                           | 0.0008     | 246.3                            | 6.5        | 241.7                            | 5.2        | 98              |
| 54           | 702                          | 1133 | 42 |  | 1.61 | 0.2783                           | 0.0083     | 0.0383                           | 0.0009     | 249.3                            | 6.6        | 242.2                            | 5.3        | 97              |
| 55           | 466                          | 352  | 22 |  | 0.76 | 0.2631                           | 0.0095     | 0.036                            | 0.0008     | 237.2                            | 7.6        | 228.2                            | 5.1        | 96              |
| 56           | 291                          | 291  | 15 |  | 1    | 0.2745                           | 0.0107     | 0.0372                           | 0.0009     | 246.3                            | 8.5        | 235.6                            | 5.3        | 96              |
| 57           | 652                          | 657  | 34 |  | 1.01 | 0.2763                           | 0.0085     | 0.0377                           | 0.0008     | 247.7                            | 6.8        | 238.4                            | 5.2        | 96              |
| 58           | 378                          | 406  | 20 |  | 1.08 | 0.2584                           | 0.0095     | 0.0367                           | 0.0008     | 233.4                            | 7.6        | 232                              | 5.2        | 99              |
| 59           | 167                          | 139  | 9  |  | 0.83 | 0.2908                           | 0.0138     | 0.0379                           | 0.0009     | 259.2                            | 10.9       | 239.7                            | 5.6        | 92              |
| 60           | 254                          | 197  | 13 |  | 0.77 | 0.2692                           | 0.0112     | 0.0376                           | 0.0009     | 242.1                            | 9          | 237.7                            | 5.4        | 98              |
| 61 *         | 124                          | 102  | 6  |  | 0.82 | 0.3296                           | 0.017      | 0.0368                           | 0.0009     | 289.3                            | 13         | 232.9                            | 5.6        | 78              |
| 62           | 374                          | 319  | 19 |  | 0.85 | 0.265                            | 0.0096     | 0.0382                           | 0.0009     | 238.7                            | 7.7        | 241.3                            | 5.4        | 99              |
| 63           | 546                          | 448  | 28 |  | 0.82 | 0.273                            | 0.0088     | 0.0377                           | 0.0008     | 245.1                            | 7          | 238.7                            | 5.2        | 97              |
| 64           | 183                          | 147  | 9  |  | 0.8  | 0.266                            | 0.0127     | 0.0371                           | 0.0009     | 239.5                            | 10.2       | 234.7                            | 5.5        | 98              |
| 65           | 153                          | 101  | 7  |  | 0.66 | 0.2625                           | 0.0134     | 0.0382                           | 0.0009     | 236.7                            | 10.8       | 241.7                            | 5.7        | 98              |
| 66           | 263                          | 264  | 14 |  | 1    | 0.262                            | 0.0109     | 0.0373                           | 0.0009     | 236.2                            | 8.8        | 235.9                            | 5.3        | 100             |
| 67           | 582                          | 489  | 31 |  | 0.84 | 0.2978                           | 0.0092     | 0.0385                           | 0.0009     | 264.7                            | 7.2        | 243.4                            | 5.3        | 92              |
| 68*          | 793                          | 749  | 41 |  | 0.94 | 0.297                            | 0.0086     | 0.0367                           | 0.0008     | 264                              | 6.7        | 232.5                            | 5.1        | 87              |
| 69           | 134                          | 83   | 7  |  | 0.62 | 0.284                            | 0.0148     | 0.0383                           | 0.0009     | 253.9                            | 11.7       | 242.5                            | 5.8        | 95              |
| 70           | 69                           | 23   | 14 |  | 0.33 | 0.2737                           | 0.0087     | 0.0372                           | 0.0008     | 245.7                            | 6.9        | 235.2                            | 5.2        | 96              |

