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Temperature Controls Initial REE Enrichment in Peraluminous Granites: Implication from the Parent Granites in the Shangyou Ion-Adsorption Type REE Deposit

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Abstract: The initial enrichment of rare earth elements (REE) in granites plays an important role for the generation of ion-adsorption type REE deposits. It has been summarized that the mineralizationrelated granitoids are mostly peraluminous, but the enrichment mechanism of REE in this peraluminous granite is currently not well understood. In this study, we conducted geochronology, petrological, and geochemical investigations on the biotite granite and muscovite granite from the Shangyou complex in Ganzhou, Jiangxi Province. Zircon U-Pb dating indicates that both the biotite granite and muscovite granite generated in the Early Silurian (ca. 433-434 Ma). The high aluminum saturation index and occurrence of muscovite and old zircon cores indicate that they belong to the S-type granite and are derived from the melting of metagreywacke. The relatively higher FeO^T contents, Mg# values, and zirconium saturation temperatures (760-873 °C) for the biotite granite resulted from hydrous melting with the involvement of mantle material. In contrast, the muscovite granite with low FeO^T contents, Mg# values, Nb/Ta ratios, and zirconium saturation temperatures (748–761 °C) indicates a purely crust-derived melt formed by muscovite dehydration melting. There is a positive correlation of REE contents with the formation temperature and Th contents in both the Shangyou granites and the data collected from global peraluminous granites. This indicates that temperature plays a key role in the REE enrichment in peraluminous granites, as the hightemperature condition could promote the melting of REE-rich and Th-rich accessory minerals of allanite and REE-phosphate and result in the increases in both REE contents and Th contents in the melts. Given the fact that the parent granites for ion-adsorbing REE deposits are mostly peraluminous and generated in the extensional setting in South China, we concluded that peraluminous granite formed under high-temperature extensional tectonic settings favors initial REE enrichment, which further contributes to the formation of ion-adsorbing REE deposits in South China.

Keywords: ion-adsorption type REE deposit; peraluminous granite; REE enrichment; formation temperature

1. Introduction

Rare earth elements (REE), which serve as "industrial vitamins", are widely used in aerospace, new energy, national defense, and military industry. Therefore, they are important strategic resources, and their supply-demand contradiction is increasingly intensifying with the development of high-tech in modern industry. The main supplies of REE are alkali-carbonate-type REE deposits and ion-adsorbing-type REE deposits [1]. The former is dominated by light REE (LREE) deposits, which are represented by Baiyunebo, Maoniuping REE deposits from China, and Mountain Pass REE deposits in America. The ion-adsorbing REE deposits account for more than 80% of the supply of heavy REE (HREE) worldwide. Ion-adsorbing REE deposits are easy to mine and have a high resource utilization rate; thus, they are of great economic value and strategic significance [2,3].



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Ion-adsorbing REE deposits were first discovered in China in the late 1960s. As unique metal deposits occurring on the surface, it is mainly formed by weathering and leaching of REE from granite, volcanic rock, and metamorphic rock under warm and humid climates and low mountain and hilly terrain conditions [3–6], among which granite is its main ore-forming parent rock. The formation of ion adsorbing REE deposits is controlled by both endogenous and hypergene processes. The former mainly affects the pre-enrichment of REE during the formation and evolution of the parent rocks and controls the type of mineralization [7–9], while the weathering processes are also vital to the REE leaching from the granites and adsorption by the clay minerals as an ion condition [6,10]. At present, the research on the ion-adsorbing REE deposits focuses on the hypergene mineralization process, including the control of groundwater, climate, microorganisms, and topography on the formation of deposits, the occurrence state of REE, and the differentiation and enrichment mechanism during weathering processes [11–14]. However, there is still a lack of systematic research on the constraints of endogenous processes on the formation of ion-adsorbing type REE deposits. A series of studies have pointed out that the high REE content of granites in the Nanling area is the key to the formation of the ion-adsorbing REE deposits [15,16], and the REE fractionation during magmatic evolution may further contribute to the HREE enrichment in the ore bodies [7,17]. Therefore, it is believed that the REE contents and patterns of granitic parent rock play a decisive role in later mineralization [3,7]. The statistics data have shown that the ore-forming parent rock of ion-adsorbing REE deposits is mainly composed of peraluminous granite [3]. However, different from alkaline granite, peraluminous granite is mostly related to the mineralization of rare metals such as tungsten, tin, niobium, and tantalum, and no large-scale independent REE ore bodies have been found yet. Therefore, the enrichment mechanism of REE in the peraluminous granite has not received sufficient attention, which restricts further understanding of the genesis of ion adsorption type REE deposits. A detailed study is needed on the mechanism of REE enrichment in peraluminous granite.

Shangyou complex is in the west of Ganzhou city, Jiangxi province, with an exposed area of more than 100 km². REE mineralization is widely distributed in the weathering profile of the Shangyou complex in the Shangpengdong, Pengdongkeng, and Yewukeng areas [18]. This article conducts geochronology, petrological, and whole-rock geochemical studies on the Shangyou granitic complex. The aims of this study are to constrain the geochemical behavior of REE and reveal the factors controlling the enrichment of REE during the formation of peraluminous granites.

2. Geological Setting

South China consists of the northwestern Yangtze Block and southeastern Cathaysian Block, which are connected along the Jiangnan Orogen in the Neoproterozoic. There are multiple stages of tectonic and magmatic activities in South China during the Paleozoic and Mesozoic [19,20], leading to the formation of widely distributed granites in South China (Figure 1a). There are also abundant rare metal deposits (W, Sn, Nb, and Ta) in South China, which are related to the widely distributed granites, making South China the most important rare metal mineralization belt in the world [21,22]. In addition, South China was characterized by a warm and humid climate and low mountain and hill terrain, admitting to the formation and preservation of the weathering crust for the granites, and many ionadsorbing REE deposits have been discovered in these weathering crusts (Figure 1a). This type of REE deposit was first found in the Zudong area in the 1960s and was endemic in South China and Southeast Asia, as little ion-adsorbing REE deposit was found in other regions. According to the relative enrichment of LREE and HREE in the weathering crust, the ion-adsorbing REE deposits could be subdivided into three types [23]: (1) HREE-type, represented by the Zudong and Zaibeiding REE deposits [10,24]; (2) Coexistence of LREE and HREE, including the Qingxi and Zhaibei REE deposits [25]; (3) LREE-type, represented by Bachi, Renju, and Heling REE deposits [26,27]. The generation of ion-adsorbing REE deposits in these different types is suggested to be associated with the REE patterns for

the parent granites [3,7], as the weathering profile usually inherits the REE patterns of the parent granite [28]. The granites related to the ion-adsorbing REE deposits are mainly generated in the Jurassic to Cretaceous extensional setting, which is induced by the slab foundering and roll-back and subsequent steep subduction of the Paleo-Pacific Ocean slab [19]. In addition, the Early Paleozoic granites also play an important role in generating the ion-adsorbing REE deposits in South China, as the parent granites for ion-adsorbing REE deposits in Shangyou, Yangbu, Ninghua, Weipu, Gutian, and Sanbiao areas are all generated in the Early Paleozoic [29]. The Shangyou granitic complex is in the west of Shangyou City and intruded in the Cambrian metamorphic rocks (Figure 1b). The main bodies of the Shangyou granitic complex are biotite granite, while locally occurred muscovite granite around by the biotite granite (Figure 1b).



