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Geochemical and Geochronological Constraints on the Genesis of Ion-Adsorption-Type REE Mineralization in the Lincang Pluton, SW China

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Abstract: Granites are assumed to be the main source of heavy rare-earth elements (HREEs), which have important applications in modern society. However, the geochemical and petrographic characteristics of such granites need to be further constrained, especially as most granitic HREE deposits have undergone heavy weathering. The LC batholith comprises both fresh granite and ion-adsorption-type HREE deposits, and contains four main iRee (ion-adsorption-type REE) deposits: the Quannei (QN), Shangyun (SY), Mengwang (MW), and Menghai (MH) deposits, which provide an opportunity to elucidate these characteristics The four deposits exhibit light REE (LREE) enrichment, and the QN deposit is also enriched in HREEs. The QN and MH deposits were chosen for study of their petrology, mineralogy, geochemistry, and geochronology to improve our understanding of the formation of iRee deposits. The host rock of the QN and MH deposits is granite that includes REE accessory minerals, with monazite, xenotime, and allanite occurring as euhedral inclusions in feldspar and biotite, and thorite, fluorite(-Y), and REE fluorcarbonate occurring as anhedral filling in cavities in quartz and feldspar. Zircon U–Pb dating analysis of the QN (217.8 ± 1.7 Ma, MSWD = 1.06; and 220.3 ± 1.2 Ma, MSWD = 0.71) and MH (232.2 ± 1.7 Ma, MSWD = 0.58) granites indicates they formed in Late Triassic, with this being the upper limit of the REE-mineral formation age. The host rock of the QN and MH iRee deposits is similar to most LC granites, with high A/CNK ratios (>1.1) and strongly peraluminous characteristics similar to S-type granites. The LC granites (including the QN and MH granites) have strongly fractionated REE patterns (LREE/HREE = 1.89–11.97), negative Eu anomalies (Eu/Eu* = 0.06–0.25), and are depleted in Nb, Zr, Hf, P, Ba, and Sr. They have high ⁸⁷Sr/⁸⁶Sr ratios (0.710194–0.751763) and low ¹⁴³Nd/¹⁴⁴Nd ratios (0.511709–0.511975), with initial Sr and Nd isotopic compositions of $({}^{87}\text{Sr}/{}^{86}\text{Sr})_i = 0.72057-0.72129$ and $\epsilon Nd(220 \text{ Ma}) = -9.57$ to -9.75. Their initial Pb isotopic ratios are: 206 Pb/ 204 Pb = 18.988-19.711; 208 Pb/ 204 Pb = 39.713-40.216; and ${}^{207}Pb/{}^{204}Pb = 15.799-15.863$. The Sr-Nd-Pb isotopic data and T_{DM2} ages suggest that the LC granitic magma had a predominantly crustal source. The REE minerals are important features of these deposits, with feldspars and micas altering to clay minerals containing Ree³⁺ (exchangeable REE), whose concentration is influenced by the intensity of weathering; the stronger the chemical weathering, the more REE minerals are dissolved. Secondary mineralization is also a decisive factor for Ree³⁺ enrichment. Stable geology within a narrow altitudinal range of 300–600 m enhances Ree³⁺ retention.



Keywords: ion-adsorption-type REE deposit; REE; Lincang batholith; isotopic ages; accessory minerals; Yunan Province

1. Introduction

Rare-earth elements (REEs) are currently a focus of global attention because of geopolitical controls on their supply, which have led to them being included in current lists of critical metals. Their importance is due to their use in high-strength magnets, which are fundamental to a range of low-carbon energy-production approaches, and in a wide range of high-technology applications [1]. REE production is currently limited to a small number of large deposits (e.g., Bayan Obo, Baotou, China; Mountain Pass, San Bernardino County, CA, USA; Mount Weld, Laverton, Australia; Lovozero, Russia [2–5]), by-products (e.g., mineral sands in India), or deposits enriched with specific elements of current high demand, such as Dy, Tb, and other heavy REEs (HREEs, e.g., the so-called ion-adsorption-type REE deposits in weathered granite in southern China [6]).

Ion–adsorption-type REE (iRee) deposits supply most of the world's REE requirements, particularly HREEs. Such deposits are often informally referred to as 'South China clays,' but similar systems have been recognized recently in Southeast Asia, Madagascar, and the southeastern USA, where deposits are generally enriched in light REEs (LREEs [6–12]). In China, iRee deposits are distributed mainly in the southeast, although exploration in other areas is ongoing. The Quannei (QN) iRee deposit, which is typically enriched in LREEs and partly enriched in HREEs, is in the Lincang (LC) area of Yunnan Province, SW China, and has an altitudinal range of 1500–2000 m. In this area, four comparable deposits have been identified recently in the LC granite: the QN, Shangyun (SY), Mengwang (MW), and Menghai (MH) iRee deposits. Both fresh and weathered granites occur in the LC area, providing an opportunity to study the effect of weathering on ion-adsorption-type HREE (iHRee) deposits. The elevation of iRee deposits (>1000 m) in SW China are higher than those in SE China, showing that there is an exploring potential of iRee (especially iHRee) deposit in high elevation areas (>1000 m) [10,13–23].

It is generally accepted that REEs are mobilized and fractionated during intense weathering of granite under warm and humid conditions [7,12,24–29]. Rare-earth element-bearing minerals ('REE minerals') are essential to the formation of iRee deposits. Moreover, fluids (organics and inorganics) also display an important role in the mobilization and accumulation of REE [30]. In host rocks, REEs occur isomorphously in the lattices of minerals such as feldspar, biotite, and apatite, or independently in minerals such as allanite, monazite, and xenotime [12]. Dissolution of these minerals is the first stage of the formation of iRee deposits, with clay being the predominant secondary mineral in which REEs are accommodated [7,24–26]. Under natural pH conditions, REEs are adsorbed on clay minerals with negatively charged layers through ion exchange, electrostatic attraction, and surface complexation, migrating into the clay structure [12]. Stable geological and tectonic conditions with a narrow altitudinal range (300–600 m) may be beneficial for retention of REEs in weathering crust [19,24,27,29,31,32].

Despite previous studies of the formation of iRee deposits, the geochemical and petrographic characteristics of granite in such deposits require further constraints. The present study focused on the geochemical characteristics of host granites in the LC area with a view to (i) determine the magma source of the host rock of iRee deposits; (ii) distinguish REE minerals in the host rock; (iii) elucidate the geodynamic mechanism of the host rock generation; and (iv) explain the REE mineralization process in weathering profiles.