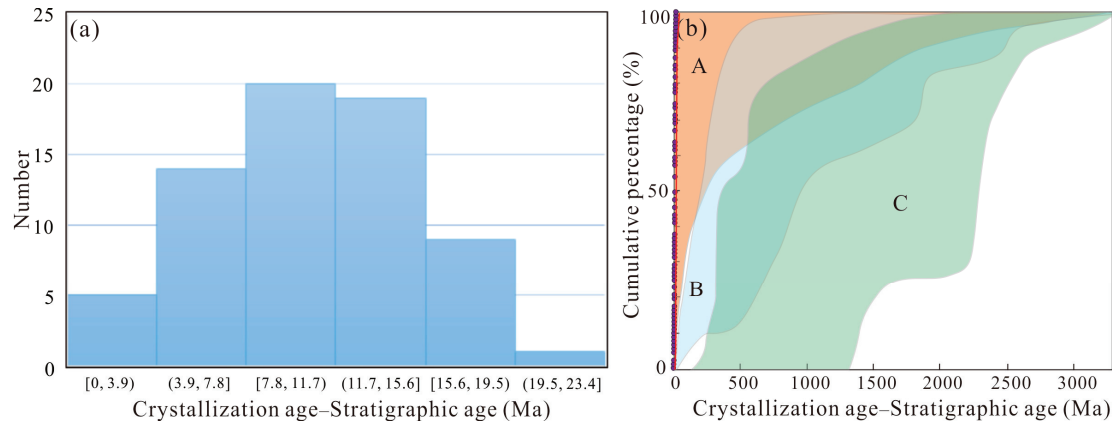


Table 4. Cont.