Figure 1. (**a**) The distributions of granitoids and ion-adsorbing REE deposits in South China [3,30]; (**b**) Simplified geological map of the Shangyou pluton.

3. Analytic Methods

Zircon U-Pb dating was conducted at the Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences, Guangzhou, using a 193 nm GeoLasPro and Agilent 7900 ICP-MS with a laser spot size of 29 μ m. Argon was used as the make-up gas mixed Helium (carrier gas) via a T-connector before entering the ICP. The samples 91,500 zircon and NIST610 glass were used as an external standard for U-Pb dating and the trace element calibration, respectively. The calculation of the age was performed using Isoplot 4.11 [31].

Whole-rock major elements analysis was conducted using X-ray fluorescence spectrometry at Wuhan Sample Solution Analytical Technology Co., Ltd. (WSSAT), Wuhan, China. The error for major element analysis is less than 5%. The trace elements were analyzed in an Agilent 7700e ICP-MS at WSSAT. The sample powder was weighed and placed in a Teflon bomb after drying for 12 h in an oven at 105 °C. The sample powders were digested in an HF+HNO₃ solution in Teflon bombs, which is subsequently putted in a stainless-steel pressure jacket and oven-heated to 190 °C for >24 h. The final solution was transferred to a polyethylene bottle and diluted to 100 g by adding 2% HNO₃. The analytical error for trace element is less than 2%. Zirconium saturation temperatures are calculated in the following equation: T_{Zr} (°C) = 12,900/(ln D_{zircon/melt} + 0.85 M + 2.95) – 273.5, D_{zircon/melt} = 496,000/Zr contents in the melts (ppm), M = molar ratio of (Na + K + 2Ca)/(Al × Si) [32].

4. Results

4.1. Petrology

The samples for this study were collected from the southeastern, central, and northwestern parts of the Shangyou pluton, including biotite granite and Shangyou muscovite granite. Shangyou biotite granite contains schlieren and mainly consists of plagioclase (25%~35%), potassium feldspar (25%~35%), quartz (30%~40%), and biotite (5%–7%), with the occurrence of slight muscovite (Figure 2). The core of some plagioclase has undergone obvious sericitization, while the later alteration of the edges is not significant (Figure 2a). Potassium feldspar usually occurs as twin crystals, with some showing obvious sericitization and containing a small amount of muscovite mineral inclusions. Biotite coexists with feldspar and includes a small amount of muscovite between grains. The appearance of muscovite indicates aluminum supersaturation in the rock, and the crystallization of a large amount of mica also indicates a high water content, which is significantly different from those of A-type granite [33,34]. The accessory minerals include zircon, apatite, and iron-titanium oxides (Figure 2a). The mineral composition of the schlieren in biotite granite is basically consistent with that of the host rock, but it has a higher proportion of mica and apatite (Figure 2b), with mica content reaching over 20%. Some mica has a harbor-like dissolution structure, indicating formation in an early stage. In addition, there is a large accumulation of apatite in the schlieren, which may be the main factor leading to a significantly higher REE content than the host rock. The Shangyou muscovite granite is composed of quartz (40%~45%), potassium feldspar (20%~30%), sodium feldspar (20%~30%), and a small amount of muscovite (~5%) (Figure 2c,d). Quartz often coexists closely with sodium feldspar and potassium feldspar, indicating that its crystallization time is relatively consistent with that of feldspar. Potassium feldspar has a twin-crystal structure and has undergone significant sericitization (Figure 2c). Sodium feldspar contains a large amount of muscovite mineral inclusions (Figure 2d).



Figure 2. Photomicrographs of the granites from Shangyou pluton. (**a**): biotite granite; (**b**): schlieren in the biotite granite; (**c**): muscovite monzogranite; (**d**): muscovite enclosed by albite. Q: quartz; Kf: K-feldspar; Pl: plagioclase; Bi: biotite; Ap: apatite; Mus: muscovite.

4.2. Zircon U-Pb Dating

Zircon U-Pb isotopic data are listed in Table S1 and illustrated in Figure 3. The zircon grains from the Shangyou biotite granite are colorless to light yellow, irregularly shaped crystals with lengths of 100–400 μ m and length–width ratios of 1–3 (Figure 3a). The zircon grains show clear oscillatory zoning, indicative of magmatic zircons in granitic systems [35]. The ²³⁸U/²⁰⁶Pb ages for the zircons are between 430 and 438 Ma with a weighted age of 433 ± 2 Ma, which is consistent with the concordia age of 433 ± 2 Ma (Figure 3b), taken as the intruded age of the Shangyou biotite granite.



Figure 3. U-Pb dating for the (a,b) Shangyou biotite granite and (b–d) muscovite granite.

The prismatic/ellipsoidal-shaped well-crystallized zircon crystals of the Shangyou muscovite granite are colorless to light yellow with lengths between 100 and 300 μ m and length-to-width ratios between 1 and 3. The zircons sometimes show a core-margin structure (Figure 3c). The cores show varied grayscale without the occurrence of oscillatory zoning and display varied 238 U/ 206 Pb ages ranging from 504 to 1540 Ma (Table S1), which may be inherited from the magmatic source (Figure 3c). The zircon margin also shows clear oscillatory zoning indicating a magmatic origin, although they are darker in the CL image (Figure 3b). All data for these magmatic zircons plot around the U-Pb concordia line yielding the same weighted mean age and concordia age of 434 ± 2 Ma (Figure 3c,d), indicating the same Early Silurian age as the biotite granite.

