

Article

Geochronology, Genesis and Redox Condition of the Lisong Granites in the Guposhan Region, Nanling Range: Constraints from Zircon U-Pb Dating, Whole-Rock Geochemistry, and Apatite Geochemistry

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Abstract

The Guposhan ore field, located in the Nanling metallogenic belt, is well known for large-scale Sn-W mineralization genetically linked to the Late Jurassic Guposhan pluton. The Lisong pluton, a product of regional magmatism, occurs in the central part of the Guposhan ore field. However, the critical factors responsible for the absence of intensive Sn polymetallic mineralization in the Lisong pluton remain poorly understood. Our geochronological results show that the coarse-grained hornblende-bearing and hornblende-free biotite monzogranites of the Lisong pluton were emplaced at 162.9 ± 1.5 Ma and 162.2 ± 2.3 Ma, respectively, which are contemporaneous with the Guposhan pluton. Geochemically, these intrusions are characterized by high SiO_2 , Al_2O_3 , and total alkalis ($\text{K}_2\text{O} + \text{Na}_2\text{O}$), high Ga/Al ratios (3.09–3.69), and peraluminous compositions ($A/\text{CNK} = 1.15\text{--}1.23$), consistent with high K calc-alkaline A-type granites. Similar to the adjacent Guposhan pluton, the Lisong granites yield variable $\epsilon_{\text{Hf}}(t)$ values from -3.0 to 5.7 , apatite $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of $0.69747\text{--}0.71190$, and old two-stage Hf model ages ($T_{\text{DM}2}$) of $0.85\text{--}1.40$ Ga. These features suggest that the Lisong and Guposhan granites may share a common magma source involving mixing of crustal and mantle-derived melts. Apatite grains from the Lisong granites display negative Eu anomalies ($\delta\text{Eu} = 0.03\text{--}0.22$) and near-normal to positive Ce anomalies ($\delta\text{Ce} = 0.99\text{--}1.07$), which we interpret to reflect plagioclase fractional crystallization and reduced melt conditions, respectively. Bulk rock geochemistry and multi-element systematics of the Lisong granites indicate that they represent early-stage magmatic products. Their relatively low differentiation signatures were unfavorable for Sn enrichment and mineralization in the melt, which likely explains the lack of intensive Sn polymetallic mineralization in the Lisong pluton.

Keywords: geochemistry; granites; apatite; Lisong pluton; Guposhan orefield



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1. Introduction

The circum-Pacific metallogenic belt, a globally significant metallogenic province, comprises several major domains, including the Southeast Asian Tin Belt (SATB) and the South China Metallogenic Belt (SCMB) [1–5]. Situated in the SCMB (Figure 1), the Nanling Metallogenic Belt (NLMB) is renowned for its intense felsic magmatism and associated W–Sn polymetallic mineralization, accounting for over 83% and 63% of China’s tungsten and tin reserves, respectively [6–10]. The mineralizing history is episodic, with temporally distinct events identified in the Neoproterozoic, Paleozoic, and Mesozoic [11–15]. Granites, products of the felsic magmatism, are mainly characterized by their highly fractionated signature, which was regarded as one of the key factors in causing the regional W–Sn polymetallic mineralization within the NLMB [7,16–19]. In addition, these highly fractionated granites, mainly formed within the range of 165–150 Ma, were widely distributed in the NLMB, e.g., the Guposhan, Dayishan, Qitianling, and Jiuyishan plutons [16–20]. Multistage magmatic evolution, dominated by fractional crystallization, was commonly identified as the major trigger for forming these highly fractionated granites in this region [12,21–24]. The formation and evolution of highly fractionated magmas within the NLMB represent a significant area of interest for geologists [25]. Nevertheless, the specific mechanisms driving the magmatic evolution process remain a critical focus of research. Elucidating these mechanisms provides the foundation for understanding the petrogenesis of these highly fractionated granites and related regional W–Sn polymetallic mineralization.

The Guposhan Sn–W polymetallic ore field, located at the western NLMB, is notable for its large-scale W–Sn polymetallic mineralization and hosting two important granitic intrusions, i.e., the Lisong and Guposhan plutons (Figure 1). Previous studies indicated that the Lisong and Guposhan granites might share a similar magma source since the ages and isotopic compositions of granites of both plutons are similar, i.e., ca. 160 Ma for ages of both granites and relatively depleted Nd–Hf isotopes [15,18,26,27]. However, Sn–W mineralization is strikingly scarce within the Lisong pluton, a feature that stands in marked contrast to the intense mineralization observed in the Guposhan pluton. The mechanism responsible for the lack of large-scale Sn–W mineralization in the Lisong pluton remains unclear, which hinders further understanding of regional Sn–W mineralization and ore prospecting. Therefore, this study presents new geochronological and geochemical data for the Lisong granites, including LA–ICP–MS zircon dating and Lu–Hf isotopes, apatite element and Sr isotopes, and whole-rock major–trace element compositions, to clarify the emplacement age, magma source, and oxidation state, as well as the genesis of the Lisong granites, which will provide critical insights into the key factors in controlling the regional Sn–W mineralization.

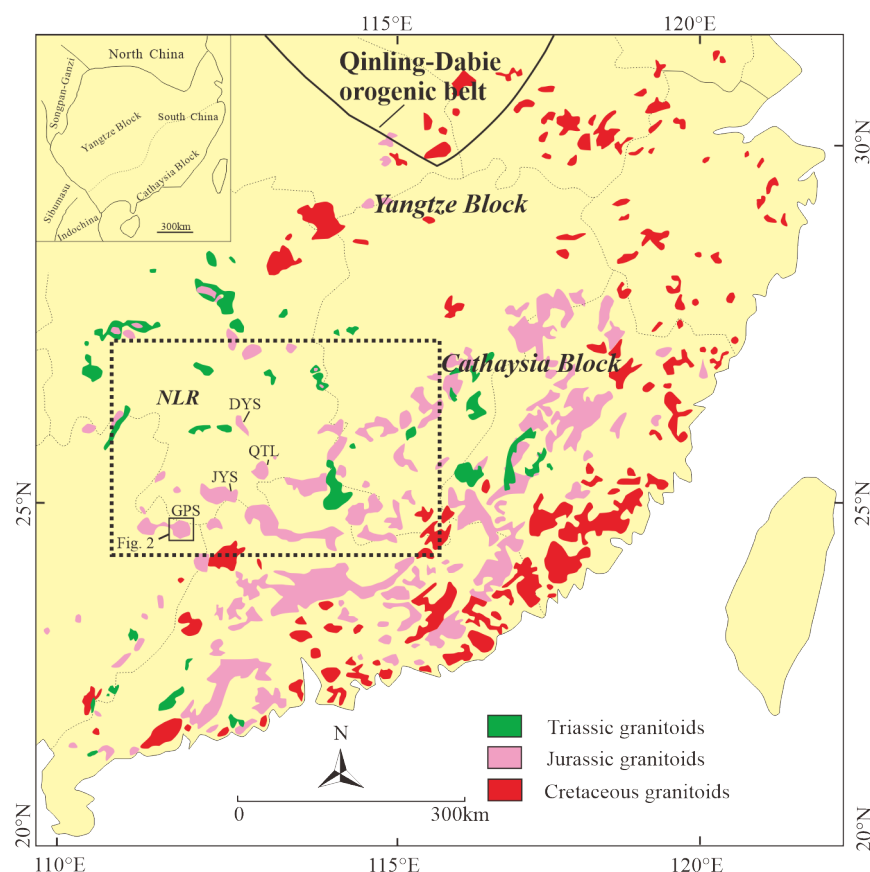


Figure 1. Simplified geological map of the South China Block, adapted from Zhou et al. (2006) [28].