| Point Number | Content ( $\times 10^{-6}$ ) |      |    |  | Th/U | $^{207}\text{Pb}/^{235}\text{U}$ |            | $^{206}\text{Pb}/^{238}\text{U}$ |            | $^{207}\text{Pb}/^{235}\text{U}$ |            | $^{206}\text{Pb}/^{238}\text{U}$ |            | Concordance (%) |
|--------------|------------------------------|------|----|--|------|----------------------------------|------------|----------------------------------|------------|----------------------------------|------------|----------------------------------|------------|-----------------|
|              | U                            | Th   | Pb |  |      | Ratio                            | 1 $\sigma$ | Ratio                            | 1 $\sigma$ | Age (Ma)                         | 1 $\sigma$ | Age (Ma)                         | 1 $\sigma$ |                 |
| 71           | 960                          | 887  | 51 |  | 0.92 | 0.2936                           | 0.0082     | 0.0382                           | 0.0008     | 261.4                            | 6.4        | 241.6                            | 5.2        | 92              |
| 72           | 838                          | 675  | 43 |  | 0.81 | 0.268                            | 0.0078     | 0.0383                           | 0.0008     | 241.1                            | 6.2        | 242.1                            | 5.2        | 100             |
| 73           | 219                          | 137  | 11 |  | 0.63 | 0.2796                           | 0.0121     | 0.0376                           | 0.0009     | 250.3                            | 9.6        | 237.6                            | 5.5        | 95              |
| 74           | 144                          | 111  | 7  |  | 0.77 | 0.27                             | 0.014      | 0.0368                           | 0.0009     | 242.7                            | 11.2       | 233                              | 5.6        | 96              |
| 75           | 313                          | 252  | 16 |  | 0.8  | 0.2534                           | 0.0099     | 0.0376                           | 0.0009     | 229.4                            | 8          | 238.1                            | 5.3        | 96              |
| 76           | 580                          | 580  | 30 |  | 1    | 0.2703                           | 0.0085     | 0.0369                           | 0.0008     | 243                              | 6.8        | 233.3                            | 5.1        | 96              |
| 77 *         | 301                          | 174  | 15 |  | 0.58 | 0.3115                           | 0.0115     | 0.039                            | 0.0009     | 275.4                            | 8.9        | 246.5                            | 5.5        | 89              |
| 78           | 438                          | 417  | 22 |  | 0.95 | 0.2641                           | 0.0092     | 0.037                            | 0.0008     | 237.9                            | 7.4        | 234.5                            | 5.2        | 99              |
| 79           | 297                          | 242  | 15 |  | 0.82 | 0.2644                           | 0.0104     | 0.0364                           | 0.0008     | 238.2                            | 8.4        | 230.6                            | 5.2        | 97              |
| 80           | 222                          | 160  | 11 |  | 0.72 | 0.2586                           | 0.0114     | 0.0375                           | 0.0009     | 233.6                            | 9.2        | 237.1                            | 5.4        | 99              |
| 81           | 158                          | 94   | 8  |  | 0.59 | 0.2689                           | 0.0134     | 0.0373                           | 0.0009     | 241.8                            | 10.7       | 236.1                            | 5.6        | 98              |
| 82 *         | 206                          | 157  | 10 |  | 0.76 | 0.2989                           | 0.0129     | 0.0371                           | 0.0009     | 265.6                            | 10.1       | 234.5                            | 5.4        | 88              |
| 83 *         | 528                          | 278  | 26 |  | 0.53 | 0.3056                           | 0.0096     | 0.0384                           | 0.0009     | 270.8                            | 7.5        | 243.1                            | 5.3        | 89              |
| 84           | 476                          | 431  | 24 |  | 0.91 | 0.2657                           | 0.009      | 0.0375                           | 0.0008     | 239.2                            | 7.2        | 237                              | 5.2        | 99              |
| 85           | 689                          | 676  | 36 |  | 0.98 | 0.2848                           | 0.0085     | 0.0376                           | 0.0008     | 254.5                            | 6.8        | 238.1                            | 5.2        | 93              |
| 86           | 409                          | 445  | 22 |  | 1.09 | 0.2539                           | 0.0092     | 0.037                            | 0.0008     | 229.8                            | 7.4        | 234                              | 5.2        | 98              |
| 87           | 285                          | 334  | 16 |  | 1.17 | 0.2649                           | 0.0106     | 0.0372                           | 0.0009     | 238.6                            | 8.5        | 235.3                            | 5.3        | 99              |
| 88           | 460                          | 408  | 23 |  | 0.89 | 0.2609                           | 0.009      | 0.0366                           | 0.0008     | 235.4                            | 7.2        | 231.5                            | 5.1        | 98              |
| 89           | 147                          | 99   | 7  |  | 0.67 | 0.267                            | 0.0137     | 0.037                            | 0.0009     | 240.3                            | 10.9       | 233.9                            | 5.6        | 97              |
| 90           | 341                          | 368  | 18 |  | 1.08 | 0.2617                           | 0.0099     | 0.0371                           | 0.0009     | 236.1                            | 8          | 235                              | 5.3        | 100             |
| 91 *         | 2011                         | 2044 | 96 |  | 1.02 | 0.2554                           | 0.0065     | 0.0331                           | 0.0007     | 231                              | 5.2        | 210                              | 4.5        | 90              |
| 92           | 613                          | 531  | 31 |  | 0.87 | 0.2576                           | 0.0082     | 0.0369                           | 0.0008     | 232.8                            | 6.6        | 233.4                            | 5.1        | 100             |
| 93           | 429                          | 239  | 20 |  | 0.56 | 0.2759                           | 0.0096     | 0.0376                           | 0.0009     | 247.4                            | 7.6        | 238.2                            | 5.3        | 96              |
| 94           | 296                          | 220  | 15 |  | 0.74 | 0.2859                           | 0.0111     | 0.0377                           | 0.0009     | 255.4                            | 8.7        | 238.6                            | 5.4        | 93              |
| 95           | 330                          | 222  | 16 |  | 0.67 | 0.2788                           | 0.0105     | 0.0376                           | 0.0009     | 249.7                            | 8.3        | 237.6                            | 5.3        | 95              |
| 96 *         | 490                          | 441  | 41 |  | 0.74 | 0.4304                           | 0.017      | 0.0386                           | 0.0009     | 363.4                            | 12.1       | 244.4                            | 5.7        | 61              |
| 97           | 611                          | 500  | 30 |  | 0.82 | 0.2628                           | 0.0083     | 0.037                            | 0.0008     | 236.9                            | 6.7        | 234                              | 5.1        | 99              |
| 98           | 666                          | 576  | 33 |  | 0.87 | 0.2535                           | 0.0079     | 0.0363                           | 0.0008     | 229.4                            | 6.4        | 229.8                            | 5          | 100             |
| 99           | 786                          | 758  | 40 |  | 0.96 | 0.2622                           | 0.0079     | 0.0366                           | 0.0008     | 236.5                            | 6.3        | 231.7                            | 5          | 98              |
| 100          | 211                          | 101  | 10 |  | 0.48 | 0.2573                           | 0.0117     | 0.0364                           | 0.0009     | 232.4                            | 9.5        | 230.7                            | 5.3        | 99              |

Note: Data with \* were discordant. Data with strikethrough were not shown in the figure due to huge discordance. \*\*\*\* were the data with huge error that couldn't be calculated.