4.3. Whole-Rock Elemental Compositions

Data for whole-rock major and trace elemental compositions are listed in Table S2 and illustrated in Figures 4–6. The CIPW (normal minerals calculation) for the biotite granite and muscovite granite are listed in Table S3. The SiO₂ contents of Shangyou biotite granite range from 72.55 to 74.59 wt.%, with total alkaline contents of 7.41 to 8.12 wt.%, belonging to subalkaline rocks (Figure 4a). This rock has high Al_2O_3 con-

tents of 13.02-13.72 wt.% and a high aluminum saturation indicator (A/CNK = 1.06-1.17), showing characteristics of peraluminous granite (Figure 4b). The samples show low contents of TiO₂, Fe₂O₃T, CaO, and MnO and relatively high K₂O contents ranging from 4.08 to 5.09 wt.%, belonging to the high potassium calcium alkaline series rocks. The schlieren in biotite granite has lower SiO₂ content (67.28 wt.%) and significantly higher TiO₂, Fe₂O₃T, Al₂O₃, CaO, MnO, and P₂O₅ contents and lower K₂O contents compared to the host granite, while their Na₂O content is similar (Figure 5). The elemental differences are consistent with a higher proportion of mica, feldspar, and apatite accumulation in the schlieren in the petrographic observations (Figure 2). The total REE content of Shangyou biotite granite is 158–303 ppm, which is significantly higher than that of continental crustal reservoirs. In addition, the biotite granite shows obvious differentiation between light REE (LREE) and heavy REE (HREE) with (La/Sm)_N ratios of 4.32–5.99 and (La/Yb)_N ratios of 5.03–11.9, and significant negative Eu anomalies with Eu/Eu* values of 0.26–0.39, but its HREE contents are relatively low with a flat HREE pattern curve (Figure 6a; HREE = 17.4-28.4 ppm; (Gd/Yb)_N = 0.91-1.38). The schlieren from the biotite granite has higher REE contents with more negative Eu anomaly and significant differentiation between LREE and HREE (Figure 6a; REE = 663 ppm; $Eu/Eu^* = 0.11$; (La/Yb)_N = 14). All the samples from the Shangyou biotite granite exhibit significant depletion of Ba, Sr, and Eu, as well as enrichment of Th, U, and Pb, with relatively high zirconium saturation temperatures (Tzr = 760–873 $^{\circ}$ C).



Figure 4. (a) TAS [36] and (b) A/CNK vs. A/NK [37] diagrams for the Shangyou biotite granite and muscovite monzogranite.

Shangyou muscovite granite has higher SiO₂ contents (76.01–77.10 wt.%) and total alkali contents (7.85–8.04 wt.%) than those of the biotite granite, belonging to subalkaline rocks (Figure 4a). It has Al₂O₃ contents of 12.36–12.64 wt.% and an aluminum saturation index (A/CNK) of 1.06–1.15, consistent with those of peraluminous rocks (Figure 4b). In addition, the Shangyou muscovite granite shows lower TiO₂, Fe₂O₃T, Al₂O₃, CaO, MnO, and P_2O_5 contents than those of the Shangyou biotite granite (Figure 5), indicating a higher degree of magmatic evolution. Its K_2O contents are 4.41–4.72 wt.%, belonging to the high potassium calcium alkaline series rocks. The REE content of the muscovite granite is relatively low (96–144 ppm), and the differentiation between LREE and HREE is not obvious (Figure 6a; (La/Sm)N = 1.76-2.59); (La/Yb)N = 1.49-2.86), but it has a more negative Eu anomaly (Eu * = 0.10-0.17) than those of the biotite granite, consistent with a higher degree of magmatic evolution. The HREE content of muscovite granite is significantly higher (23.9–45.1 ppm) than that of biotite granite (17.4–28.4 ppm), and there is a weak enrichment trend in the HREE $(Gd/Yb)_N = 0.80-0.89)$. The muscovite granite exhibits significant depletion in Ba, Nb, Sr, and Eu (Figure 6b), with Nb/Ta and Zr/Hf ratios of 4.63–5.69 and 21.8–26.3, respectively, which are significantly lower than those of



the Shangyou biotite granite and continental crust. In addition, the muscovite granite has a relatively lower zirconium saturation temperature (Tzr = $748-761 \text{ }^{\circ}\text{C}$).

Figure 5. Harker diagrams for the Shangyou biotite granite and muscovite monzogranite.



Figure 6. Chondrite-normalized REE patterns (**a**) and primitive mantle-normalized trace element patterns (**b**) for the Shangyou biotite granite and muscovite monzogranite. Chondrite and primitive mantle data from Sun et al. (1989) [38].

5. Discussion

5.1. Petrogenesis

Granite is the most important component of continental crust and is classified according to their chemistry, isotopic signature, and mineralogical components into I-, S-, A-, or M-types in order to infer their source characteristics [39–41]. M-type granite is formed by crystallization differentiation of mantle-derived magma and is mostly found in the middle ocean ridges [42,43]. M-type granite generally shows relatively low SiO₂ contents, which are different from those of the Shangyou biotite granite and muscovite granite. The classification of I-type and S-type granites is based on their source characteristics, as I-type granites generally originate from igneous rock while S-type granites are from sedimentary sources [44,45]. The conspicuous characteristics of A-type granite are the high formation temperatures and high contents of high field strength element (HSFE), with definitions from "alkaline, anhydrous, and anorogenic settings [46]. A-type granite is usually marked by the appearance of mafic alkaline minerals such as arfvedsonite, and its source area can be sediments or igneous rocks [47,48]. The whole rock Ga/Al ratio is an important parameter for distinguishing A-type granite, as A-type granites generally show high Ca/Al ratios >2.6 [39]. The Ga/Al ratios of Shangyou biotite granite and Shangyou muscovite granite are 2.29–2.74 and 2.54–2.72, respectively, which are close to or slightly higher than the typical ratio of A-type granite. However, the contents of HFSE in the Shangyou granites are relatively low, with Ze+Ce+Nb+Y content of 228–544 ppm and 194–250 ppm for the biotite granite and muscovite granite, respectively, which are lower than the values for A-type granite (Figure 7a). Combined with their lower zirconium saturation temperatures (Table S2; biotite granite is 760–873 °C, with an average value of 810 °C; biotite diorite granite is 745–764 °C, with an average value of 755 °C) and the absence of the alkaline minerals, indicating that the Shangyou granite does not belong to A-type granite. In addition, mica in A-type granite usually crystallizes at a late stage and are intergranular distribution due to the anhydrous condition of the primitive magma for A-type granite [42]. However, the mica in the Shangyou granites is mainly symbiotic with other minerals or crystallized in an earlier stage (Figure 2), further indicating that they do not belong to A-type granite.