2. Geological Background and Sampling

The Guposhan region in eastern Guangxi Province is notable for its large-scale W-Sn polymetallic mineralization, genetically related to the Jurassic Guposhan granites (Figure 1). This region has experienced multi-stage tectonic events, resulting in the formation of the regional structural frame, particularly its NE-trending fault systems, which reflect a complex tectonic history involving the Caledonian, Indosinian, and Yanshanian orogenies [29,30]. Intense granitic magmatism occurs in the Yanshanian event and forms the Guposhan and Lisong plutons, covering approximately 678 km² and 70 km², respectively. The Guposhan plutons are genetically related to the regional Sn-polymetallic mineralization, hosting a series of Sn-polymetallic deposits, e.g., Helukou, Xinlu, and Shuiyanba Sn deposits [15,31]. The Guposhan pluton, dated at 162.8 ± 1.3 Ma, is predominantly composed of fine- and medium-grained biotite granite that intrudes the Devonian marine clastic-carbonate sequences, inducing extensive silicification, marmorization, and skarnization of the surrounding rocks and intense W-Sn polymetallic mineralization [15,18]. The Lisong pluton, located within the Guposhan pluton, has an age of 163.3 ± 1.3 Ma and consists of coarse-grained biotite monzonitic granites [32]. The Lisong pluton is overlain by the Guposhan pluton, exhibiting a sharp change in lithology from coarse-grained to fine-grained texture [33]. In addition, a considerable amount of mafic microgranular enclave (MME) is widespread within the granitoids of the Lisong pluton. The stratigraphic sequence is composed of: (1) Sinian greywacke; (2) Cambrian quartz sandstone, dolomite, bioclastic limestone, and epimetamorphic sandshales; (3) Devonian shallow marine clastic and carbonate rocks; Carboniferous carbonate rocks; (4) Jurassic carbonate rocks and quartz sandstones; and (5) Neogene shaly sandstone and Quaternary conglomerate (Figure 2).

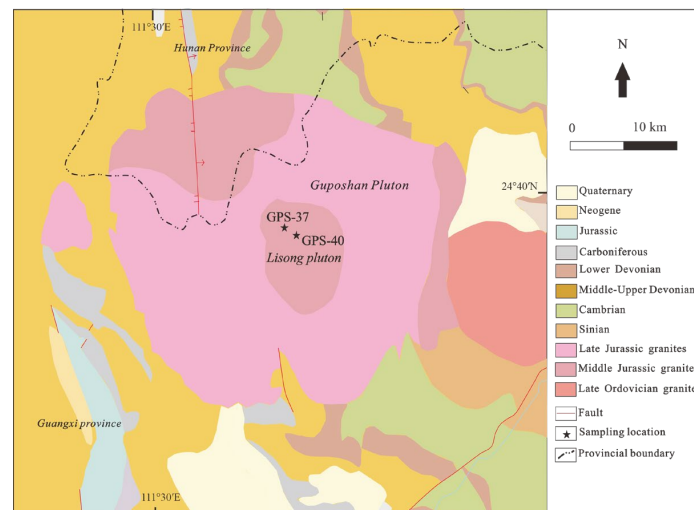


Figure 2. Simplified geological map of the Guposhan ore field, adapted from Li et al. (2015) [31].

Samples of biotite monzonitic granites (hornblende-bearing) and biotite monzonitic granites (hornblende-free) were collected from two drilling cores within the Lisong pluton (Figure 2). The former exhibits a massive structure and is characterized by the occurrence of the mafic microgranular enclaves (MMEs) (Figure 3a). The mineral assemblages contain K-feldspar (~30%), plagioclase (~25%), quartz (~30%), biotite (~10%), hornblende (~5%), and accessory minerals (less than 1%; e.g., zircon, apatite, rutile) (Figure 3c,d). In contrast, the latter lacks hornblende and has a higher quartz content (~35%), while the proportions of other minerals remain similar (Figure 3e,f).

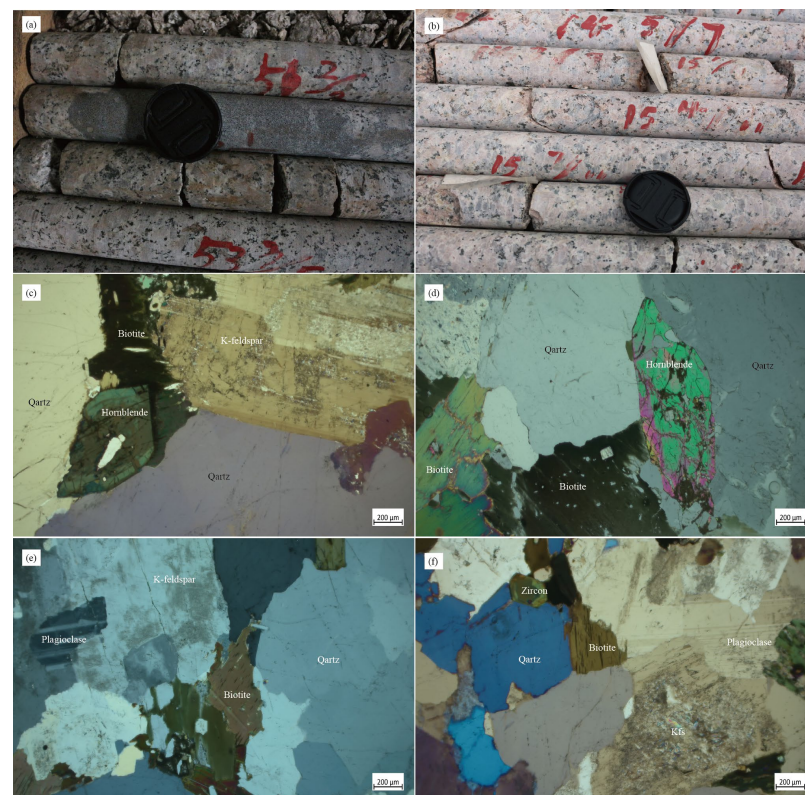


Figure 3. Hand specimen photograph and photomicrographs of the Lisong coarse-grained hornblende-bearing biotite monzonitic granites (a,c,d) and coarse-grained hornblende-free biotite monzonitic granite (b,e,f). Mineral abbreviations: Bi, biotite; Hbl, hornblende; Kfs, K-feldspar; Pl, plagioclase; Qtz, quartz.

3. Analytical Techniques

3.1. LA-ICP-MS Zircon U-Pb Dating

Separation of zircon grains was achieved by combining standard magnetic and heavy liquid methods with final manual picking under a binocular microscope. The preparation of the selected grains involved first mounting them in epoxy resin blocks, then polishing the mounts to reveal flat internal surfaces. Cathodoluminescence (CL) imaging of zircon grains was conducted to examine their internal structures before geochemical analysis. The imaging was performed using a TESCAN MIRA 3 LMH FE-SEM (TESCAN Brno, s.r.o., Brno, Czech Republic) scanning electron microscope at Sample Solution Analytical Technology Co., Ltd. (Wuhan, China). Zircon U-Pb dating was carried out by the LA-ICP-MS instrument at the In Situ Mineral Geochemistry Laboratory, Ore Deposit and Exploration Centre (ODEC), Hefei University of Technology, Hefei, China. The analytical system comprised an Agilent 7900 quadrupole ICP-MS (Agilent Technologies, Santa Clara, CA, USA) coupled with a Photon Machines Analyte HE 193-nm ArF excimer laser ablation system (Photon Machines, Inc., Bozeman, MT, USA). External standards included zircon 91,500 with an age of 1062 ± 4 Ma [34] and NIST SRM610 silicate glass (National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA). Zircon U-Pb dating employed the decay constants from [35]. Results for individual analyses, reported with 1σ uncertainties in the accompanying data tables and Concordia diagrams, are based on a 95% confidence level (2σ) for age uncertainties. Data processing was conducted with ICPMSDataCal 10.7 [36], with common Pb corrections applied following Andersen (2002) [37]. Weighted mean ages and Concordia diagrams were generated using ISOPLOT 3.0 [38].

3.2. Zircon Lu-Hf Isotopic Analyses

In situ Hf isotope measurements for zircon Lu-Hf analysis were performed on the previously dated grains using a Geolas Pro laser ablation system (Thermo Fisher Scientific, Bremen, Germany) coupled to a Neptune MC-ICP-MS (Thermo Fisher Scientific, Bremen, Germany) at the Key Laboratory of Focused Magmatism and Giant Ore Deposits, Xi'an Center of Geological Survey, Xi'an, China. Analytical conditions and data acquisition protocols followed the procedures [39,40]. The zircon reference material GJ-1 was utilized for external calibration, yielding a weighted-average $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282030 ± 40 (2σ). Isobaric interference corrections for ^{176}Yb on ^{176}Hf were applied using a mean βYb value and a $^{176}\text{Yb}/^{172}\text{Yb}$ ratio of 0.5887. The decay constant for ^{176}Lu ($1.865 \times 10^{-11} \text{ year}^{-1}$) [41] and present-day chondritic ratios ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$; $^{176}\text{Lu}/^{177}\text{Hf} = 0.0332$) [42] were used to calculate $\epsilon_{\text{Hf}}(t)$ values. Single-stage Hf model ages (T_{DM1}) were calculated relative to the depleted mantle present-day values ($^{176}\text{Hf}/^{177}\text{Hf} = 0.28325$; $^{176}\text{Lu}/^{177}\text{Hf} = 0.0384$) [43,44]. Two-stage Hf model ages (T_{DM2}) were calculated assuming derivation from the average continental crust ($^{176}\text{Lu}/^{177}\text{Hf} = 0.015$) [45].