2. Study Areas and Sampling

2.1. Geological Background

The LC batholith and the Triassic volcanic belt constitute the southern Lancangjiang zone of SW China. The southern Lancangjiang tectonic zone in the central part of the Sanjiang orogenic belt

includes the Jinsha, Lancang, and Nu rivers. The Lanping–Simao Block and Jinshajiang–Ailaoshan suture lie east of the Sanjiang orogenic belt, which represents a Paleo-Tethyan block–arc oceanic basin. The Changning–Menglian suture belt is a remnant of the main Paleo–Tethyan ocean crust in SW China and extends to the south of the Nan and Sr Kaeo sutures.

The LC batholith intrudes the Lancang, Damenglong, and Chongshan groups. The Lancang Group comprises sandstones, mudstones, slates, phyllites, minor chlorite schists, and blueschists. The Danmenglong and Chongshan groups comprise banded gneiss, quartz–feldspathic-mica schist, amphibolite, migmatite, and marble. These three groups are considered to represent Proterozoic basement and have undergone several stages of metamorphism and deformation [33–35].

2.2. The Lincang Granitic Batholith

The LC batholith comprises different types of granitic rock with an area of over 7400 km², and measures 350 km long by 10–48 km wide. It extends from Yunxian county in the north to Menghai county in the south, with intermittent southward connection to Thailand, the Malay Peninsula, and Sumatra granites (Figure 1a,b). The exposed area represents the largest batholith in Yunnan and is separated into three segments by the Xiaojie–Nadong and Nanling–Chengzi faults (Figure 1c). The altitude of the LC batholith is in the range of 1000–2500 m, with the topography of the region dominated by low hills of 300–600 m in height. Denudation rates are fairly low and weathering profiles are well preserved. The region has a temperate subtropical monsoon climate with an annual-average temperature, rainfall, and humidity of 17.3 °C, 1504.5 mm, and 72.54%, respectively [33].

Four iRee deposits have been recognized in the weathering crust of LC granites, and are distributed in the central and southern areas of the batholith. The QN and SY deposits are in the central part of the batholith, and the MH and MW deposits in the southern area (Figure 1c). The parent rock of the QN deposit (QN granite) is sandwiched between the Tanyao and Jianshitou faults, granodiorite intrudes in the east, and the western area contains light-colored granite. The area of SY, MW, and MH deposits are bounded by the lowest industrial-grade of REE content (REE = 0.05-0.1%) in the weathering crust. The four medium–large-sized deposits have similar mineralization systems with LREE enrichment and host rocks of biotite granite.

2.3. Sampling and Methods

2.3.1. Sampling

As shown in Figure 1c, four QN granite samples (lc2-j2, lc2-j3, lc3-j1, and lc4-j1) were taken from the QN iRee deposit in the central LC batholith, and one MH granite sample (mh-j1) from the MH iRee deposit in the southern batholith. The corresponding granite weathering profile was separated to three horizons, A, B, and C. Horizon A, the upper weathering profile, comprises mainly soil and organic matter with some detrital quartz. Horizon B comprises weathered granite, with most minerals being altered to secondary minerals, such as clay, oxides, and phosphates. This sample contains K-feldspar and detrital quartz, and was crushed easily by hand. Horizon C represents a weathering zone where the sample was sandier and stonier than horizon B, and could be crushed by a hammer. Sample numbers in each weathering profile followed Lu et al. (2019, 2020) [28,29].

2.3.2. Methods

Whole rock major and trace element compositions were determined at the National research center of Geoanalysis, Beijing, China (NRCG, CAGS). Major elements of the analyses were determined by X-ray fluorescence spectrometry (XRF) using fused glass discs, with precisions of 1–2%. Trace element analyses were determined by inductively coupled plasma-mass spectrometry (ICP-MS) (PE-300D).



Figure 1. The distribution of LC batholith in China (**a**) and Southeast Asia (**b**), and regional geology of QN, SY, MW and MH iRee deposits showing the location of the samples (**c**) (modified from references [33,36]). 1—granite; 2—porphyritic biotite granite; 3—granodiorite; 4—metamorphic rock; 5—fault; 6—national boundaries; 7—river; 8—iRee deposit; 9—Sampled location.

Chemical compositions of minerals in the granites from the LC granite were determined by a JEOL-8230 electronmicroprobe at the Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing. Trace elements of minerals were carried out by fs-LA-ICP-MS, using a femto-second laser ablation system (ASI J200) coupled to an inductively-coupled mass spectrometer (Thermo X series II).

Meanwhile, the zircon U-Pb age and Sr-Nd-Pb isotope of LC granite were examined. Measurements of U, Th, and Pb isotopes of zircon grains were conducted using a Camera IMS–1280HR SIMS at the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing. Sr-Nd and Pb isotope analyses were performed on a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Dreieich, Germany) at the Wuhan Sample Solution Analytical Technology Co., Ltd, Hubei, China. For the details on the analysis methods, we refer to the Supplementary Materials.

3. Petrography

3.1. Petrographic Characteristics of LC Granite

The granite samples are all biotite granite, barring sample lc2-j2, which is granodiorite. Granodioritic xenoliths occur in the monzonitic granites at several locations (Figure 2A). The biotite granite has either a medium–coarse-grained (samples lc4-j1) or medium–fine-grained (samples lc2-j3, lc3-j1, and mh-j1) texture.



Figure 2. Petrological diagram of QN and MH granites: (**A**) granodiorite was intruded by medium–fine-grained biotite granite; (**B**) medium–coarse-grained biotite granite; (**C**,**D**) granodioritc xenoliths are observed in the monzonitic granites; (**a**) crosshatch twins of microline; (**b**) carlsbad twin of plagioclase; (**c**,**g**) quartz occurs as anhedron fill into the interspace of plagioclase; (**d**,**g**) plagioclase altered to serisite and (**d**) biotite altered to chlorite; (**e**) albite occurs as anhedron; (**f**) biotite was replaced and altered to muscovite; (**h**) muscovite occurs as sheet structure; Qtz—Quartz; Pl—Plagioclase; Ab—Albite; Bt—Biotite; Ms—Muscovite; Chl—Chlorite; Ep—Epidote; Ilm—Ilmenite; Aln—Allanite; Ap—Apatite; Mnz—monazite; Py—Pyrite; Zrn—Zircon.

Granodiorite lc2-j2 (Figure 2A,a) has a porphyritic medium–coarse-grained structure and comprises mainly plagioclase (An_{28–36}; 28–32%), biotite (27–29%), quartz (16–20%), and K-feldspar (8–10%). These rock-forming minerals have similar grain sizes of 0.1–1 mm. Accessory minerals include minor magnetite (0.1–0.3%), apatite (1–2%), and zircon (0.5–1%; Figure 3a).