Figure 7. $Zr + Nb + Ce + Y vs. K_2O + Na_2O)/CaO [40] (a) and ACF classification [40] (b) diagrams of the Shangyou biotite granite and muscovite monzogranite.$

Both Shangyou biotite granite and muscovite granite have high aluminum saturation indices (Table S2, Figure 3b) and contain aluminum-saturated minerals such as muscovite and corundum but lack amphibole, which are consistent with those of the S-type granite but different from those of I-type granites [49–51]. In addition, there are old zircon cores in the Shangyou granites with varied ages, which are common in the S-type granites that should be inherited in the sedimentary source, also indicating the classification to S-style for the Shangyou granites. In the source area discrimination diagram, both Shangyou biotite granite and muscovite granite are plotted in the metamorphic sandstone source area, manifesting a sediment-derived source and S-type genetic type for the Shangyou granites (Figure 8). It is noticeable that Proterozoic to Paleozoic metamorphic sandstones are widely distributed in the southern Jiangxi region, with relatively high REE contents



(average values 302 ppm, Wang et al., 2018 [52]), which favors the formation of REE-rich granite in the region.

Figure 8. Discrimination diagrams of source region of (a) $Al_2O_3 + MgO + TiO_2 + FeO^T$ vs. $Al_2O_3/(MgO + TiO_2 + FeO^T)$, and (b) CaO + MgO + TiO_2 + FeO^T vs. CaO/(MgO + TiO_2 + FeO^T) for Shangyou biotite granite and muscovite monzogranite (after Douce, 1999 [49]).

Although the Shangyou biotite granite and muscovite granite have the same genetic type and similar source areas, their different geochemical properties may indicate different petrogenesis for them. Granite is mainly formed by dehydration melting under conditions of water unsaturation or hydrous melting due to the addition of external fluid [53,54]. The Na_2O+K_2O and FeO^T contents of the biotite granites are consistent with hydrous melting due to the addition of external fluid (Figure 8a). Studies have shown that mafic rocks formed in subduction zones have a high water content of >10%. During the processes of cooling, rising, and the underlying process of the mafic magma, they would undergo dehydration to form fluid, which is added to the continental crust and promotes crustal melting, thereby leading to the formation of S-type granite [54]. There is a significant amount of hypersthene in the samples from the Shangyou biotite granite (mostly >1.0 vol.%), and the samples display high $Fe_2O_3^T + MgO + TiO_2$ contents (2.47–4.06 wt.%) and $Mg^{\#}$ values (30–33), indicating that it was not from a pure crustal source [55,56] (Figure 8). In addition, it has been reported that Shangyou intrusion has a relatively depleted Nd isotope composition and a younger Nd two-stage model age ($\varepsilon_{Nd(t)} = -4.06 - 7.00$, T_{DM2} = 1491–1735 Ma) compared with other Caledonian granites ($\epsilon_{Nd(t)} = -8.64 - 13.3$, $T_{DM2} = 1838 - 2252$ Ma) in the Nanling area [57]. Therefore, the addition of mantle material may have provided fluid-dominated materials for the formation of Shangyou biotite granite, but the origin of the fluid is indeed elusive at this point and needs more constraints.

Different from the Shangyou biotite granite, the muscovite granite exhibits similar geochemical characteristics with those rocks derived from the dehydration melting of crustal sources (Figure 9). Biotite, muscovite, and amphibole are the main dehydrated minerals in such a process. The dehydration melting of amphibole usually needs temperatures higher than 850 °C and generally forms alkaline granite [58], while the dehydration temperature of biotite also mostly exceeds 750 °C [53]. Miller et al. (2003) [59] proved that the zirconium saturation temperature of granite with inherited zircons can effectively reflect the melting temperature of its source region and could represent the underestimate of their initial temperature for these granites without inherited zircons. Collins et al. (2021) [60] also suggest that crust-derived granites exhibit characteristics of zirconium supersaturation, and their zirconium saturation temperature reflects the melting temperature in the source region. Therefore, the occurrence of abundant inherited zircon cores and high Zr contents of Shangyou muscovite granite (85.4–108 ppm) indicates that zirconium saturation temperature can reflect its melting temperature. The zirconium saturation temperature of the Shangyou muscovite granite is 745–764 °C, which is significantly lower than the dehydration temperature of biotite and amphibole but similar to the dehydration temperature of muscovite [53,58]. Therefore, we inferred that the generation of the Shangyou muscovite granite is associated with muscovite dehydration in the source area.



Figure 9. (a) Na_2O/K_2O vs. FeO^T [61] and (b) SiO₂ vs. Mg# [62] diagrams for Shangyou biotite granite and muscovite monzogranite.

5.2. The Controls of Temperature on REE Enrichment in Peraluminous Granites

The Ordovician to Devonian magmatic event in South China was proved to be triggered by intracontinental orogeny in the Middle Ordovician and subsequent post-orogenic extension in the Silurian [20,63,64]. In this period, the granitic rocks are mostly generated due to the reworking of crustal materials and are peraluminous [65]. In the postorogenic extension stage in Silurian, the detachment of the lithospheric mantle induced high-temperature asthenosphere upwelling in the regional extensional setting, which provides heat for crustal melting and generation of the A-, S-, and I- type granites in this period [66]. In addition, the shortening and thickening of the crust allow sediments such as sandstone to enter the deep crust, which is conducive to the accumulation of heat, leading to the melting of sediments and the formation of S-type granite [45]. Obviously, there are relatively high-temperature conditions in the continental crust in South China during the Silurian responsible for the generation of the Shangyou granites.

The formation temperature of granite plays an important role in its geochemical characteristics [67]. Experimental petrological studies have confirmed that the formation temperature of most granitic magmas is between 700 and 1100 °C [68,69]. Finger et al. (2022) [70] defined the formation temperature of granite based on zirconium saturation temperature, zircon Ti thermometer, and zircon structural characteristics and classified granite into ultra-low-temperature granite (VLT: <750 $^{\circ}$ C), low-temperature granite (LT: 750–800 °C), medium-temperature granite (MT: 800–850 °C), high-temperature granite (HT: 850–900 °C), and ultra-high-temperature granite (UHT: >900 °C). According to the zirconium saturation temperature of the Shangyou granites, the biotite granite belongs to medium-high temperature granite, which may be closely related to the involvement of mantle material, while the muscovite granite belongs to low-temperature granite. It is noticeable that the REE contents for the Shangyou granites show a positive correlation with the formation temperature, indicating that the temperature may influence the REE contents in the Shangyou granites (Figure 10a). In addition, in granitic systems, aluminum-rich minerals such as aluminosilicates and garnet are insensitive to the changes in temperature, while titanium-containing minerals such as mica and ilmenite will decompose with increasing temperature, resulting in a gradual increase in TiO₂ content in the melts and leading to a negative correlation between the Al₂O₃/TiO₂ ratio and the temperature [71]. Therefore, the

temperature of peraluminous granites can also be qualitatively limited by their Al₂O₃/TiO₂ ratio [71]. The Al_2O_3/TiO_2 ratio of Shangyou biotite granite and Shangyou muscovite granite are different and show a significant negative correlation with REE contents (Figure 10b), further indicating a significant difference in their formation temperature, and the REE contents are related to the formation temperature for the Shangyou granites. The relationship between the temperature condition and REE contents in granites is that the high temperature could promote the melting of REE-rich accessory minerals such as allanite, monazite, and xenotime in the source area, thus increasing the REE contents in the melts [72,73]. It is noticeable that these REE-rich accessory minerals are prevailing in the sediments in South China [52], which are the magmatic source for the S-type granites, supporting the inference that the melting of REE-rich accessory minerals in high-temperature conditions may be the reason for REE enrichment in the Shangyou S-type granites. Furthermore, in addition to REE contents, these REE-rich accessory minerals also contain abundant Th, and melting of these minerals would lead to an increase in Th contents in the melts and a positive correlation between REE contents and Th contents in the granites, which are consistent with those observed in the Shangyou granites (Figure 10c). Thus, the high-temperature condition promotes the melting of REE-rich accessory minerals, accounting for the REE enrichment for the Shangyou granites.