3.3. LA-ICP-MS Major and Trace Element Analyses of Apatite

Upon separation, individual grains of high optical clarity were meticulously hand-picked under a binocular microscope. We conducted measurements of apatite element concentrations using LA-ICP-MS at the School of Resources and Environmental Engineering, Hefei University of Technology. The analyses utilized a system that consists of a Resonetics 193 nm ArF-excimer laser coupled with an Agilent 7500a ICP-MS, operating with a $30 \mu\text{m}$ spot size, 5 Hz frequency, and $4 \text{ J}/\text{cm}^2$ fluence. To ensure precision and accuracy, external calibration was performed using the standard references, i.e., SRM 610 and BCR-2G. Raw data were processed offline using the ICPMSDataCal software (version 10.7) [36].

3.4. LA-MC-ICP-MS Sr Isotopic Analyses of Apatite

Apatite strontium isotope compositions were analyzed using a Thermo Fisher Scientific Neptune Plus multi-collector ICP-MS (Waltham, MA, USA) coupled with a Coherent GeoLas HD excimer ArF laser ablation system (Coherent, Inc., Saxonburg, PA, USA) at Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. The instrument was configured with nine Faraday cups ($10^{11} \Omega$ resistors) to monitor Kr, Rb, Er, Yb, and Sr isotopes. A high-sensitivity X-skimmer cone and a Jet-sample cone were used, with helium as the carrier gas. Single-spot laser ablation employed a 60 μm spot size at a repetition rate of 8–15 Hz and a fluence of $\sim 10 \text{ J}/\text{cm}^2$. The detailed analytical methodology and data processing protocols for apatite Sr isotopic analysis followed Cao et al. (2023) [46].

3.5. Bulk-Rock Major and Trace Element Analyses

A total of ten granite samples from the study area were analyzed for bulk-rock major and trace element compositions at ALS Chemex, Guangzhou, China. Samples without MMEs were crushed to pass through a 200-mesh sieve. Major element concentrations were determined using an XRF spectrometer (PANalytical B.V., Almelo, The Netherlands), with an analytical accuracy of 1%–5%. The analysis of trace element compositions was conducted on an ICP-MS spectrometer (Agilent Technologies, Santa Clara, CA, USA), achieving an analytical accuracy greater than 5%.

4. Results

4.1. Zircon Ages

Zircons from the coarse-grained biotite monzonitic granites (hornblende-free) are characterized by euhedral, colorless crystals. These grains have lengths of 120–200 μm and exhibit aspect ratios of 1:1 to 2:1. Furthermore, cathodoluminescence (CL) imaging shows that the majority of zircons possess distinct oscillatory zoning, confirming a magmatic origin (Figure 4a–d) [47]. Geochemically, the zircons display U and Th concentrations of 178–1272 ppm and 73–889 ppm, respectively, resulting in relatively high Th/U ratios of 0.35–0.93 (mean = 0.49); this compositional signature further affirms their magmatic origin (Table S1) [47]. Consequently, a set of twenty-two analyses yielded a concordant $^{206}\text{Pb}/^{238}\text{U}$ age of $163.6 \pm 5.7 \text{ Ma}$ (MSWD = 1.6) (Figure 5a), which is consistent with the weighted-average $^{206}\text{Pb}/^{238}\text{U}$ age of $162.2 \pm 1.5 \text{ Ma}$ (MSWD = 1.18) (Figure 5b). Hence, the weighted-average $^{206}\text{Pb}/^{238}\text{U}$ age is interpreted as the crystallization age of the coarse-grained biotite monzonitic granites (hornblende-free).

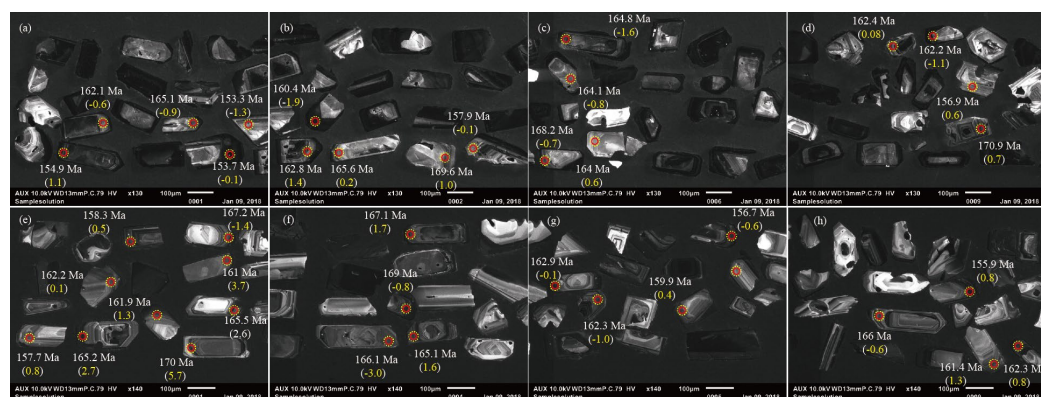


Figure 4. Cathodoluminescence (CL) characteristics of zircons. (a–d) Coarse-grained hornblende-free biotite monzonitic granite; (e–h) Coarse-grained hornblende-bearing biotite monzonitic granite. The $^{206}\text{Pb}/^{238}\text{U}$ age and $\epsilon_{\text{Hf}}(t)$ values were marked in white and yellow, respectively. The beam spot diameters for zircon U–Pb dating and Lu–Hf isotopic analyses were 32 and 44 μm , respectively.

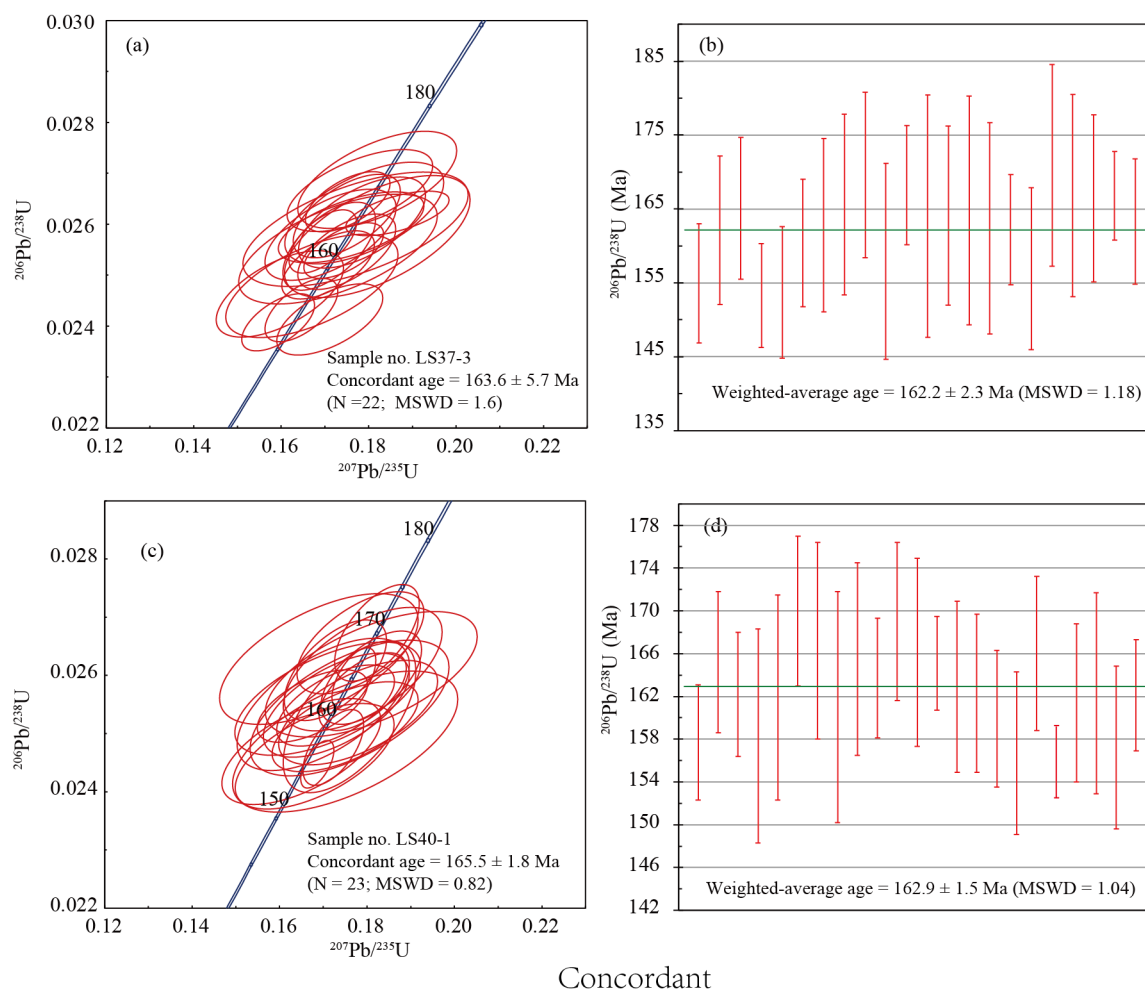


Figure 5. U-Pb ages for zircon grains from the Lisong granites. (a,c): zircon U-Pb concordia diagrams; (b,d): weighted average diagrams.