The conglomeratic sandstone samples from the Dajianggang Formation were subjected to statistical analysis of their ages, and a frequency distribution histogram of crystallization age–stratigraphic age was constructed in order to visualize the zircon age data (Figure 11a). The results show that the zircon ages are highly concentrated within a narrow range of 220–250 Ma, indicating a uniform provenance. The youngest single grain age of  $226.8 \pm 5$  Ma in 88 concordant zircons is interpreted as the maximum depositional age of the strata. The cumulative probability graph demonstrates a steep line almost perpendicular to the horizontal line, indicating a sharp increase in the sedimentation rate during the period of zircon crystallization. Based on the empirical curve proposed by Cawood, Hawkesworth [56] for the relationship between detrital zircon ages and tectonic settings, and the cumulative probability distribution diagram of the difference between zircon crystallization age and the maximum deposition age (Figure 11b), it can be inferred that the zircon ages in the conglomeratic sandstone samples are closely linked to the maximum depositional age (227 Ma) and indicative of a convergent tectonic setting.



**Figure 11.** (a) Histogram of crystallization age–stratigraphic age frequency distribution of sandstone in the Dajianggang Formation and (b) cumulative probability graph. Summative drop point region: A—convergence plate edge background; B—synclinal tectonic setting; C—Extensional basin setting. Purple dot—plot of the difference between the measured crystallization age and the depositional age of the succession in this study. Red line—variation of the difference between the measured crystallization age and the depositional age of the succession in which it occurs in this study.

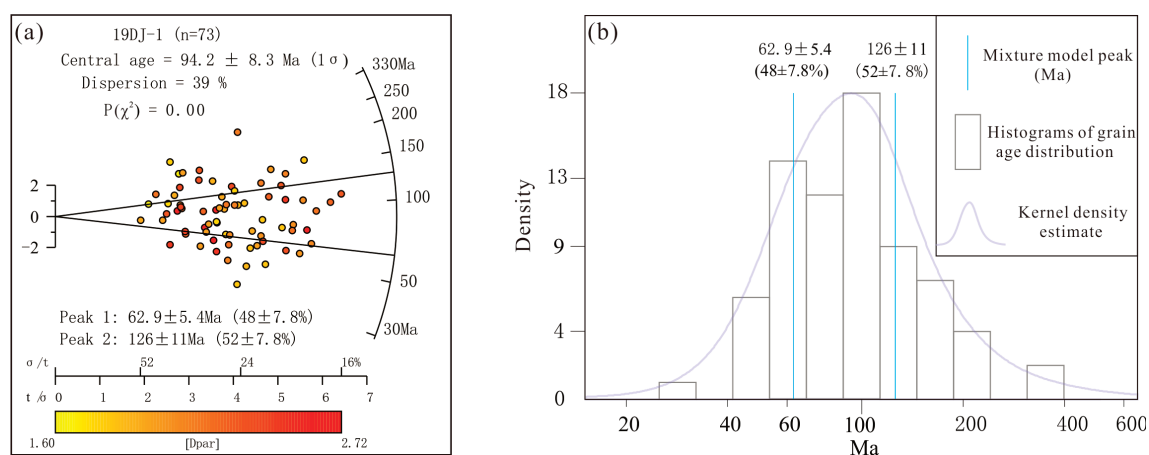
7. Analysis of Apatite Fission Track Results

This study employed apatite fission track analysis in order to investigate the thermal history of sandstone sample 19DJ-1 from the Late Triassic Dajianggang Formation. A total of 73 apatite grains were analyzed, and the results are presented in Table 5. In order to further interpret the data, the results were processed using RadialPlotter [57], which produced a radar radiogram and age histogram with which to visualize the age components of the apatite grains in the sample. The results are presented in Figure 12.