To further constrain the relationship between the formation temperature and REE contents in the granites, we collect global data for the peraluminous granites, which are plotted in Figure 10. The results also show that the REE contents in these peraluminous granites display a positive correlation with their formation temperature and Th contents, and the rocks with high REE contents generally generate in a high-temperature condition, supporting our inference that temperature has controlled the enrichment of REE in peraluminous granites by promoting the melting of REE-rich accessory minerals.

Previous studies have suggested different factors to account for the REE enrichment and activation in the parent granites for the ion-adsorbing REE deposits in South China. Studies on the parent granites in Guanxi ion-adsorbing REE deposits suggested that the involvement of enriched mantle materials in the source area at Jurassic extensional setting had contributed to the relatively high REE contents in these granites [8,74], which is also supported by regional Hf isotope mapping [75]. Xu et al. (2017) [24] and Fan et al. (2023) [76] suggest that subducting slab-derived REE-rich fluids contribute to the HREE enrichment in the parent granites for Zudong ion-adsorbing REE deposit. Other studies based on the Jurassic to Cretaceous granites from the Bachi, and Renju ion-adsorbing REE deposits found that these granites are peraluminous, but show similar geochemical features with those of A-type granites, which are generated in high-temperature extensional conditions [26]. However, although there are different factors resulting in the REE enrichment in some specific granites, the same feature for the parent granites that could generate the ion-adsorption is the high-temperature extensional setting. The granites related to the generation of ion-adsorbing REE deposits are generated in three stages. The Silurian, Late Permian to Triassic, and Jurassic, and Cretaceous [3,66]. The Silurian granites, such as the Shangyou biotite granite and muscovite granite are generated in the high-temperature setting related to the post-orogenic extension, and the Jurassic to Cretaceous granites are related to the extensional setting induced by the slab-foundering and rollback and subsequent steep subduction of the Paleo-Pacific Ocean slab [19,20]. Although the tectonic framework during the Late Permian to Triassic in South China was controlled by the collisional events between the South China Block and Indochina Block, and only local extensional events occurred [51], studies have indicated that the Late Permian to Triassic peraluminous granite, such as the Darongshan S-type granite and Shanglong peraluminous A-type granites associated with the ion-adsorbing REE deposits [77], are also generated in the high-temperature extensional setting, while the rocks generated in a relatively low-temperature compressional setting (such as the Triassic Beitou granite) show relatively REE contents and failed to generate ion-adsorbing deposit in its weathering profile [51]. The fact that the parent granites for ion-adsorbing REE deposits are all generated in high-temperature extensional



settings is consistent with our points that high temperature is the key to the REE enrichment in the peraluminous granites.

Figure 10. TZr (**a**), Al₂O₃/TiO₂ (**b**), and Th (**c**) vs. REE plots of the Shangyou biotite granite and muscovite monzogranite and peraluminous granitoids from worldwide. The data for global peraluminous granitoids are from Georoc: "http://georoc.mpch-mainz.gwdg.de/georoc (accessed on 12 June 2024)".

6. Conclusions

Shangyou granites, which are the parent rocks for ion-adsorbing REE deposits in the Shangyou area, comprise biotite granite and muscovite granite, which are both intruded in Silurian and belong to peraluminous S-type granite. The Shangyou biotite granite is formed by the melting of sediment-dominated crustal members in a relatively high-temperature

condition with the addition of mantle-derived fluid-rich materials. The source area for the muscovite granite is only the sediment-dominated crustal member, and the generation of it is associated with muscovite dehydration in the source area. The muscovite granite shows lower formation temperature and lower REE contents than those of the biotite granite; in combination with the data from global peraluminous granites, it is concluded that REE contents in peraluminous granites show a positive correlation with their formation temperature. There are facts that all the parent granites for ion-adsorbing REE deposits in South China with relatively high REE contents generated in high-temperature conditions. Therefore, we concluded that the high-temperature extensional setting is more conducive to the formation of REE-rich peraluminous granite, which further favors the generation of ion-adsorbing REE deposits.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/min14121222/s1, Table S1: Zircon U-Pb dating for the Shangyou granites; Table S2: Major and trace chemical composition for the Shangyou biotite granite and muscovite granite; Table S3: CIPW norm minerals for the Shangyou biotite granite and muscovite granite.

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References

- 1. He, H.P.; Yang, W.B. REE Mineral Resources in China: Review and Perspective. *Geotecton. Metallog.* **2022**, *46*, 829–841. (In Chinese with English Abstract)
- 2. Chi, R.A.; Tian, J. Review of Weathered Crust Rare Earth Ore. *J. Chin. Rare Earth Soc.* 2007, 25, 641–650. (In Chinese with English Abstract)
- 3. Li, M.Y.H.; Zhao, W.W.; Zhou, M. Nature of Parent Rocks, Mineralization Styles and Ore Genesis of Regolith-Hosted REE Deposits in South China: An Integrated Genetic Model. J. Asian Earth Sci. 2017, 148, 65–95. [CrossRef]
- 4. Bao, Z.; Zhao, Z. Geochemistry of mineralization with exchangeable REY in the weathering crusts of granitic rocks in South China. *Ore Geol. Rev.* 2008, *33*, 519–535. [CrossRef]
- 5. Sanematsu, K.; Watanabe, Y. Characteristics and genesis of ion adsorption-type rare earth element deposits. *Rev. Econ. Geol.* 2016, 18, 55–79.
- 6. Fu, W.; Li, X.T.; Feng, Y.Y.; Feng, M.; Peng, Z.; Yu, H.X.; Lin, H. Chemical weathering of S-type granite and formation of Rare Earth Element (REE)-rich regolith in South China: Critical control of lithology. *Chem. Geol.* **2019**, *520*, 33–51. [CrossRef]
- Zhao, X.; Li, N.B.; Niu, H.C.; Wang, J.; Yan, S.; Yang, Y.Y.; Fu, R.X.; Huizenga, J.M. HREE enrichment during magmatic evolution recorded by apatite: Implication for the ion-adsorption HREE mineralization in South China. *Lithos* 2022, 432–433, 106896. [CrossRef]
- Feng, Y.Z.; Xiao, B.; Chu, G.B.; Li, S.S.; Wang, J.; Wen, Z.Q. Late Mesozoic magmatism in the Gucheng district: Implications for REE metallogenesis in South China. Ore Geol. Rev. 2022, 148, 105034. [CrossRef]
- Chu, G.; Chen, H.; Feng, Y.; Wu, C.; Li, S.; Zhang, Y.; Lai, C.K. Are South China granites special in forming regolith-hosted REE deposits? *Gondwana Res.* 2024, 125, 82–90. [CrossRef]
- 10. Li, M.Y.H.; Zhou, M.F.; Williams-Jones, A.E. The genesis of regolith-hosted heavy rare earth element deposits: Insights from the world-class Zudong deposit in Jiangxi Province, South China. *Econ. Geol.* **2019**, *114*, 541–568. [CrossRef]