Zircon grains from the coarse-grained biotite monzonitic granite (hornblende-bearing) occur as euhedral crystals and have lengths of 100–300 μm and aspect ratios of 1:1–3:1. Features of CL images indicate that most of the zircon grains have internal oscillatory zoning, which is of magmatic origin (Figure 4e–h) [47]. Zircon grains have variable U (216–2888 ppm) and Th (87–2290 ppm) concentrations, with relatively high Th/U ratios of 0.19–0.99 (mean = 0.48) (Table S1 in the Supplementary Materials). The selected analyses of zircon grains yield a concordant $^{206}\text{Pb}/^{238}\text{U}$ age of $165.5 \text{ Ma} \pm 1.8 \text{ Ma}$ (MSWD = 0.82) (Figure 5c), consistent with the weighted-average $^{206}\text{Pb}/^{238}\text{U}$ age of $162.9 \pm 1.5 \text{ Ma}$ (MSWD = 1.04) (Figure 5d). This weighted-average $^{206}\text{Pb}/^{238}\text{U}$ age could be interpreted as the crystallization age of the coarse-grained biotite monzonitic granites (hornblende-bearing).

4.2. Zircon Lu–Hf Isotopes

Zircon Lu–Hf isotopes for the granitic rocks of the Lisong pluton are summarized in Table S2 in the Supplementary Materials. The coarse-grained biotite monzonitic granites (hornblende-free) have zircon $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of 0.282619–0.282717 (mean = 0.282672) with initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of 0.282617–0.282712 (mean = 0.282669). Based on the zircon age of 162.2 Ma, it yields calculated $\epsilon_{\text{Hf}}(t)$ values of -1.9 to 1.4 (mean = -0.1) and two-stage Hf model ages ($T_{\text{DM2}} = 1.12$ – 1.34 Ga; mean = 1.22 Ga). In contrast, zircons from the coarse-grained biotite monzonitic granites (hornblende-bearing) exhibit a wider range of $^{176}\text{Hf}/^{177}\text{Hf}$ ratios (0.282589–0.282841; mean = 0.282697). Based on the zircon age of

162.9 Ma, the calculated initial ratios (0.282587–0.282832; mean = 0.282693) yield variable $\epsilon_{\text{Hf}}(t)$ values (−3.0 to 5.7; mean = 0.8) and old T_{DM2} ages (0.85–1.40 Ga; mean = 1.16 Ga).

4.3. Apatite Chemical and Sr Isotopic Compositions

The chemical and Sr isotopic compositions of apatite grains are presented in Tables S3 and S4 in the Supplementary Materials, respectively. Apatite grains (apatite-1) from the coarse-grained hornblende-bearing biotite monzonitic granites exhibit lower CaO (53.1–54.3 wt%) and higher P_2O_5 (43.0–44.8 wt%) contents, comparable to those in apatite grains from the coarse-grained hornblende-bearing biotite monzonitic granites (apatite-2; 53.8–55.5 wt% CaO and 41.4–43.1 wt% P_2O_5). However, apatite-1 displays higher MnO (0.14–0.40 wt%) and FeO (0.13%–0.37%) concentrations relative to apatite-2, with MnO content of 0.05%–0.07% and FeO content of 0.05%–0.13%.

In trace element compositions, apatite-1 shows variable Sr (50.6–127 ppm) and Y (1560–4382 ppm) concentrations, which are consistent with apatite-2 (Sr content of 85.8–114.4 ppm; Y content of 1418–5193 ppm). Apatite-1 also exhibits lower total rare earth element (ΣREE) abundances (2925–8403 ppm) and lower δEu values (0.03–0.22) than apatite-2 (ΣREE = 4173–16,119 ppm and δEu = 0.04–0.07). Apatite from both samples is defined by enrichment in light rare earth elements (LREE) and depletion in heavy rare earth elements (HREE), with high LREE/HREE ratios of 1.5 to 5.7 and 3.0 to 6.3, respectively (Figure 6).

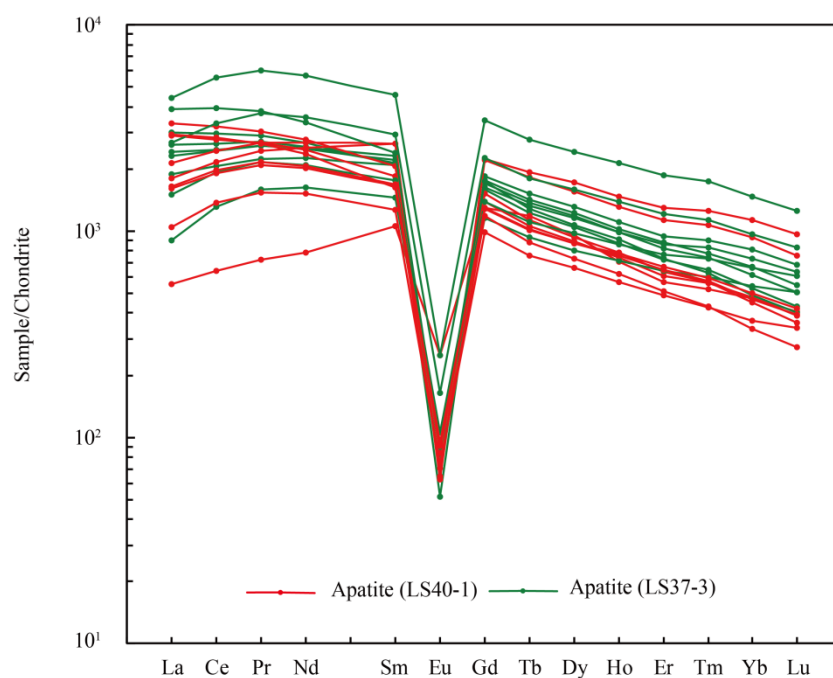


Figure 6. Chondrite-normalized REE patterns for apatite grains of the Lisong granites. Normalizing factors are from Taylor and McLennan (1985) [48].

The low apatite $^{87}\text{Rb}/^{86}\text{Sr}$ ratios of 0.00003–0.00813 (apatite-1) and 0.01335–0.06074 (apatite-2) confirm the measured $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.69747–0.70568 and 0.70152–0.71190, respectively) faithfully represent initial melt compositions.

4.4. Bulk-Rock Chemical Compositions

Bulk-rock chemical compositions of the Lisong granites are summarized in Table S5 in the Supplementary Materials. The biotite monzonitic granites (hornblende-free) are characterized by high SiO_2 (73.0–75.8 wt%), Al_2O_3 (12.1–13.8 wt%), Na_2O (3.33–3.75 wt%), and K_2O (3.62–5.40 wt%), alongside low TiO_2 (0.13–0.17 wt%), TFe_2O_3 (1.81–2.34 wt%), MnO (0.03–0.04 wt%), MgO (0.15–0.18 wt%), CaO (0.88–1.14 wt%),

and P_2O_5 (0.03–0.04 wt%). A comparable geochemical trend is observed for the biotite monzonitic granites (hornblende-bearing) with 72.8–75.7 wt% SiO_2 , 0.18–0.25 wt% TiO_2 , 11.9–13.3 wt% Al_2O_3 , 2.11–2.59 wt% TFe_2O_3 , 0.04–0.05 wt% MnO , 0.21–0.28 wt% MgO , 0.94–1.35 wt% CaO , 3.10–3.73 wt% Na_2O , 4.26–4.96 wt% K_2O , and 0.05–0.07 wt% P_2O_5 , respectively (Figure 7). Elevated $Na_2O + K_2O$ and K_2O contents classify these granites as high-K calc-alkaline (Figure 8a,b). They are further identified as peraluminous due to the high A/CNK ratios (1.15 to 1.23; Figure 9a). Collectively, these geochemical features, including their $Na_2O + K_2O$ versus CaO systematics, support an A-type granite affinity (Figure 9b).