Figure 3. Optical (**d**,**e**) and back scattered electron (BSE, **a**–**c** and **f**–**i**) images of REE minerals in the host rock of QN and MH iRee deposit: (**a**,**c**) monazite and zircon occur as anhedron associated with apatite; (**b**) monazite and thorite occur as anhedron associated with fluorapatite; (**d**,**g**) monazite and allanite zircon occur as subhedral—anhedral associated with biotite, which altered to chlorite; (**e**,**h**) apatite and zircon occur as euhedron associated with biotie, which altered to chlorite; (**e**,**h**) apatite occurs as anhedron filled into the interspace of feldspar; Mnz—Monazite; Xtm—Xenotime; Aln—Allanite; Ap—Apatite; Fl-Ap—Fluorapatite; Trt—Thorite; Zrn—Zircon; Fl—Fluorite.

Biotite granite lc4-j1 (Figure 2B,c,d) has a porphyritic, medium–coarse-grained structure and comprises K-feldspar (20–40%), plagioclase (25–40%), quartz (20–30%), and biotite (4–8%). Phenocrysts include K-feldspar (5–25%) with grain sizes of 0.5–10 cm. The matrix comprises K-feldspar, plagioclase, quartz, and biotite, with grain sizes of 1–5 mm. Mineral crystals are subhedral–anhedral. The K-feldspar comprises microcline and perthite, the former of which has a cross-hatched twin texture and the latter a perthitic texture. Plagioclase is mainly andesine (An_{28–36}) with carlsbad twinning and a zoned texture. Alteration in the granite includes chloritization, epidotization, and sericitization, with biotite replaced by chlorite (ink-blue interference color; Figure 2d), and the central part of plagioclase replaced by epidote or sericite (Figure 2d,g). Accessory minerals include ilmenite (0.2–0.5%), sphene (0.2–0.3%), epidote (3–5%), apatite (or fluorapatite, 1–2%), allanite (1–2%), monazite (0.5–1%), zircon (0.5–1%), and pyrite (0.3–0.5%). Accessory minerals occur as euhedral crystals barring allanite, which is anhedral.

The biotite granites lc2-j3, lc3-j1, and mh-j1 (Figure 2A,C,D,b,e–h) comprise plagioclase (31–42%, including oligoclase (An_{15–20}) and albite (An_{0–6})); K-feldspar (19–35% microcline); quartz (20–34%), and mica (including 4–6% biotite and 0.2–3% muscovite), all with grain sizes of 0.5–2 mm. Accessory minerals include epidote (0.5–1%), apatite (or fluorapatite, 0.2–0.5%), and zircon (0.6–1%). Quartz, albite, and muscovite contents are higher than those of the granite, and the allanite content lower, but REE minerals such as fluorite(–Y) and REE fluorcarbonate occur. Alteration includes silicification (Figure 2g), albitization (Figure 2e), and muscovitization, with biotite replaced and altered to muscovite (Figure 2f). Fluorapatite is associated with monazite, thorite, and xenotime. Most REE minerals occur as anhedral crystals filling fissures in fluorapatite (Figure 3b,i). Allanite(–Y) is associated with fluorite(–Y) and REE fluorcarbonates that fill fissures between plagioclase and quartz.

3.2. REE Minerals

In the LC granite, REEs are concentrated in accessory minerals such as sphene, apatite, and zircon, or occur as independent REE minerals such as monazite, xenotime, and allanite. Sphene, apatite, zircon, monazite, and xenotime occur as subhedral–euhedral crystals associated with quartz, feldspar, and mica (biotite and muscovite) (Figure 3a,d,e,g,h), whereas allanite, monazite, fluorite(–Y) and REE fluorcarbonate occur as anhedral crystals (Figure 3b,c,g–i). In our samples, different mineral assemblages are observed in each type of granite. For example, in granodiorite lc2-j2, accessory minerals are ilmenite, sphene, apatite, and zircon with minor monazite and xenotime; in the medium–coarse-grained biotite granites lc4-j1 (Figure 3d,e,g,h), allanite is associated with monazite, apatite, and zircon, fluorapatite contents are higher, and monazite, thorite, and zircon occur as anhedral crystals filling fissures (Figure 3b,c); in the medium–fine-grained biotite granite (lc3-j1) of REE mineral are present, such as allanite(–Y), fluorite(–Y), and REE fluorcarbonate (Figure 3f,i).

The REE concentrations for each REE mineral are listed in Table 1. The accessory minerals allanite, monazite, and xenotime have relatively high REE contents (>5 wt.%). Based on their LREE/HREE ratios, REE minerals can be divided into two categories: LREE-type and HREE-type. For example, allanite and monazite are relatively enriched in LREE (LREE/HREE > 1) and are therefore 'LREE minerals,' whereas xenotime and fluorite(-Y) are relatively enriched in HREE, and are therefore 'HREE minerals.'

Allanite, monazite, apatite, and zircon are the main accessory minerals in the LC granite, with minor cerite and xenotime associated with feldspar and quartz. In medium–fine-grained biotite granite (lc3-j1), allanite(–Y) is an HREE mineral with Y_2O_3 contents of up to 30 wt.%. More fluorapatites are found. Monazite and thorite have been re-crystallized and occur as anhedral fillings in fissures in fluorapatite which increasing the REE contents to up to 8.46 wt.%. The REE fluorcarbonates associated with fluorite(–Y) that fill fractures or crystal cleavages in quartz and plagioclase (Figure 3f,i) are LREE minerals, but have high Dy_2O_3 and Y_2O_3 contents of up to 4.6 wt.% and 16.6 wt.%, respectively.

3.3. Weathering Profile of the LC Granite

It is generally considered that weathering crusts are formed by the weathering of granite in a humid environment, with the crust comprising detrital and secondary minerals. Detrital minerals can be subdivided into two groups: (1) quartz, feldspar, and biotite; and (2) heavy minerals that are relatively stable during weathering, such as zircon, monazite, and xenotime. The REE minerals such as allanite, fluorapatite, fluorite, and fluorcarbonate may occur in host rocks, but not in the weathering crust.

Secondary minerals carrying exchangeable REE (Ree³⁺) include clay minerals and Fe–Mn oxides. Here, the secondary-mineral content of the LC weathering profile ranges from 21% to 33%, from top to bottom. The clay mineral content is highest in horizon A, with most clay minerals finally altering to gibbsite (~7%) in this horizon [28,29]. Horizon B is the most important for Ree³⁺ enrichment. Kaolinite, montmorillonite, and illite are the main clay minerals in the LC granite weathering profile. The proportion of clay minerals varies between horizons based on the intensity of weathering. The horizon A kaolinite content is up to 85%, with 4% illite and 5% vermiculite. Horizon B contains 74–81% kaolinite, 9% illite, and 8–17% montmorillonite (mixed with illite). Horizon C contains 36% kaolinite, 12% illite, and 13% chlorite [29].