- 11. Wang, D.H.; Zhao, Z.; Yu, Y.; Wang, C.H.; Dai, J.J.; Sun, Y.; Zhao, T.; Li, J.K.; Huang, F.; Chen, Z.Y.; et al. A Review of the Achievements in the Survey and Study of Ion-absorption Type REE Deposits in China. *Acta Geosci. Sin.* **2017**, *38*, 317–325. (In Chinese with English Abstract)
- Zhou, M.F.; Li, X.X.; Wang, Z.C.; Li, X.C.; Liu, J.C. The genesis of regolith-hosted rare earth element and scandium deposits: Current understanding and outlook to future prospecting. *Chin. Sci. Bull.* 2020, 65, 3809–3824. (In Chinese with English Abstract) [CrossRef]
- Borst, A.M.; Smith, M.P.; Finch, A.A.; Estrade, G.; Villanova-de-Benavent, C.; Nason, P.; Marquis, E.; Horsburgh, N.J.; Goodenough, K.M.; Xu, C.; et al. Adsorption of rare earth elements in regolith-hosted clay deposits. *Nat. Commun.* 2020, *11*, 4386. [CrossRef] [PubMed]
- 14. Huang, J.; He, H.P.; Tan, W.; Liang, X.L.; Ma, L.Y.; Wang, Y.Y.; Qin, X.R.; Zhu, J.X. Groundwater controls REE mineralisation in the regolith of South China. *Chem. Geol.* 2021, 577, 120295. [CrossRef]
- 15. Hua, R.M.; Zhang, W.L.; Gu, S.Y.; Chen, P.R. Comparison between REE granite and W-Sn granite in the Nanling region, South China, and their mineralizations. *Acta Petrol. Sin.* **2007**, *23*, 2321–2328. (In Chinese with English Abstract)
- 16. Ishihara, S.; Hua, R.; Hoshino, M.; Murakami, H. REE abundance and REE minerals in granitic rocks in the Nanling range, Jiangxi Province, southern China, and generation of the REE-rich weathered crust deposits. *Resour. Geol.* 2008, *58*, 355–372. [CrossRef]
- Wang, H.; He, H.P.; Yang, W.B.; Bao, Z.W.; Liang, X.L.; Zhu, J.X.; Ma, L.Y.; Huang, Y. Zircon texture and composition fingerprint HREE enrichment in muscovite granite bedrock of the Dabu ion-adsorption REE deposit, South China. *Chem. Geol.* 2023, 616, 121231. [CrossRef]
- Huang, Y.F.; Tan, W.; Bao, Z.W.; He, H.P.; Liang, X.L.; Huang, J.; Wang, H. Constraints of Parent Rocks on the Formation of Ion Adsorption HREE Deposit in the Weathering Crust of the Shangyou Granite Batholith. *Geotecton. Metallog.* 2022, 46, 303–317. (In Chinese with English Abstract)
- 19. Li, Z.X.; Li, X.H. Formation of the 1300-km-wide intracontinental orogen and postorogenic magmatic province in Mesozoic South China: A flat-slab subduction model. *Geology* 2007, *35*, 179–182. [CrossRef]
- Charvet, J.; Shu, L.; Faure, M.; Choulet, F.; Wang, B.; Lu, H.; Le Breton, N. Structural development of the Lower Paleozoic belt of South China: Genesis of an intracontinental orogen. J. Asian Earth Sci. 2010, 39, 309–330. [CrossRef]
- 21. Xie, L.; Wang, Z.J.; Wang, R.C.; Zhu, J.C.; Chen, X.D.; Gao, J.F.; Zhao, X. Mineralogical constraints on the genesis of W–Nb–Ta mineralization in the Laiziling granite (Xianghualing district, south China). *Ore Geol. Rev.* **2018**, *95*, 695–712. [CrossRef]
- 22. Wang, X.N.; Chen, X.L.; Zou, S.H.; Jia, Z.W.; Li, B.; Wang, H.; Xu, D.R. Geochronology, geochemistry, and mineral chemistry of the Lingshan-Huangshan complex, South China: Insights into Nb and Ta enrichment. *Ore Geol. Rev.* 2023, 157, 105433. [CrossRef]
- 23. Fu, W.; Zhao, Q.; Luo, P.; Li, P.Q.; Lu, J.P.; Zhou, H.; Yi, Z.B.; Xu, C. Mineralization diversity of ionadsorption type REE deposit in southern China and the critical influence of parent rocks. *Acta Geol. Sin.* 2022, *96*, 3901–3923. (In Chinese with English Abstract)
- 24. Xu, C.; Kynický, J.; Smith, M.P.; Kopriva, A.; Brtnický, M.; Urubek, T.; Yang, Y.; Zhao, Z.; He, C.; Song, W. Origin of heavy rare earth mineralization in South China. *Nat. Commun.* **2017**, *8*, 14598. [CrossRef]
- 25. Zhao, Z.; Wang, D.H.; Bagas, L.; Chen, Z.Y. Geochemical and REE mineralogical characteristics of the Zhaibei Granite in Jiangxi Province, southern China, and a model for the genesis of ion-adsorption REE deposits. *Ore Geol. Rev.* 2022, 140, 104579. [CrossRef]
- 26. Zhao, X.; Li, N.B.; Huizenga, J.M.; Yan, S.; Yang, Y.Y.; Niu, H.C. Rare earth element enrichment in the ion-adsorption deposits associated granites at Mesozoic extensional tectonic setting in South China. *Ore Geol. Rev.* **2021**, 137, 104317. [CrossRef]
- 27. Zhao, X.; Li, N.B.; Niu, H.C.; Jiang, Y.H.; Yan, S.; Yang, Y.Y.; Fu, R.X. Hydrothermal alteration of allanite promotes the generation of ion-adsorption LREE deposits in South China. *Ore Geol. Rev.* **2023**, *155*, 105377. [CrossRef]
- 28. Yusoff, Z.M.; Ngwenya, B.T.; Parsons, I. Mobility and fractionation of REEs during deep weathering of geochemically contrasting granites in a tropical setting, Malaysia. *Chem. Geol.* **2013**, *349*, 71–86. [CrossRef]
- 29. Zhao, Z.; Wang, D.H.; Chen, Z.H.; Chen, Z.Y. Progress of Research on Metallogenic Regularity of Ion-adsorption Type REE Deposit in the Nanling Range. *Acta Geol. Sin.* **2017**, *91*, 2814–2827, (In Chinese with English Abstract).
- Zhou, X.M.; Sun, T.; Shen, W.Z.; Shu, L.S.; Niu, Y.L. Petrogenesis of Mesozoic granitoids and volcanic rocks in South China: A response to tectonic evolution. *Epis. J. Int. Geosci.* 2006, 29, 26–33. [CrossRef]
- 31. Ludwig, K.R. Isoplot: A Geochronological Toolkit for Microsoft Excel. Berkeley Geochronol. Center. Spec. Publ. 2012, 5, 75.
- 32. Watson, E.B.; Harrison, T.M. Zircon saturation revisited: Temperature and composition effects in a variety of crustal magma types. *Earth Planet. Sci. Lett.* **1983**, *64*, 295–304. [CrossRef]
- Zhang, F.; Wang, Y.; Zhang, A.; Fan, W.; Zhang, Y.; Zi, J. Geochronological and geochemical constraints on the petrogenesis of Middle Paleozoic (Kwangsian) massive granites in the eastern South China Block. *Lithos* 2012, 150, 188–208. [CrossRef]
- 34. Thomas, R.; Davidson, P. Water in granite and pegmatite-forming melts. Ore Geol. Rev. 2012, 46, 32–46. [CrossRef]
- 35. Hoskin, P.W.; Schaltegger, U. The composition of zircon and igneous and metamorphic petrogenesis. *Rev. Mineral. Geochem.* 2003, 53, 27–62. [CrossRef]
- 36. Wilson, M. Review of Igneous Petrogenesis: A Global Tectonic Approach. Terra Nova 1989, 1, 218–222. [CrossRef]
- 37. Maniar, P.D.; Piccoli, P.M. Tectonic discrimination of granitoids. Geol. Soc. Am. Bull. 1989, 101, 635–643. [CrossRef]
- 38. Sun, S.S.; McDonough, W. Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes. *Geol. Soc. Lond. Spec. Publ.* **1989**, 42, 313–345. [CrossRef]
- Whalen, J.B.; Currie, K.L.; Chappell, B.W. A-type granites: Geochemical characteristics, discrimination and petrogenesis. Contrib. Mineral. Petr. 1987, 95, 407–419. [CrossRef]