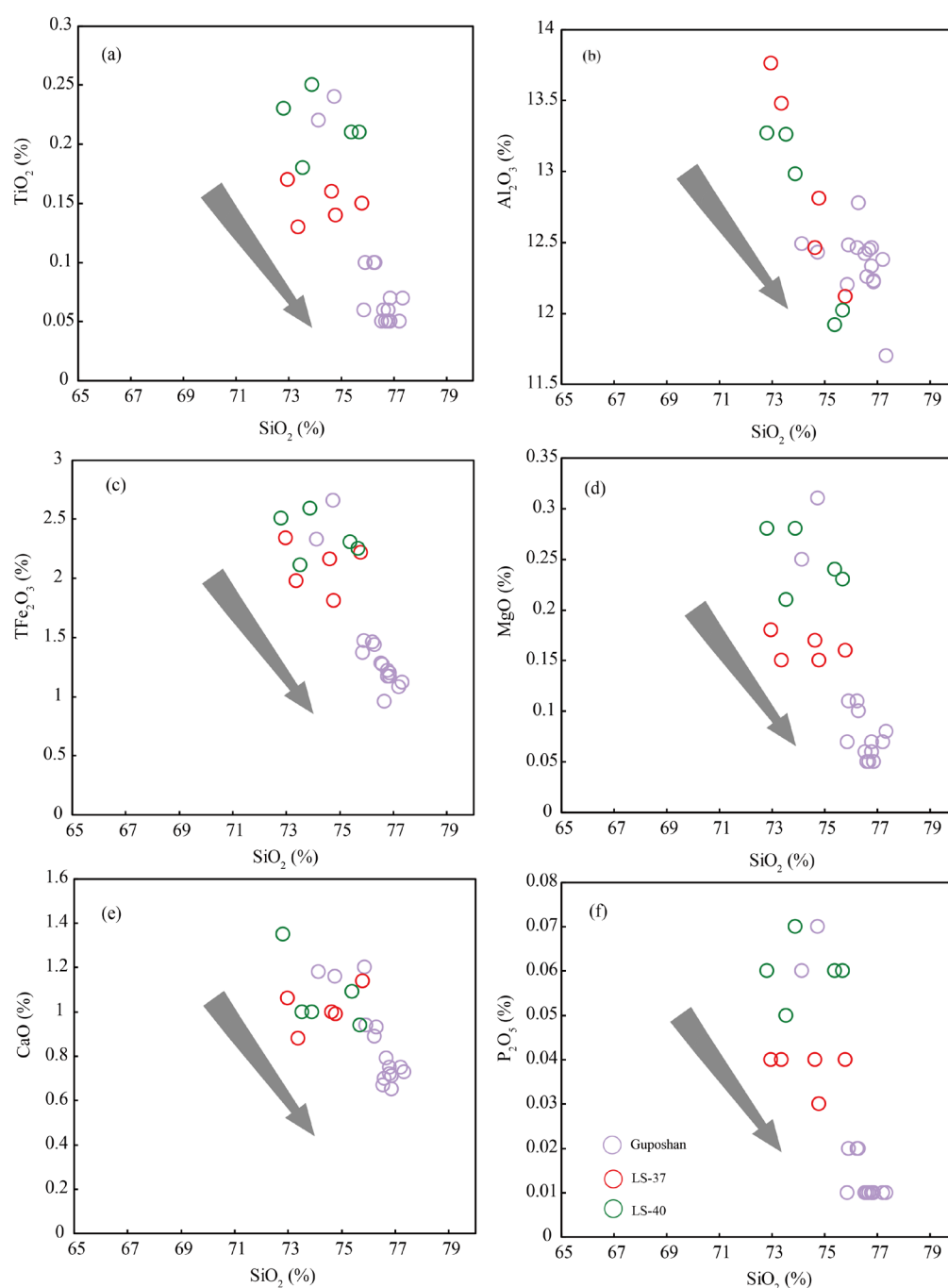


Figure 7. Geochemical plots of the Lisong granites. (a) TiO_2 – SiO_2 diagram; (b) Al_2O_3 – SiO_2 diagram; (c) TFe_2O_3 – SiO_2 diagram; (d) MgO – SiO_2 diagram; (e) CaO – SiO_2 diagram; (f) P_2O_5 – SiO_2 diagram.

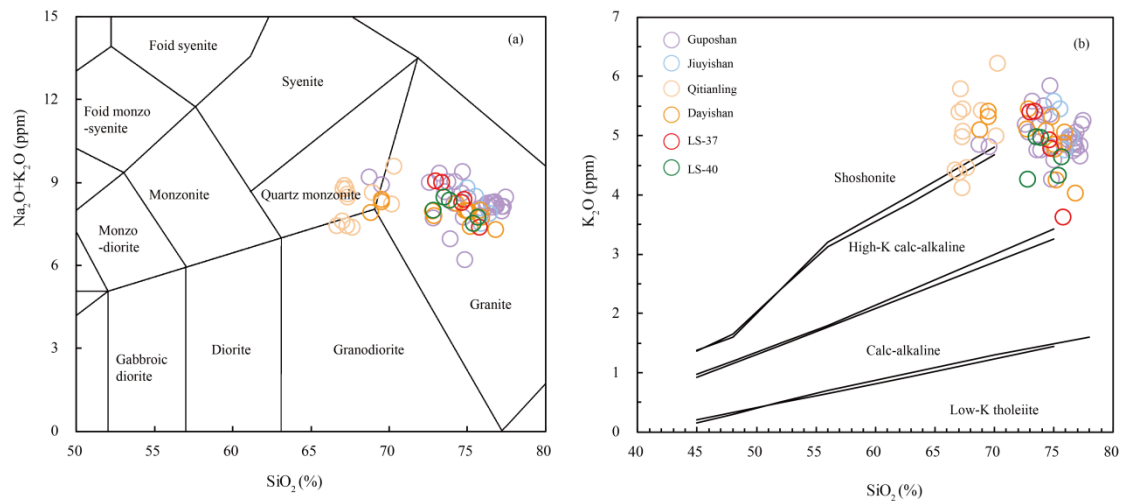


Figure 8. (a) SiO_2 vs. $\text{K}_2\text{O} + \text{Na}_2\text{O}$ and (b) SiO_2 vs. K_2O diagrams, revised from Middlemost (1994) [49] and Peccerillo and McLennan (1985) [50]. Data of the Guposhan, Qitianling, Jiuyishan, and Dayishan plutons are from Cao et al. (2020) [18], Zhao et al. (2012) [20], Liu et al. (2021) [51], and Lu et al. (2021) [19].