**Table 5.** Apatite fission track analysis results of sample 19DJ-1 of the Dajianggang Formation.

| Sample | Longitude<br>(°E) | Latitude<br>(°N) | Elevation<br>(m) | Lithology/<br>Strata                 | Nc | $\rho_s$<br>( $10^5/\text{cm}^2$ )<br>(Ns) | $\rho_i$<br>( $10^5/\text{cm}^2$ )<br>(Ni) | $\rho_d$<br>( $10^5/\text{cm}^2$ )<br>(Nd) | U<br>( $\times 10^{-6}$ ) | P( $\chi^2$ )<br>/% | Central Age<br>(Ma)<br>1 $\sigma$ | Dpar<br>( $\mu\text{m}$ ) | MTL<br>( $\mu\text{m}$ )<br>1 $\sigma$ | N  |
|--------|-------------------|------------------|------------------|--------------------------------------|----|--------------------------------------------|--------------------------------------------|--------------------------------------------|---------------------------|---------------------|-----------------------------------|---------------------------|----------------------------------------|----|
| 19DJ-1 | 125° 49′ 25″      | 43° 22′ 53″      | 309              | pebbly<br>sandstone/T <sub>3</sub> d | 73 | 7.922<br>(1777)                            | 19.759<br>(4432)                           | 17<br>(15,655)                             | 15.77                     | 0                   | 94.2 $\pm$ 8.3                    | 2.15                      | 11.53 $\pm$ 1.47                       | 89 |

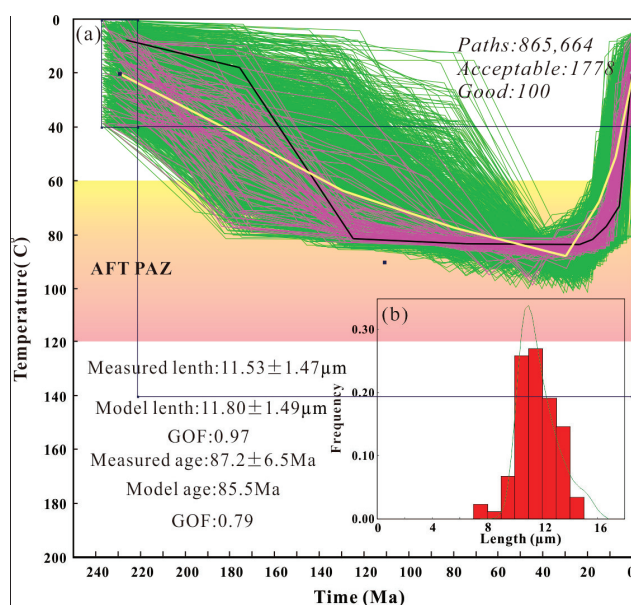
Abbreviations: Nc—number of grains;  $\rho_s$  and Ns—spontaneous track density of the sample ( $\times 10^6$  tracks  $\text{cm}^{-2}$ ) and number of spontaneous tracks counted;  $\rho_i$  and Ni—induced track density in external detector (muscovite) ( $\times 10^6$  tracks  $\text{cm}^{-2}$ ) and number of induced tracks counted;  $\rho_d$  and Nd—induced track density of dosimeter glass ( $\times 10^6$  tracks  $\text{cm}^{-2}$ ) and number of tracks counted; MTL and N—mean confined fission track length and number of lengths measured.



**Figure 12.** (a) Age distribution radar map of AFT particles from 19DJ-1 clastic rock of the Triassic Dajianggang Formation. (b) Age distribution density map of AFT particles from 19DJ-1 clastic rock of the Triassic Dajianggang Formation.

The sample did not pass the Chi-square test, as  $P(\chi^2) < 5\%$ , indicating that the age of sample particles was dispersed. This may be attributed to several factors, including changes in the chemical composition of apatite grains in a single sample [37,58], and difficulties in accurately identifying fission tracks and lengths due to a large number of fission tracks being shortened by the annealing process [34,59,60].