Mineral	Formula	REO	LREO	HREO	LREO/HREO	Nd ₂ O ₃ /REO	Ce ₂ O ₃ /REO	Eu ₂ O ₃ /REO	Dy ₂ O ₃ /REO	Y ₂ O ₃ /REO
Sphene $(n = 2)$	CaTi[SiO ₄]O	0.37	0.21	0.39	0.78	0.12	0.25	0.00	0.13	0.19
apatite $(n = 3)$	Ca ₅ (PO ₄) ₃ F	8.46	7.59	1.56	6.49	0.21	0.50	0.00	0.09	0.41
allanite ($n = 17$)	(Ce,Ca) ₂ (Al,Fe ³⁺) ₃ (SiO ₄) ₃ (OH)	16.92	14.53	5.78	8.25	0.22	3.42	0.01	0.03	0.25
Monazite ($n = 21$)	(Ce,La,Nd,Th)PO ₄	61.03	57.55	17.01	16.80	0.22	12.89	0.00	0.00	1.03
xenotime $(n = 5)$	YPO_4	53.05	0.77	52.28	0.01	0.01	0.00	0.00	0.07	0.74
thorite $(n = 2)$	(Y,Th,Ca,U)(Ti,Fe ³⁺) ₃ (O,OH) ₄	17.61	16.55	1.07	10.67	0.39	0.31	0.00	0.00	0.00
zircon(n = 2)	$(Zr,Y)(Si,P)O_4$	0.67	0.11	0.56	0.26	0.00	0.15	0.00	0.18	0.11
allanite-Y ($n = 7$)	$(Ce,Ca,Y)_2(Al,Fe^{3+})_3(SiO_4)_3(OH)$	31.83	20.89	10.95	1.80	0.34	0.02	0.00	0.09	0.16
flourite-Y ($n = 1$)	$(Ca,Y)F_2$	15.56	9.38	6.18	1.52	0.30	0.03	0.00	0.06	0.21
REE-flourcarbonate ($n = 1$)		59.20	31.94	27.26	1.17	0.27	0.06	0.00	0.08	0.28

Table 1. REE geochemical characteristics in REE minerals from the QN and MH granites (%).

4. Results

4.1. Geochemistry of the QN Granite

Results of geochemical analysis of representative samples of the QN and MH granites are listed in Table 2. The average loss on ignition was <1.5 wt.%. The samples have high SiO₂ (62.67–75.12 wt.%) and K₂O (4.45–4.85 wt.%) contents; low MgO (0.39–0.87 wt.%) and FeOt (total Fe oxides; 1.71–6.44 wt.%) contents; and MnO and P₂O₅ contents of 0.05–0.07 wt.% and 0.05–0.07 wt.%, respectively. Their K₂O/Na₂O ratios of 0.88–2.36 indicate that the QN and MH granites are high-K calc-alkaline series rocks (Figure 4a, b). Their peraluminous nature is indicated by A/CNK ratios (mol. Al₂O₃/(CaO + $K_2O + Na_2O$) of generally >1.1 (Figure 4c). In the ternary classification diagram (Figure 5), the samples plot within the S-type granite field (with one exception in the I-type field), close to the boundary of the A-type field. In the Harker diagrams (Figure 6), FeO, MgO, TiO₂, CaO, MnO, and P₂O₅ contents exhibit strong negative correlations with SiO₂ content. Five samples (lc2-j2, lc2-j3, lc3-j1, lc4-j1, and mh-j1) have REE contents of 212–749 ppm with similar chondrite-normalized REE patterns that are relatively enriched in LREEs (LREE/HREE = 1.89–7.74), and obvious negative Eu anomalies (Eu/Eu* = 0.14–0.2). The Eu/Eu* ratios are negatively related to HREE contents. The sample lc3-j1 with the highest REE content exhibits a notable negative Ce anomaly (Figure 7a). Five samples are enriched in large-ion lithophile elements, and display negative Ba, Nb, Sr, Zr, Hf, and Ti anomalies in primitive-mantle-normalized trace-element spidergrams (Figure 7b).

Sample	lc2-j2	lc2-j3	lc3-j1	lc4-j1	mh1-j1
		(wt	.%)		
SiO ₂	62.7	75.4	72.7	74.7	67.7
Al_2O_3	15.9	12.1	13.7	12.9	0.53
CaO	2.37	1.44	1.46	1.59	14.7
Fe ₂ O ₃	6.44	2.77	0.12	0.09	4.29
FeO	5.28	2.14	2.18	1.62	3.53
K ₂ O	2.27	0.87	0.68	0.39	0.09
MgO	0.08	0.05	0.07	0.05	1.94
MnO	2.12	1.88	2.66	2.35	1.76
Na ₂ O	5.40	4.45	4.52	4.85	2.42
P_2O_5	0.85	0.32	0.27	0.20	4.61
TiO ₂	0.25	0.05	0.07	0.05	0.19
CO ₂	0.36	0.20	0.23	0.20	0.48
H_2O^+	0.87	0.65	0.70	0.44	0.92
LOI	0.83	0.50	0.63	0.49	0.90
		(×1	0 ⁻⁶)		
Li	37.8	14.8	36.0	16.2	39.1
Be	2.27	1.46	5.00	1.40	6.03
Cr	41.4	41.4	19.1	17.6	64.6
Co	15.4	5.68	4.09	3.00	10.2
Ni	16.0	10.8	6.71	2.61	21.9
Cu	17.2	11.1	10.2	4.25	13.2
Zn	93.4	38.4	36.0	23.0	63.4
Ga	26.1	15.9	16.6	13.3	19.0
Rb	277	163	257	159	268
Sr	181	136	85.5	119	126
Mo	1.06	0.84	0.39	0.68	0.82
Cd	0.07	< 0.05	0.07	0.03	0.10
In	0.13	< 0.05	0.05	0.02	0.07
Cs	8.66	3.77	9.51	4.47	16.4

Table 2. Major (wt.%), trace elements ($\times 10^{-6}$), and rare earth elements ($\times 10^{-6}$) of QN and MH granites.