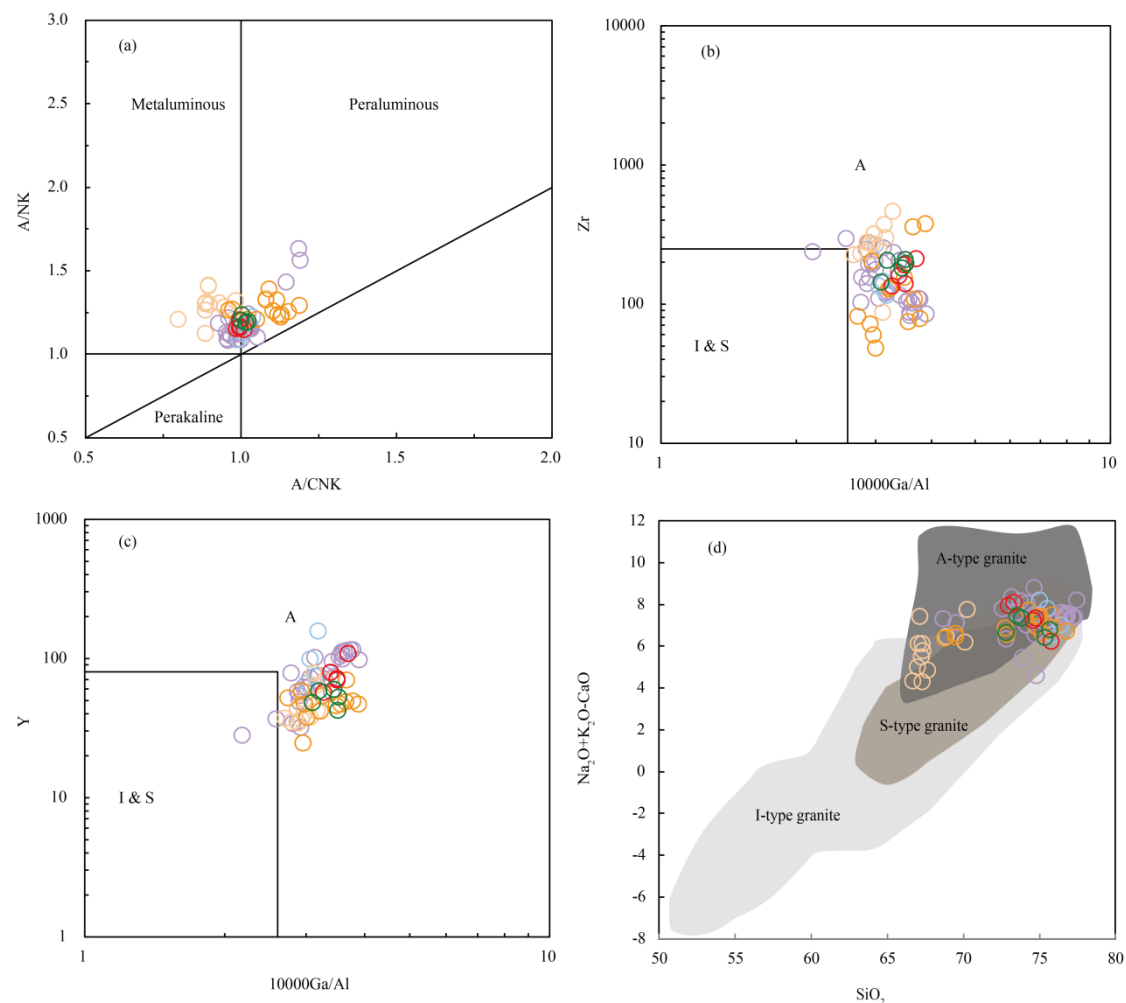


Figure 9. (a) A/CNK vs. A/NK , (b) $10,000\text{Ga}/\text{Al}$ vs. Zr , (c) $10,000\text{Ga}/\text{Al}$ vs. Y , and (d) SiO_2 vs. $\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO}$ diagrams. (a,b) are adapted from Maniar and Piccoli (1989) [52] and Frost et al. (2001) [53], respectively. (c,d) are adapted from Whalen et al. (1987) [54]. Symbols are the same as in Figure 8.

The granites display variable concentrations of Ga (21.7–24.7 ppm), Rb (306–404 ppm), Sr (66.4–92.1 ppm), Ba (150–256 ppm), Th (40.1–63.2 ppm), U (13.6–22.9 ppm), Nb (27.0–65.3 ppm), Ta (4.4–7.0 ppm), and Y (42.0–108 ppm; Table S5 in the Supplementary Materials). The Lisong granites are distinguished by high $10,000 \times \text{Ga}/\text{Al}$ ratios (3.09 to 3.69), falling within the field of A-type granites (Figure 9c,d). Geochemically, these rocks are distinguished by depletions in specific large ion lithophile elements (LILEs; e.g., Sr, Ba) and high field strength elements (HFSEs; e.g., P, Ti), a pattern analogous to that observed in the Guposhan granites (Figure 10a). They have ΣREE contents of 248–344 ppm and exhibit significant light REE (LREE) enrichment relative to heavy REEs (HREEs), with LREE/HREE ratios between 4.10 and 10.7. Their chondrite-normalized REE patterns are distinct from those of the Guposhan suite and are marked by pronounced negative Eu anomalies ($\delta\text{Eu} = 0.14\text{--}0.25$; Figure 10b).

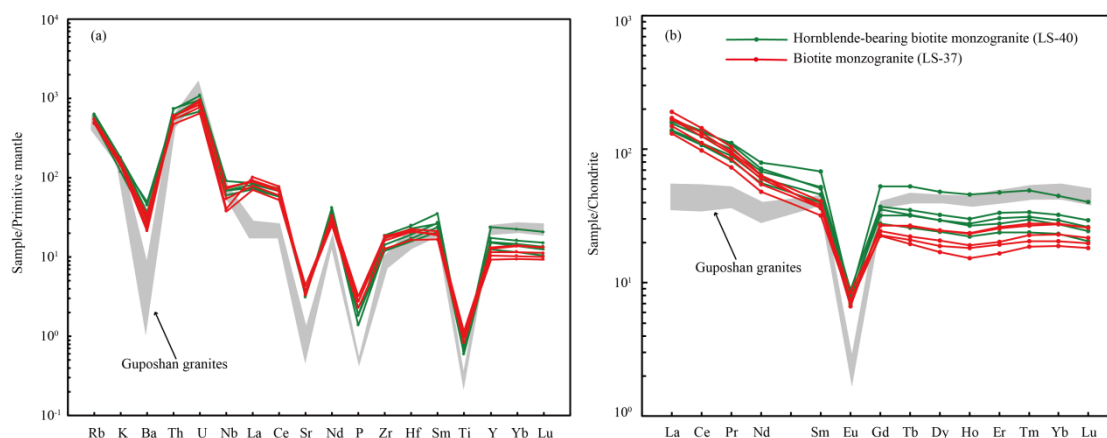


Figure 10. (a) Primitive mantle-normalized multi-element spider diagram and (b) chondrite-normalized REE diagram for the Guposhan granites. Normalizing values are from Sun and McDonough (1989) [55] and Taylor and McLennan (1985) [48], respectively. The data of the Guposhan granites are from Cao et al. (2020) [18].

5. Discussion

5.1. Geochronology of the Lisong Granites

The Guposhan region, which constitutes a key part of the NLMB, is marked by a complex geological history involving multi-phase Jurassic magmatism, which is genetically linked to significant W–Sn polymetallic mineralization [15,18,27,31,32]. The NLMB underwent a critical geodynamic transition from a post-collisional compression to an extensional tectonic regime induced by the roll-back of the subducted Paleo-Pacific slab, which subsequently led to an asthenosphere upwelling event [56–58]. This event induced large-scale crustal melting and intense mantle-crust interaction and generated a NE-trending A-type granite belt, including the Guposhan, Jiuyishan, and Xitian plutons [18,59,60].

While the NLMB is widely recognized for its peak granitic magmatism and mineralization between 165 and 150 Ma [7,12], the Guposhan region preserves an extended record of magmatic-hydrothermal activity, providing critical insights into the magmatic-hydrothermal mineralization events. A magmatic event in Guposhan, dated at 184 ± 3.6 Ma [7], thus constitutes one of the earliest recorded Jurassic granitic intrusions associated with W–Sn mineralization in the NLMB. A subsequent magmatic pulse at ca. 165 Ma marks a major mineralization episode, with magmatic-hydrothermal deposits constrained to 165–160 Ma [31–33,61]. A third phase of magmatism occurred at ca. 154 Ma, though no associated mineralization ages have been identified to date [27]. In the present study, zircon geochronological studies on the Lisong granites yielded ages of 162.0 ± 2.4 Ma

and 162.1 ± 2.2 Ma, which are consistent with the previously reported age of 163 ± 1.3 Ma for the Lisong pluton [32]. These ages align closely with the emplacement age of the nearby Guposhan pluton (162.8 ± 1.3 Ma) [18,32], suggesting synchronicity in the emplacement of the Lisong and Guposhan plutons. This temporal consistency supports the notion that the Guposhan and Lisong plutons are also potentially genetically related. Furthermore, the coeval mineralization and rock-forming ages suggest that both the Lisong and Guposhan plutons are important components of the Jurassic regional magmatic-mineralization event in South China. However, most of the W-Sn deposits are hosted within the Guposhan plutons, indicating that the W-Sn mineralization is closely related to the Guposhan pluton rather than the Lisong pluton.