Using the age of apatite grains and the length of confined fission track obtained in this study, we carried out thermal history inversion modelling in order to infer the time–temperature evolution history of the sample [61,62]. We used HeFTy v1.9.1 thermal history simulation software in order to conduct thermal history inversion modelling [42,61,63], considering apatite fission track data such as grain age, confined fission track length, Dpar value, and C-axis Angle. The modelling results are shown in Figure 13 using two criteria, including (1) the first box constrained the deposition time of the strata, indicating that the surface temperature of the strata was 0–40 °C during the diagenesis; (2) the second box is the search box that allows the model to search for potential paths of the sample when it was deposited to the present time between the temperatures of 40 and 140 °C. We set the model to continuously run until it generated 100 good paths. The thermal history for the sample indicates the subsequent to deposition between ~230 and 30 Ma. After deposition, the sample showed rapid continuous cooling of 0.67–7.29 °C/Ma since 30 Ma.



**Figure 13.** (a) Modelling result of AFT thermal history of clastic rock 19DJ-1 of Triassic Dajianggang Formation and (b) length distribution of fission tracks. (a) shows the results of the thermal history simulation based on grain age and track length. (b) shows the length distribution of the confined fission track and the comparison with the simulation results in (a); the purple lines represent simulated paths with good fit ( $GOF > 0.5$ ), and the green lines represent simulated paths with acceptable fit ( $0.5 > GOF > 0.05$ ). The blue boxes are used to constrain the Time–Temperature paths. The black solid line represents the optimal solution in the simulation result. The yellow solid line represents the weighted mean path. Abbreviation: AFT PAZ—partial annealing zone of apatite fission track.

## 8. Discussion

### 8.1. Provenance and Tectonic Setting Reflected by Clastic Components of Sandstone

The petrographic analysis of sandstone from the Dajianggang Formation in the study area reveals that it predominantly consists of feldspar lithic sandstone with low structural and compositional maturity. This indicates intense tectonic activity in the provenance area, where detrital material was rapidly eroded and deposited after being transported for a short distance. The Dickinson diagram analysis of the sandstone detrital components suggests that the primary provenance of the Dajianggang Formation sandstone in the Shuangyang area is an island arc orogenic belt. It is possible that the clastic material from the volcanic island arc mixed with the subduction complex material in the forearc basin, resulting in some sandstone samples showing the characteristics of recycled orogenic and subduction complex belts.

### 8.2. Provenance and Tectonic Setting Reflected by Geochemical Characteristics of Sandstone

Based on a comprehensive analysis of the geochemical characteristics of the sandstone samples, it has been determined that the tectonic setting and provenance of the Dajianggang Formation in the Shuangyang area is predominantly from a continental island arc environment, with a provenance type of feldspar island arc. In some samples, the structural diagram of La/Sc-Ti/Zr suggests an active continental margin provenance, indicating that materials from the active continental margin may have been mixed in the provenance. Along with receiving materials from the Late Triassic Changchun–Yanji suture zone island arc, the Dajianggang Formation in the Shuangyang area may also have received materials

from the northern margin of the North China Craton or exhumed recycled orogenic belt, suggesting a complex provenance history for the formation.

### *8.3. Provenance and Tectonic Setting Reflected by LA-ICP-MS Analysis of Detrital Zircons from Sandstone*

LA-ICP-MS analysis of detrital zircons from sandstone samples of the Dajianggang Formation in the study area provides valuable information about the age and origin of the formation. The peak  $^{206}\text{Pb}/^{238}\text{U}$  age range of 226.8–246.5 Ma and the weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of  $237.4 \pm 1.1$  Ma suggest that the formation of the Dajianggang Formation occurred later than  $226.8 \pm 5$  Ma, corresponding to the Carnian in the early Late Triassic period, based on the revised International Geological time scale of 2023. The high Th/U values of all detrital zircons ( $>0.3$ ) indicate that most of the zircons are magmatic in origin, which is supported by the characteristics of the CL image. This suggests that the provenance area experienced magmatic events that resulted in the crystallization of zircons. These findings provide significant insights into the geological history of the study area and contribute to our understanding of Late Triassic sedimentation and tectonic evolution in this region.