- 40. Chappell, B.W.; White, A. I- and S-type granites in the Lachlan Fold Belt. Earth Environ. Sci. Trans. R. Soc. Edinb. 1992, 83, 1–26.
- 41. Chappell, B.W. Aluminium saturation in I- and S-type granites and the characterization of fractionated haplogranites. *Lithos* **1999**, 46, 535–551. [CrossRef]
- 42. Collins, W.J.; Beams, S.D.; White, A.J.R.; Chappell, B.W. Nature and origin of A-type granites with particular reference to southeastern Australia. *Contrib. Mineral. Petr.* **1982**, *80*, 189–200. [CrossRef]
- 43. Pitcher, W.S. Granite Type and Tectonic Environment; Mountain Building Processes; Academic Press: London, UK, 1983; pp. 19-40.
- 44. Clemens, J.D. S-type granitic magmas-petrogenetic issues, models and evidence. Earth Sci. Rev. 2003, 61, 1–18. [CrossRef]
- Zhao, X.; Wei, J.H.; Fu, L.B.; Huizenga, J.M.; Santosh, M.; Chen, J.J.; Wang, D.Z.; Li, A.B. Multi-stage crustal melting from Late Permian back-arc extension through Middle Triassic continental collision to Late Triassic post-collisional extension in the East Kunlun Orogen. *Lithos* 2020, 360–361, 105446. [CrossRef]
- 46. Bonin, B. A-type granites and related rocks: Evolution of a concept, problems and prospects. Lithos 2007, 97, 1–29. [CrossRef]
- Li, X.W.; Mo, X.X.; Zhao, Z.D.; Zhu, D.C. A discussion on how to discriminate A-type granite. *Geol. Bull. China* 2010, 29, 278–285. (In Chinese with English Abstract)
- Huang, H.Q.; Li, X.H.; Li, W.X.; Li, Z.X. Formation of high δ¹⁸O fayalite-bearing A-type granite by high-temperature melting of granulitic metasedimentary rocks, southern China. *Geology* 2011, 39, 903–906. [CrossRef]
- 49. Douce, A. What do experiments tell us about the relative contributions of crust and mantle to the origin of granitic magmas? *Geol. Soc. Lond. Spec. Publ.* **1999**, *168*, 55–75. [CrossRef]
- 50. Jiao, S.J.; Li, X.H.; Huang, H.Q.; Deng, X.G. Metasedimentary melting in the formation of charnockite: Petrological and zircon U-Pb-Hf-O isotope evidence from the Darongshan S-type granitic complex in Southern China. *Lithos* **2015**, *239*, 217–233. [CrossRef]
- 51. Zhao, X.; Li, N.B.; Niu, H.C.; Tan, S.C.; Fu, R.X.; Yang, Y. Extension settings favour initial REE enrichment in the parent granites of ion-adsorption REE deposits: Implication from Late-Permian to Triassic granites in South China. *J. Geol. Soc.* 2024, *in press.* [CrossRef]
- 52. Wang, Z.; Zhao, Z.; Zou, X.Y.; Chen, Z.Y.; Tu, X.J. Petrogeochemical Characteristics and Metallogenetic Potential of Epimetamorphic Rocks in South Jiangxi Province. *Rock Miner. Anal.* **2018**, *37*, 96–107. (In Chinese with English Abstract)
- 53. Weinberg, R.F.; Hasalová, P. Water-fluxed melting of the continental crust: A review. Lithos 2015, 212–215, 158–188. [CrossRef]
- 54. Collins, W.J.; Murphy, J.B.; Johnson, T.E.; Huang, H. Critical role of water in the formation of continental crust. *Nat. Geosci.* 2020, 13, 331–338. [CrossRef]
- 55. Jiang, Y.H.; Jia, R.Y.; Liu, Z.; Liao, S.Y.; Zhao, P.; Zhou, Q. Origin of Middle Triassic high-K calc-alkaline granitoids and their potassic microgranular enclaves from the western Kunlun orogen, northwest China: A record of the closure of Paleo-Tethys. *Lithos* **2013**, *156–159*, 13–30. [CrossRef]
- Lu, L.; Zhang, K.J.; Yan, L.L.; Jin, X.; Zhang, Y.X. Was Late Triassic Tanggula granitoid (central Tibet, western China) a product of melting of underthrust Songpan-Ganzi flysch sediments? *Tectonics* 2017, 36, 902–928. [CrossRef]
- 57. Zhang, F.R. The Geological and Geochemical Characteristics and Its Petrogenesis for Caledonian Granites in the Central-Southern JiangXi Province. Ph.D. Thesis, Nanjing University, Nanjing, China, 2011. (In Chinese with English Abstract)
- Huang, C.; Chen, B.; Sun, K.K. A-type granites derived from dehydration melting of calc-alkaline granitoids in East Junggaer (NW China): Implications for the origin of aluminous and peralkaline A-types. *Lithos* 2023, 440–441, 107043. [CrossRef]
- Miller, C.F.; McDowell, S.M.; Mapes, R.W. Hot and cold granites? Implications of zircon saturation temperatures and preservation of inheritance. *Geology* 2003, *31*, 529–532. [CrossRef]
- 60. Collins, W.J.; Murphy, J.B.; Blereau, E.; Huang, H.Q. Water availability controls crustal melting temperatures. *Lithos* **2021**, 402–403, 106351. [CrossRef]
- 61. Mo, J.; Xia, X.P.; Li, P.F.; Spencer, C.J.; Lai, C.K.; Xu, J.; Yang, Q.; Sun, M.D.; Yu, Y.; Milan, L. Water-in-zircon: A discriminant between S- and I-type granitoid. *Contrib. Mineral. Petr.* **2023**, *178*, 5. [CrossRef]
- 62. Sisson, T.W.; Ratajeski, K.; Hankins, W.B.; Glazner, A.F. Voluminous granitic magmas from common basaltic sources. *Contrib. Mineral. Petr.* **2005**, *148*, 635–661. [CrossRef]
- 63. Faure, M.; Shu, L.; Wang, B.; Charvet, J.; Choulet, F.; Monie, P. Intracontinental subduction: A possible mechanism for the Early Palaeozoic Orogen of SE China. *Terra Nova* **2009**, *21*, 360–368. [CrossRef]
- Wang, X.L.; Zhou, J.C.; Wan, Y.S.; Kitajima, K.; Wang, D.; Bonamici, C.; Qiu, J.S.; Sun, T. Magmatic evolution and crustal recycling for Neoproterozoic strongly peraluminous granitoids from southern China: Hf and O isotopes in zircon. *Earth Planet. Sci. Lett.* 2013, *366*, 71–82. [CrossRef]
- 65. Hua, R.M.; Zhang, W.L.; Chen, P.R.; Zhai, W.; Li, G.L. Relationship Between Caledonian Granitoids and Large-scale Mineralization in South China. *Geol. J. China Univ.* **2013**, *19*, 1–11, (In Chinese with English Abstract).
- 66. Zhang, Q.; Jiang, Y.H.; Wang, G.C.; Liu, Z.; Ni, C.Y.; Qing, L. Origin of Silurian gabbros and I-type granites in central Fujian, SE China: Implications for the evolution of the early Paleozoic orogen of South China. *Lithos* **2015**, 216–217, 285–297. [CrossRef]
- 67. King, P.L.; White, A.J.R.; Chappell, B.W.; Allen, C.M. Characterization and Origin of Aluminous A-type Granites from the Lachlan Fold Belt, Southeastern Australia. *J. Petrol.* **1997**, *38*, 371–391. [CrossRef]
- 68. Duan, M.; Niu, Y.L.; Sun, P.; Chen, S.; Kong, J.J.; Li, J.Y.; Zhang, Y.; Hu, Y.; Shao, F.L. A simple and robust method for calculating temperatures of granitoid magmas. *Miner. Petrol.* 2022, 116, 93–103. [CrossRef]
- 69. Gao, P.; Zheng, Y.F.; Zhao, Z.F. Experimental melts from crustal rocks: A lithochemical constraint on granite petrogenesis. *Lithos* **2016**, 266–267, 133–157. [CrossRef]