5.2. Magma Source

Apatite commonly crystallizes during the early phase of the magma and serves as a sensitive petrogenetic tracer for constraining magma origin and rock-forming processes due to its capacity to incorporate specific trace elements into its crystal lattice, e.g., Sr, REE, Fe, Mg, Mn, and Y [62,63]. The ionic radius of Ca^{2+} (1.00 Å) is similar to Sr^{2+} (1.18 Å) and different from Rb^{+} (1.52 Å), making Sr^{2+} much easier to fit into the apatite lattice than Rb^{+} [64] and indicating that the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio of apatite will not be significantly influenced by the radioactive decay of the $^{87}\text{Rb}/^{86}\text{Sr}$ [46,65]. It is rendering that its $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios are representative of the Sr isotopic signature of the primary melt [66,67]. Moreover, apatite remains stable through subsequent geological events [68]. This durability makes it an ideal tracer for tracking multi-stage magma evolution without significant overprinting [46,65,69–71]. In this study, apatite grains from the Lisong granites exhibit low $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.69747–0.71190), consistent with those of the nearby Guposhan pluton (0.67983–0.70900) and Sn-bearing granites in the NLMB, such as Qitianling, Jiuyishan, and Dayishan (Figure 11a). These isotopic signatures suggest a mantle-crust hybrid source for the Lisong granites, analogous to Sn-bearing granites in the NLMB [7], corroborated by the variable zircon $\varepsilon_{\text{Hf}}(t)$ signatures (−3.02 to 5.66), which agree with those of the Guposhan pluton and other Sn-bearing Nanling granites, reflecting isotopic evidence of crust-mantle interaction [7,32]. Additionally, the presence of mafic microgranular enclaves (MMEs), commonly interpreted as evidence of felsic-mafic magma mixing within the coarse-grained hornblende-bearing biotite monzonitic granites (Figure 3a), reinforces the hypothesis of hybrid magmatism. Despite these mantle-like isotopic signatures, the Lisong granites also exhibit geochemical characteristics typical of crustal-derived melts: (1) high SiO_2 (72.8%–75.8%), Al_2O_3 (12.1%–13.8%), Th (40.1–62.8 ppm), U (13.6–22.9 ppm), Nb (27.0–65.3 ppm), and Ta (4.4–7.0 ppm); low Fe_2O_3 and MgO ; and (2) old T_{DM2} ages of 0.85–1.40 Ga [72–75]. The consistent emplacement ages and isotopic compositions between the Lisong and Guposhan plutons (Figure 11b) suggest derivation from a shared magmatic chamber. Collectively, these data support that the Lisong and Guposhan granites originated primarily from a mixed melt composed of ancient crustal and mantle-derived material sources.

5.3. Fractional Crystallization Processes

Fractional crystallization (FC), a fundamental mechanism in magmatic evolution, facilitates the enrichment of ore-forming elements in the evolved melt [76,77]. Furthermore, mineral fractional crystallization during magma evolution is essential for the formation of granitic rocks [78,79]. As mentioned earlier, the Lisong and Guposhan granites may be products of a common magma chamber; therefore, their chemical compositions should provide essential evidence of their magma evolution process. The negative correlation between Rb and V attests to intense fractional crystallization in the Lisong and Guposhan granites

(Figure 12a), as evidenced by Rb-Sr, Rb-Ba, and Eu-Yb systematics, which fingerprint the roles of biotite, K-feldspar, and plagioclase, respectively (Figure 12b–d). The Lisong and Guposhan granites exhibit negative SiO_2 correlations with TiO_2 , Al_2O_3 , MgO , CaO , and P_2O_5 (Figure 7), which are consistent with the magma evolution trend, which was dominated by the mineral fractional crystallization. Furthermore, the more pronounced depletion of Eu, Sr, Ba, P, and Ti in the Guposhan granites compared to the Lisong granites suggests more extensive fractional crystallization of minerals such as plagioclase, apatite, and rutile/ilmenite during magmatic evolution (Figure 10a). Additionally, the shift from higher LREE/HREE ratios in the Lisong granites to lower ratios in the Guposhan granites indicates fractional crystallization of LREE-enriched minerals throughout this process (Figure 10b).

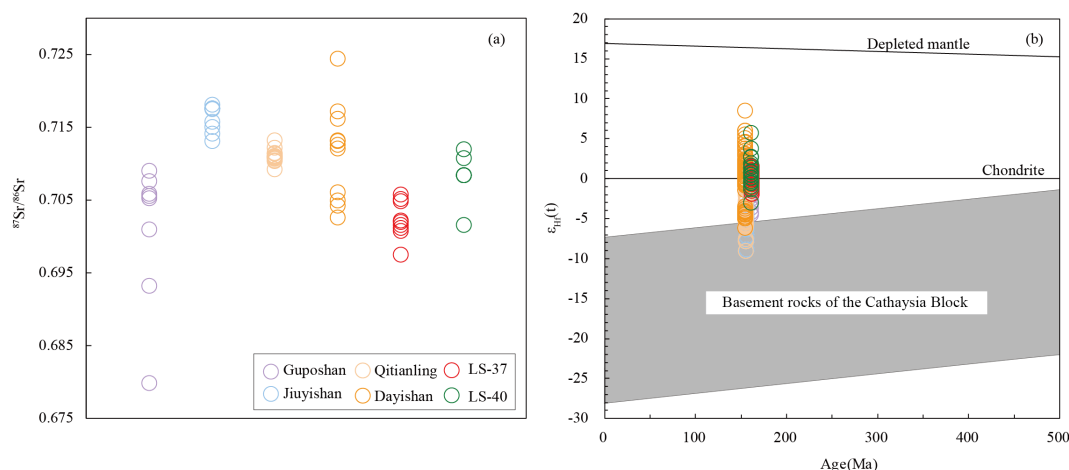


Figure 11. (a) Apatite $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and (b) zircon age vs. $\epsilon_{\text{Hf}}(t)$ values of the Lisong granites. Data sources of the Guposhan, Qitianling, Jiuyishan, and Dayishan plutons are the same as in Figure 8.

As a major reservoir for Eu, plagioclase fractional crystallization is responsible for Eu depletion in the evolving magma [65], which will be recorded by the apatite [46,65,69,80]. Both the apatite-1 and apatite-2 contain low Eu contents of 4.47–21.8 ppm (mostly lower than 8.0 ppm) and 6.17–21.7 ppm, respectively, with corresponding low δEu values from apatite-1 (0.03–0.22; mostly within the range of 0.03–0.05) to apatite-2 (0.04–0.07). The pronounced negative Eu anomalies further indicate an intense plagioclase fractional crystallization for the primary magma (Figure 6). Consequently, the Lisong and Guposhan plutons form as products of the early and late stages of magmatic evolution, respectively, dominantly through fractional crystallization. This conclusion was certified by a decrease in Rb/Sr ratios from the Guposhan granites (4.03–25.7) to the Lisong granites (3.32–5.77) and an elevation in Zr/Hf ratios from the Guposhan granites (15.6–29.4) to the Lisong granites (26.4–30.9), which indicates that the Lisong granites belong to the highly fractionated granites.

The multistage magma evolution favors the W-Sn enrichment in the magma system, which might be one of the key factors in controlling the intense W-Sn mineralization of the Guposhan region. Being incompatible elements in the magma melt, tungsten and tin are commonly enriched in the late-stage magmatism [81]. However, the Lisong granites belong to the product of the early-stage magma evolution, which is unfavorable to the Sn and other metal enrichment in the magma. Therefore, the low differentiated signatures of the Lisong granites are one of the key factors for the absence of intense Sn mineralization.