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Sample	lc2-j2	lc2-j3	lc3-j1	lc4-j1	mh1-j1
Ва	1972	1322	638	792	754
Tl	1.47	0.82	1.38	0.90	1.50
Pb	43.3	55.2	41.1	37.6	42.4
Bi	0.19	0.17	1.13	0.11	1.10
Th	25.2	22.9	28.6	40.5	24.2
U	3.45	3.53	6.03	3.53	7.90
Nb	19.7	8.66	10.9	3.96	13.6
Та	1.70	0.91	1.47	0.48	1.54
Zr	339	153	96.1	92.9	172
Hf	9.21	4.74	3.71	3.27	5.21
Sn	5.06	2.73	10.5	3.89	10.9
Sb	0.16	0.09	0.09	0.07	0.07
W	2.82	0.68	2.48	0.95	2.44
As	2.51	1.03	1.01	1.09	11.5
V	116	36.1	20.8	16.4	73.5
Sc	16.1	6.60	5.42	3.68	10.8
La	56.5	41.5	154	59.5	41.5
Ce	115	83.8	81.1	112	87.1
Pr	12.4	9.35	41.3	13.5	9.89
Nd	45.6	34.1	166	50.1	36.3
Sm	9.65	6.52	41.7	7.93	7.52
Eu	1.45	1.27	6.18	1.03	1.14
Gd	9.11	5.17	38.9	6.28	6.11
Tb	1.79	0.80	6.38	0.78	0.95
Dy	10.5	4.24	33.5	3.68	5.07
Ho	1.92	0.70	5.78	0.70	0.83
Er	5.29	1.87	14.2	1.89	2.28
Tm	0.64	0.26	1.87	0.23	0.31
Yb	3.53	1.65	13.6	1.71	2.02
Lu	0.51	0.25	1.47	0.20	0.29
Y	54.3	21.1	143	16.0	24.0
ΣREE	328	212	749	275	225
LREE	240	176	490	244	183
HREE	87.6	36.0	258	31.5	41.8
LREE/HREE	2.75	4.90	1.89	7.74	4.38
δΕυ	0.15	0.22	0.15	0.15	0.17

Table 2. Cont.



Figure 4. Plots of SiO₂ *versus* K_2O (**a**), Na_2O *versus* K_2O (**b**) and A/CNK *versus* A/NK (**c**) for the LC granite (modified from references [37–39]; the LC batholith data after e.g., [40–45]).





Figure 5. Plots of Zr+Nb+Ce+Y *versus* (Na₂O+K₂O)/CaO (**a**), 1000×Ga/Al *versus* (Na₂O+K₂O)/CaO (**b**) and A(Al—Na—K)-C(Ca)-F(Fe³⁺+Mg) (**c**) for the LC granite (modified from reference [46]).



Figure 6. Harker diagrams (SiO₂ *versus* FeO (**a**), MgO (**b**), TiO₂(**c**), CaO (**d**), MnO (**e**), P₂O₅ (**f**)) for the major elements in the LC granite.



Figure 7. Chondrite-normalized REE patterns (**a**), primitive mantle-normalized elements diagrams (**b**) of the LC granite (normalization values after [47]; the LC batholith data after, e.g., [40–45]).

4.2. Zircon U-Pb Dating

Zircons from the QN porphyritic biotite granite sample (lc4-j1) are predominantly yellow to colorless euhedral crystals, 50–150 μ m long with aspect ratios of 1–3, and exhibit oscillatory magmatic zoning in cathodoluminescence (CL) images. Their U and Th contents are 117–21,152.8 and 69–28,873 ppm, respectively, with Th/U ratios of 0.19–1.36, which is typical of magmatic zircons. Twenty analyses yielded concordant ²⁰⁶Pb/²³⁸U ages of 231.4–215.2 Ma, with a weighted-mean age

of 220.3 ± 1.2 Ma (mean squared weighted deviation, MSWD = 0.71), which is interpreted as the crystallization age of the central part of the LC batholith (Table 3; Figure 8a,b).

Zircons from biotite granite lc2-j3 are a similar color to those of sample lc4-j1, with lengths of 50–200 μ m and aspect ratios of 1.5–2.5, and magmatic oscillatory zoning in CL images. Their U and Th contents are 107–4335 and 48–1146 ppm, respectively, with Th/U ratios of 0.05–1.59. The 12 youngest ages are concordant with a weighted-mean ²⁰⁶Pb/²³⁸U age of 217.8 ± 1.7 Ma (MSWD = 1.06). Older ages were obtained from cores and xenocrysts. Three analysis yielded Concordia ²⁰⁶Pb/²³⁸U ages of 443.1 ± 13.9 to 384.7 ± 12.1 Ma, and 10 analyses yield ages of 1575.1 ± 45.0 to 509.0 ± 15.8 Ma (Table 3; Figure 8c,d).

Zircons from the MH biotite granite mh-j1 are similar to the QN zircons and are yellow to colorless, with lengths of 50–250 μ m and aspect ratios of 1–4, and magmatic oscillatory zoning in CL images. Their U and Th contents are 98–709 and 16–294 ppm, respectively, with Th/U ratios of 0.18–0.85. One xenocryst analysis yielded a ²⁰⁶Pb/²³⁸U age of 410.6 ± 13.2 Ma. Four other xenocryst analyses yielded ²⁰⁶Pb/²³⁸U ages of 1015.1 ± 30.0 to 902.4 ± 26.8 Ma, possibly indicating the existence of early Proterozoic basement in the region, similar to that in the Yangtze Block [48,49]. These ages suggest that the petrogenesis of the LC granite was associated with anatexis of crustal materials. The 19 youngest analyses are concordant, with a weighted-mean age of 232.2 ± 1.7 Ma (MSWD = 0.58; Table 3; Figure 8e,f).