Through statistical analysis of the age distribution of conglomeratic sandstone samples from the Dajianggang Formation, it is evident that the detrital zircon ages are predominantly clustered within a narrow range of 200–300 Ma. This high degree of concentration is further supported by the steep slope of the cumulative probability curve, which suggests a relatively uniform and consistent provenance for the sedimentary material. The nearly vertical trend of the curve near the age of the sedimentary strata indicates that the tectonic setting of the provenance area was likely convergent in nature.

Wang, Zhou [64] identified a zircon with an age of  $2516 \pm 18$  Ma from the 238 zircons they dated from the Dajianggang Formation, indicating that the North China Craton was also a source of detrital materials. Consistent with previous studies, the Changchun–Yanji suture zone in central Jilin was believed to be the main source of the Dajianggang Formation, which is a subduction complex [7,16,23,65], while the Changchun–Yanji suture belt is not only an eastward extension of the Soloker–Xilamulon–Changchun suture belt [1,2,66–69] towards the east, but also the southern margin of the Jihei high pressure belt, which formed via the subduction of the Jiamusi–Xingkai Block to the northern margin of the North China Craton during the Late Triassic and Early Jurassic periods [16,65]. Based on the LA-ICP-MS results of detrital zircons from sandstone samples, it can be concluded that the provenance of the Dajianggang Formation may be mainly from the Late Triassic magmatic arc of the Changchun–Yanji suture zone, with possible contributions from the northern margin of the North China Craton, indicating a convergent tectonic setting during that time. Combining the previous report in the vicinity of the study area, the Paleo-Asian Ocean finished its closure before the Late Triassic period [70,71].

### *8.4. Tectonic Setting and Evolution History Reflected by Apatite Fission Track Results in Sandstone*

The detritus apatite fission track (AFT) age analysis of sample 19DJ-1 shows a relatively dispersed age distribution, as indicated by a low  $P$  ( $\chi^2$ ) value of less than 5%. The central age of the detrital AFT in sample 19DJ-1 is  $94.2 \pm 8.3$  Ma (Figure 12), which is younger than the corresponding stratigraphic age. The thermal evolution history of sample 19DJ-1 indicates that the early thermal events (240–30 Ma) may have been caused by burial, while the rapid cooling in the late stage reflects regional exhumation events (since 30 Ma). This indicates that the orogenic process of the Central Asian Orogenic Belt had ceased, and the study area had not been uplifted since the Late Triassic period. The rapid uplift of 30 Ma may correspond to the temporary squeezing of the northeast Asian continental margin and a series of inversion structures in basins caused by the subduction of the Pacific plate during the Middle Himalayan movement, reflecting a regional uplift event [72–74]. These findings suggest that the study area has experienced complex tectonic activities, including burial,



subduction, and uplift events, and their effects on the region have been felt at different times throughout geological history [73,74].

## 9. Conclusions

- (1) The Dajianggang Formation sandstone in the Shuangyang area is mainly feldspar lithic sandstone, and the lithic type is mainly volcanic lithic. Petrographic studies suggest that the clastic grains are angular, indicating near-source sedimentary characteristics. Dickinson diagram analysis reveals that the sandstone's main provenance is from island arcs, with some samples showing mixed characteristics from recycled orogenic belts and subduction complex belts.
- (2) The geochemical analysis of sandstone samples from the Shuangyang area suggests a continental island arc environment, with felsic rocks dominating the provenance, mixed with active continental margin materials.
- (3) The U-Pb chronology of detrital zircon LA-ICP-MS shows that the Dajianggang Formation has a maximum depositional age of  $226.8 \pm 5$  Ma, indicating that it formed in the Carnian of the middle Late Triassic period, at the earliest. The distribution of zircon ages suggests that the main source of the Dajianggang Formation was the Late Triassic magmatic arc of the Changchun–Yanji suture zone, possibly mixed with materials from the northern margin of the North China Craton, in a convergent tectonic setting.
- (4) The apatite fission track analysis reveals that the Dajianggang Formation underwent a thermal history that started around 240 Ma and experienced rapid exhumation to the surface since 30 Ma. This implies that the orogenic process in the study area ceased during the Late Triassic period, and the remote effect of Pacific subduction did not impact the study area until 30 Ma.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13070975/s1>. Figure S1: The strata column section of Dajianggang Formation in Dajianggang area.

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