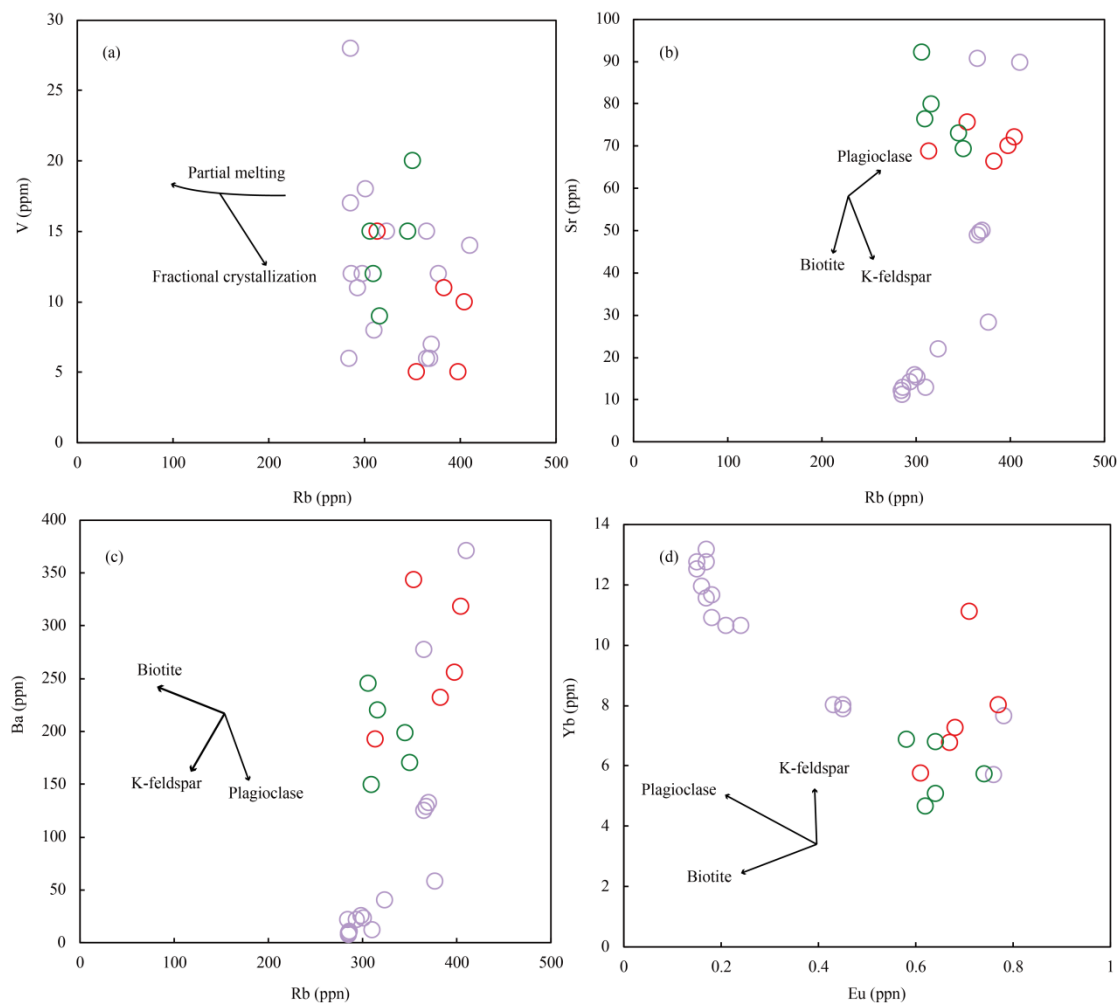


Figure 12. Binary plots of (a) Rb vs. V, (b) Rb vs. Sr, (c) Rb versus Ba, and (d) Eu vs. Yb for the Lisong granites. Symbol conventions follow those in Figure 7.

5.4. Magma Oxidation State and Its Implications for the Sn Mineralization

Apatite commonly crystallizes during the early stages of magma evolution, serving as an important tracer of the parental magma's chemical composition and magma oxidation state [46,63,65,69,82]. Previous studies suggest that certain valence-variable elements (e.g., Fe, Mn, S, Eu, and Ce) in apatite can be used as indicators of the redox conditions of magmas [63,83]. Under reduced magmatic conditions, the concentrations of Ce^{3+} and Eu^{2+} increase relative to Ce^{4+} and Eu^{3+} in the melt. Consequently, apatite preferentially incorporates Ce^{3+} and Eu^{2+} due to their ability to substitute for Ca^{2+} within its crystal structure, resulting in the Eu and Ce enrichment and positive and/or normal Eu and Ce anomalies in the apatite [63,80]. However, variations in a single element within apatite are not a reliable indicator of magmatic oxidation state, primarily because other factors, such as fractional crystallization, melt composition, and/or structure, can significantly influence elemental compositions [84]. For example, the fractional crystallization of plagioclase, one of the Eu reservoirs, will lead to the depletion of Eu in the melt and consequently negative Eu anomalies in apatite, indicating that apatite Eu anomalies are not an ideal indicator in reflecting the redox conditions of the melt [85]. In this study, both apatite-1 and apatite-2 are characterized by normal and/or positive Ce anomalies with $\delta\text{Ce} = 0.99\text{--}1.03$ and $1.02\text{--}1.09$, respectively, indicating that the apatite probably crystallized from a reduced melt. This conclusion was confirmed by the relatively low $\text{FeOT}/\text{MgO}/\text{SiO}_2$ ($0.11\text{--}0.16$) and $\text{CaO}/\text{Al}_2\text{O}_3$ ($0.07\text{--}0.10$) ratios of the Lisong granites, which are similar to the Guposhan

granites with $(\text{FeOT}/\text{MgO})/\text{SiO}_2$ and $\text{CaO}/\text{Al}_2\text{O}_3$ ratios of 0.10–0.30 and 0.05–0.09, respectively, indicating that Lisong granites originated from a reduced magma rather than an oxidized melt (Figure 13) [86].

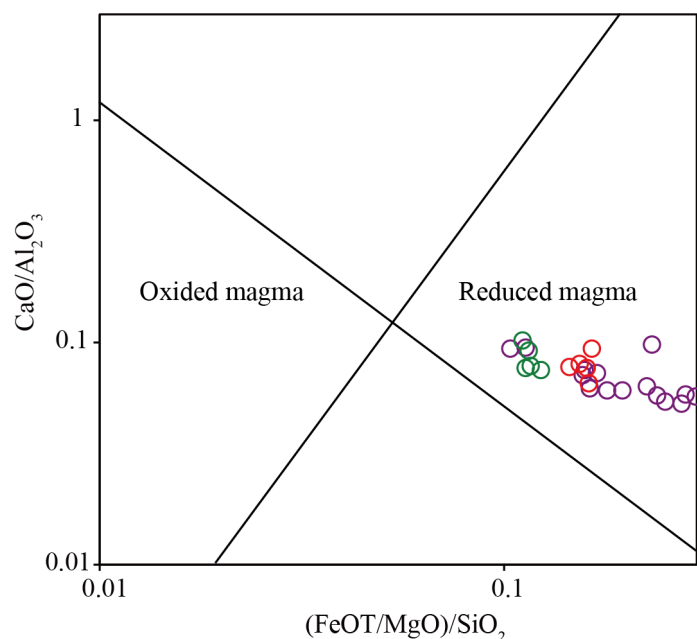


Figure 13. $(\text{FeOT}/\text{MgO})/\text{SiO}_2$ versus $\text{CaO}/\text{Al}_2\text{O}_3$ [86]. Symbol conventions follow those in Figure 7.

It is well accepted that redox conditions and magma evolution patterns are key factors for Sn mineralization, such that reduced, highly evolved magmas are deemed particularly critical [17,81,87]. As a multivalent element, the solubility of Sn in melts is governed by the magmatic redox conditions [88]. Under oxidizing conditions, Sn primarily exists as Sn^{4+} , which can substitute for Ti^{4+} in minerals such as titanite, leading to the depletion of Sn in the melt. In contrast, under reducing conditions, Sn occurs as incompatible Sn^{2+} , resulting in its progressive enrichment in the residual melt during magmatic evolution. As aforementioned, the Lisong and Guposhan granites are generated from a reduced melt, thereby favoring the partitioning of Sn into residual melt [18]. Therefore, the redox of the magma may not be a key factor responsible for the absence of large-scale Sn mineralization in the Lisong pluton.

6. Conclusions

Zircon U-Pb dating reveals that the Lisong pluton was emplaced at ~162 Ma. Their relatively low apatite $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and variable zircon Hf isotopes suggest a magmatic origin that was derived from the partial melting of Cathaysia Block crustal rocks with the involvement of mantle-derived magmas. Furthermore, the Lisong granites might share a common magma chamber with the nearby Guposhan pluton. Apatite and whole-rock geochemistry indicate that the Lisong granites are generated from a reduced melt. The whole-rock geochemistry reveals that the Lisong granites belong to the low-differentiated granites. Therefore, the low differentiated nature of the primary magma is unfavorable for the enrichment of Sn and other metals and consequently influences the Sn mineralization potential of the Lisong granites.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min16030313/s1>, Table S1. LA-ICP-MS zircon U-Pb dating for the Lisong granites; Table S2. LA-MC-ICP-MS zircon Lu-Hf isotopes of the Lisong granites; Table S3. LA-ICP-MS apatite major and trace element compositions of Lisong granites;

Table S4. LA-MC-ICP-MS apatite Sr isotope compositions of the Lisong granites; Table S5. Major and trace element compositions of the Lisong granites.

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