Communite /Nice	U	Th	Pb(t)	Th/U	²⁰⁷ Pb	/ ²³⁵ U	²⁰⁶ Pb/ ²³⁸ U		²⁰⁷ Pb/ ²³⁵ U		²⁰⁸ Pb/ ²³² Th	
Sample/10.		(×10 ⁻⁶)			Ratio	1σ	Ratio	1σ	Ma	1σ	Ma	1σ
					lc4-j1	, N = 25						
1	21153	28873	1703	1.36	0.2496	0.0081	0.0365	0.0012	226.2	6.60	230.9	7.30
2	1341	467	44.2	0.35	0.2516	0.0082	0.0364	0.0012	227.9	6.70	230.5	7.30
3	285	125	10.8	0.44	0.2599	0.0093	0.0366	0.0012	234.6	7.50	231.4	7.40
4	326	182	13.8	0.56	0.2552	0.0088	0.0361	0.0012	230.8	7.20	228.6	7.30
5	285	163	11.9	0.57	0.2362	0.0083	0.0342	0.0011	215.3	6.80	216.6	6.90
6	967	443	35.4	0.46	0.2367	0.0078	0.0342	0.0011	215.7	6.40	216.9	6.90
7	475	295	21.9	0.62	0.2361	0.0079	0.0344	0.0011	215.2	6.50	217.8	6.90
8	1076	660	48.5	0.61	0.2366	0.0078	0.0343	0.0011	215.6	6.40	217.2	6.90
9	242	132	10.0	0.54	0.2376	0.0084	0.0343	0.0011	216.4	6.90	217.6	6.90
10	358	189	14.4	0.53	0.2337	0.0118	0.0341	0.0012	213.3	9.70	216.1	7.30
11	334	342	21.5	1.02	0.2519	0.0085	0.0361	0.0012	228.1	6.90	228.3	7.20
12	1248	232	30.2	0.19	0.2506	0.0082	0.0365	0.0012	227.1	6.70	230.9	7.30
13	117	72.0	5.1	0.62	0.2563	0.0154	0.0361	0.0013	231.7	12.50	228.9	8.10
14	395	251	18.4	0.64	0.2545	0.0086	0.0362	0.0012	230.2	6.90	229.1	7.20
15	784	494	36.2	0.63	0.2375	0.0081	0.0344	0.0011	216.4	6.70	218.2	6.90
16	520	278	20.7	0.53	0.2356	0.0079	0.0341	0.0011	214.8	6.50	216.3	6.80
17	276	139	10.6	0.50	0.2348	0.0087	0.0344	0.0011	214.2	7.20	218.0	7.00
18	137	69.4	5.3	0.51	0.2382	0.0106	0.0343	0.0011	217.0	8.70	217.6	7.10
19	165	92.6	7.2	0.56	0.2402	0.0107	0.034	0.0011	218.6	8.80	215.2	7.10
20	196	116	9.2	0.60	0.2403	0.0135	0.0344	0.0012	218.7	11.00	218.1	7.50
21	694	254	21.9	0.37	0.2364	0.0078	0.0343	0.0011	215.5	6.40	217.5	6.90
22	785	336	28.1	0.43	0.2341	0.0077	0.0344	0.0011	213.5	6.30	218.0	6.90
23	182	78.1	6.5	0.43	0.2399	0.0178	0.034	0.0013	218.3	14.60	215.4	8.10
24	133	74.6	5.6	0.56	0.2364	0.0089	0.0343	0.0011	215.5	7.30	217.2	6.90
25	577	167	16.6	0.29	0.2352	0.0082	0.0343	0.0011	214.5	6.80	217.2	6.90

Table 3. LA-ICP-MS zircon U-Pb analytical data of the QN and MH granites.

Table 3. Cont.

	II	ть	Ph(t)	Th/II	207 ph	/23511	206 ph	/23811	207 ph	/23511	208 ph/2	32Th
Sample/No.	U	(×10 ⁻⁶)	10(1)	1140	Ratio	, υ 1σ	Ratio	, υ 1σ	Ma	1σ	Ma	1σ
					lc2-i3	, N = 25						
1	1027	309	32.1	0.30	0.217	0.0073	0.0321	0.0010	199	6.10	204.50	4.50
2	974	331	32.2	0.34	0.2237	0.0075	0.0322	0.0011	205	6.20	196.60	4.30
3	689	256	22.3	0.37	0.239	0.0080	0.0348	0.0011	218	6.50	205.40	4.50
4	271	136	10.5	0.50	0.2407	0.0084	0.0348	0.0011	219	6.80	203.40	4.70
5	1159	75.0	21.4	0.06	0.2471	0.0082	0.0349	0.0011	224	6.70	213.30	5.80
6	597	48.2	11.1	0.08	0.2418	0.0081	0.0349	0.0011	220	6.60	226.10	6.20
7	449	23.4	7.9	0.05	0.247	0.0094	0.0349	0.0012	224	7.70	252.00	13.9
8	2237	1146	104	0.51	0.2393	0.0078	0.0350	0.0011	218	6.40	212.00	4.40
9	171	81.0	6.2	0.47	0.2496	0.0089	0.0350	0.0011	226	7.30	192.40	4.80
10	425	161	13.6	0.38	0.2452	0.0083	0.0351	0.0011	223	6.70	194.60	4.40
11	383	166	13.8	0.43	0.2444	0.0083	0.0351	0.0011	222	6.80	207.00	4.80
12	4335	1110	142.7	0.26	0.2443	0.0080	0.0351	0.0011	222	6.50	243.20	5.10
13	1931	381	91.5	0.20	0.452	0.0147	0.0615	0.0020	379	10.3	368.50	7.70
14	1036	529	79.2	0.51	0.48	0.0157	0.0644	0.0021	398	10.8	402.80	8.40
15	1038	94.1	51.0	0.09	0.6739	0.0223	0.0712	0.0023	523	13.5	588.20	14.1
16	1808	813	150	0.45	0.5983	0.0195	0.0822	0.0027	476	12.4	450.40	9.40
17	1153	115	82.8	0.10	0.9613	0.0319	0.1055	0.0034	684	16.5	784.80	18.8
18	58.0	80.0	16.5	1.37	1.0337	0.0491	0.1180	0.0041	721	24.5	692.60	19.4
19	517	136	58.6	0.26	1.3384	0.0438	0.1415	0.0046	863	19.0	745.60	16.0
20	464	263	84.9	0.57	1.4514	0.0475	0.1499	0.0048	911	19.7	817.10	17.1
21	629	109	68.2	0.17	1.45	0.0471	0.1504	0.0048	910	19.5	898.80	18.9
22	976	169	157	0.17	2.2981	0.0751	0.1733	0.0056	1212	23.1	1240.80	26.3
23	356	238	118	0.67	2.2211	0.0731	0.1963	0.0064	1188	23.0	1136.30	23.5
24	107	170	52.7	1.59	2.2998	0.0760	0.2039	0.0066	1212	23.4	1004.40	20.8
25	377	122	97.8	0.32	3.7222	0.1205	0.2768	0.0089	1576	25.9	1329.70	27.1
					mh1-j	1, N = 25	;					
1	286	163	13.8	0.57	0.2632	0.0243	0.0364	0.0015	237.2	19.5	230.5	9.6
2	283	215	15.4	0.76	0.2627	0.0158	0.0365	0.0013	236.8	12.7	231.2	8.1
3	403	267	23.1	0.66	0.2593	0.0101	0.0366	0.0012	234.1	8.1	231.6	7.4
4	136	80.8	6.20	0.60	0.2606	0.0111	0.0366	0.0012	235.1	9.0	231.9	7.5
5	520	271	24.7	0.52	0.2593	0.0144	0.0366	0.0013	234.1	11.6	232.0	7.9
6	459	294	25.4	0.64	0.2611	0.0103	0.0367	0.0012	235.5	8.3	232.1	7.4
7	297	196	16.0	0.66	0.2638	0.0101	0.0367	0.0012	237.7	8.1	232.3	7.4
8	295	15.9	5.40	0.05	0.2622	0.0135	0.0367	0.0013	236.5	10.8	232.3	7.8
9	142	99.4	7.00	0.70	0.2568	0.0122	0.0367	0.0012	232.0	9.8	232.5	7.6
10	297	159	12.7	0.53	0.2611	0.0094	0.0367	0.0012	235.6	7.6	232.5	7.3
11	98.0	55.7	4.4	0.57	0.2577	0.0114	0.0367	0.0012	232.8	9.2	232.6	7.5
12	511	180	19.6	0.35	0.2535	0.0090	0.0368	0.0012	229.4	7.3	232.9	7.3
13	497	217	20.7	0.44	0.2533	0.0102	0.0368	0.0012	229.3	8.2	233.1	7.5
14	238	81.8	7.40	0.34	0.2627	0.0134	0.0369	0.0013	236.8	10.8	233.4	7.8
15	108	50.7	4.10	0.47	0.2579	0.0117	0.0369	0.0012	233.0	9.5	233.7	7.6
16	179	49.6	6.60	0.28	0.2705	0.0204	0.0369	0.0014	243.1	16.3	233.9	8.9
17	445	184	18.6	0.41	0.2604	0.0097	0.037	0.0012	235.0	7.8	234.1	7.4
18	510	251	25.9	0.49	0.2618	0.0137	0.0371	0.0013	236.1	11.0	234.6	7.9
19	181	154	10.5	0.85	0.2598	0.0122	0.0373	0.0013	234.5	9.8	235.8	7.7
20	284	52.5	8.80	0.18	0.2976	0.0244	0.0405	0.0016	264.6	19.1	256.2	10.0
21	709	127	35.5	0.18	0.5302	0.0230	0.0658	0.0022	432.0	15.2	410.6	13.2
22	332	265	79.7	0.80	1.4443	0.0485	0.1503	0.0048	907.5	20.2	902.4	26.8
23	540	253	109	0.47	1.4412	0.0462	0.1507	0.0048	906.2	19.2	904.7	26.7
24	167	44.0	28.4	0.26	1.9706	0.0636	0.1509	0.0048	1105.5	21.8	905.8	26.8
25	136	40.6	22.8	0.30	2.1645	0.0730	0.1706	0.0055	1169.7	23.4	1015.1	30.0