- 70. Finger, F.; Schiller, D.; Lindner, M.; Hauzenberger, C.; Verner, K.; Žák, J. Ultrahigh-temperature granites and a curious thermal eye in the post-collisional South Bohemian batholith of the Variscan orogenic belt (Europe). *Geology* **2022**, *50*, 542–546. [CrossRef]
- 71. Sylvester, P.J. Post-collisional strongly peraluminous granites. Lithos 1998, 45, 29–44. [CrossRef]
- 72. Skjerlie, K.P.; Johnston, A.D. Vapor-absent melting at 10 kbar of a biotite-and amphibole-bearing tonalitic gneiss: Implications for the generation of A-type granites. *Geology* **1992**, *20*, 263–266. [CrossRef]
- 73. Villaros, A.; Stevens, G.; Moyen, J.-F.; Buick, I.S. The trace element compositions of S-type granites: Evidence for disequilibrium melting and accessory phase entrainment in the source. *Contrib. Mineral. Petr.* **2009**, *158*, 543–561. [CrossRef]
- 74. He, C.; Xu, C.; Zhao, Z.; Kynicky, J.; Song, W.; Wang, L. Petrogenesis and mineralization of ree-rich granites in Qingxi and Guanxi, Nanling Region, South China. *Ore Geol. Rev.* 2017, *81*, 309–325. [CrossRef]
- 75. Zhang, Z.Y.; Hou, Z.Q.; Lü, Q.T.; Zhang, X.W.; Pan, X.F.; Fan, X.K.; Zhang, Y.Q.; Wang, C.G.; Lü, Y.J. Crustal architectural controls on critical metal ore systems in South China based on Hf isotopic mapping. *Geology* **2023**, *51*, 738–742. [CrossRef]
- 76. Fan, C.X.; Xu, C.; Shi, A.G.; Smith, M.P.; Kynicky, J.; Wei, C.W. Origin of heavy rare earth elements in highly fractionated peraluminous granites. *Geochim. Cosmochim. Acta* 2023, 343, 371–383. [CrossRef]
- 77. Gao, P.; Zheng, Y.F.; Zhao, Z.F. Triassic granites in South China: A geochemical perspective on their characteristics, petrogenesis, and tectonic significance. *Earth Sci. Rev.* 2017, 173, 266–294. [CrossRef]

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