4.3. Sr-Nd-Pb Isotopic Compositions

Results of whole-rock Sr–Nd isotope analyses of the QN and MH granites are shown in Table 4 and plotted in the ϵ Nd(t)–(⁸⁷Sr/⁸⁶Sr) diagram (Figure 9a). The QN and MH granites have variable ⁸⁷Sr/⁸⁶Sr ratios of 0.733459–0.733626, and ¹⁴³Nd/¹⁴⁴Nd ratios of 0.511982–0.511990. Their initial Sr and Nd isotopic compositions are indicated by (⁸⁷Sr/⁸⁶Sr)_i = 0.72057–0.72129 and ϵ Nd(232 Ma) = –9.57 to –9.75.

Sample	t (Ma)	Rb (ppm)	Sr (ppm)	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr	2σ	I _{Sr}	$\varepsilon_{\mathrm{Sr}}$ (t)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	2σ	I _{Nd}	εNd (0)	εNd (t)	f _{Sm/Nd}	T _{2DM}
YNlc3-j1	220	257	85.5	3.919	0.733514	0.000007	0.72058	232.2	0.09349	0.511982	0.000003	0.51184	-12.8	-9.75	-0.52	1801
YNlc4-j1	220	159	119	3.905	0.733459	0.000008	0.72057	232.1	0.09267	0.51199	0.000007	0.511849	-12.64	-9.57	-0.53	1787
YNmh-j1	220	246	146	3.918	0.733616	0.000006	0.72069	233.8	0.09349	0.511982	0.000006	0.51184	-12.8	-9.75	-0.52	1801

Table 4. Sr-Nd isotope ratios of the QN and MH granites.





Figure 9. Diagrams of $({}^{87}\text{Sr}/{}^{86}\text{Sr})_i - \varepsilon \text{Nd}(t)$ (**a**) and Pb-isotopic composition (**b**) of biotite granite obtained from the LC granite (the LC batholith data after e.g., [41,50]).

The initial Pb isotopic compositions of the QN and MH granites are moderately radiogenic, with isotopic ratios of 206 Pb/ 204 Pb = 18.988–19.711, 208 Pb/ 204 Pb = 39.713–40.216, and 207 Pb/ 204 Pb = 15.799–15.863. In (207 Pb/ 204 Pb)–(206 Pb/ 204 Pb) diagrams (Table 5; Figure 9b), the LC granites are clustered towards the upper-crust field.

Sample	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	$(^{206}\text{Pb}/^{204}\text{Pb})_i$	$(^{207}\text{Pb}/^{204}\text{Pb})_i$	$(^{208}\text{Pb}/^{204}\text{Pb})_i$
YNlc3-j1	19.346	0.0000	15.823	0.00001	39.690	0.001	18.993	15.805	39.145
YNlc4-j1	18.988	0.0000	15.799	0.00001	39.819	0.001	18.763	15.788	38.979
YNmh-j1	19.326	0.0000	15.817	0.00001	39.713	0.001	18.293	15.765	39.107

Table 5. Pb isotope ratios of the QN and MH granites.

5. Discussion

5.1. The Timing of REE Mineralization in the LC Granite

Previously published ages for the LC granite have generally been in the range of 252–199 Ma (e.g., [17–19,33,40–45,50,51]; Figure 10). Our zircon U–Pb dating in the central LC batholith, which contains HREE mineralization, yielded an age of ca. 220.3 Ma, and zircons from the southern area yielded an age of ca. 233.2 Ma, both of which are within this range, suggesting that the main LC granitic body intruded during the middle–late Triassic.

Zircon usually crystallizes during the early stages of rock formation and can survive temperatures as high as 3000 °C. Zircon U–Pb ages may, therefore, reflect those of their host granite [52]. However, REE minerals such as monazite, allanite, and xenotime crystallize later in granite than zircon. Furthermore, the types and amounts of REE mineral (including HREE minerals) increase with hydrothermal alteration after crystallization being [30,53]. Hence, zircon U–Pb ages should be considered upper limits of the REE-mineralization age; i.e., 220.3 Ma in the QN granite, and 233.2 Ma in the MH granite.



Figure 10. Plots of Al₂O₃/TiO₂ *versus* CaO/Na₂O (**a**), Rb/Sr *versus* Rb/Ba (**b**), Ca/(MgO+FeO^T) *versus* Al₂O₃/(MgO+FeO^T) (**c**), Ba *versus* Rb/Sr (**d**) for the potential magma source of the LC granite (modified from references [54,55]).

5.2. Petrogenesis and Tectonic Setting of the LC Pluton

The decrease in FeOt, MgO, TiO₂, CaO, MnO, and P₂O₅ contents of the LC granites with increasing SiO₂ content suggests that the magmas underwent continuous crystallization during magmatic evolution, and their peraluminous nature (A/CNK > 1.1) indicates S-type affinity (Section 4.1; Figure 4, Figure 5c, and Figure 6; [54–58]). Geochemical, isotopic, and petrological constraints confirm that most large-volume peraluminous granites originate from the melting of crustal rocks (e.g., [54]). Here, the strong negative Eu, Ba, Nb, Sr, P, and Ti anomalies, and positive Rb, Th, and U anomalies of the LC granite are similar to those of magma derived from the partial melting of crustal rocks [56,59].

S-type granites are produced mainly from the melting of metasediments such as psammite and pelite [60], and their CaO/Na₂O ratios are influenced by their magma source. The CaO/Na₂O ratios in psammite-derived melt are generally > 0.3 (average 0.8), whereas in pelite-derived melt the ratios are <0.5 [54]. Here, most LC granite samples have CaO/Na₂O ratios of 0.06–2.67 (n = 147), with only 21 samples having ratios of <0.5, and Al₂O₃/TiO₂ ratios of 9.29–150.9, with only four samples having ratios of >79. In the $(CaO/Na_2O)-(Al_2O_3/TiO_2)$ diagram (Figure 10a), most samples plot in the field of psammite-derived melt. The Rb/Ba and Rb/Sr ratios in psammite-derived melt are lower than those in pelite-derived melt [56]. In the (Rb/Ba)–(Rb/Sr) diagram ([61]; Figure 10b), most LC granite samples plot close to the psammite-derived melt field, with such melt having a clay-poor source, including minor shale. Some samples plot near the clay-rich field with a mixed source dominated by quartz-feldspathic psammites. In the (Al₂O₃/(MgO + FeOt))–(CaO/(MgO + FeO^T)) diagram (Figure 10c), most samples plot in the field of psammite-derived melt. Furthermore, Sr and Eu are enriched mainly in plagioclase, whereas K-feldspar is enriched in Ba. The strong negative Eu, Ba, and Sr anomalies in LC granite samples indicate that plagioclase and K-feldspar are the main residual phase in partial melting. In the (Rb/Sr)–Ba diagram (Figure 10d), most LC granite samples plot with 20–60% plagioclase, suggesting that at least 20–60% plagioclase was present in the magma source [54,55]. It follows that the parental magma source for the LC granites involved mainly quartz-feldspathic materials such as psammite-dominated clastic metasediments, with minor shales.

The high initial ⁸⁷Sr/⁸⁶Sr ratios, low $\varepsilon_{Nd}(231 \text{ Ma})$ values and Pb isotopic compositions, consistent with the isotopic composition of the field of remelting granites of SCB (South China Block; [62]; Figure 9), indicates that the LC granitic magma was derived from partial melting of ancient crystallized basement.

The compositions of the Changning–Menglian suture belt in the Lancangjiang zone of SW China, the Chiang Mai–Inthanon suture belt in northern Thailand, and the Bentong–Raub suture belt in the Malay Peninsula indicate that the Paleo-Tethys Ocean opened in the early Devonian and closed in the Middle–Late Triassic [33,34,40–43,63–65]. The LC batholith, exposed to the east of the Changning–Menglian suture zone, represents a tectono-magmatic zone that records the evolution of the Paleo-Tethys Ocean from subduction to post-collisional regimes [41,64].

The LC granite exhibits peraluminous and S-type characteristics and, with psammite-derived upper-crustal melt being the main source of S-type granites, some studies have concluded that the LC batholith formed in a syn-collisional setting [33,51,55–57]. This is supported by most LC granites being peraluminous (Figure 5c) and plotting in the volcanic arc and syn-collision fields in the Nb-Y diagram (Figure 11a). Peralkaline and alkaline granites are commonly associated with post-tectonic within-plate extension [55]. In the SiO_2-K_2O diagram (Figure 5a), most LC granite samples plot in the peralkaline and alkaline fields, while in the Rb-(Y+Nb) diagram (Figure 11c), all but one plot in the post-collision field, consistent with a post-collision tectonic setting. Our zircon U-Pb ages of 233.2-217.8 Ma from the LC granite are consistent with those found in most other studies (252–199 Ma), and the common absence of Early Triassic strata in the Lancangjiang zone reflects pronounced uplift and erosion at that time [33,40]. Moreover, in the Rb–(Y+Ta) diagram (Figure 11b), all LC granites plot in the within-plate granite field, indicating a within-plate extensional environment. Experimental studies have demonstrated that bimodal igneous suites comprising mafic members of tholeiitic gabbros and basalts, and felsic members displaying A-type characteristics, are common in such a setting [37,40,66]. We, therefore, conclude that closure of the Paleo-Tethys Ocean at ca. 295 Ma was followed by syn-collisional extension accompanied by crustal melting and a degree of mantle-material ascent, with magmatism occurring mainly at ca. 199 Ma within a post-collision extensional environment. The LC granite, thus, originated from the partial melting of early Paleozoic crustal basement.



Figure 11. Plots of Y *versus* Nb (**a**), Y+Ta *versus* Rb (**b**) and Y+Nb *versus* Rb (**a**) for the LC granite (modified from references [67,68]).

5.3. Key Factors in REE Mineralization

5.3.1. Rare-Earth Element Minerals

Surface water and groundwater may contain little Ree³⁺, and bedrock is considered the main source of iRee deposits [24–26]. The Nangling (NL) granites are the host rocks for most iRee deposits in SE China, and in both the NL and LC granites, accessory rare-earth element (REE) minerals are critical for the formation of iRee deposits [7,24–27]. However, fewer types and lower quantities of REE minerals occur in the LC granite than in, for example, the Zudong and Longnan granites that are enriched in prisite (–Y), bastnaesite, samarskite, eschynite, monazite, and allanite. The behavior of REE minerals during chemical weathering is a critical factor that affects the accumulation and differentiation of REEs in the weathering profile. Minerals in weathering crust can be divided into three groups: (1) strongly stable during chemical weathering; e.g., quartz, monazite, xenotime, and zircon; (2) moderately stable during weathering; e.g., feldspar, biotite, apatite, and allanite; and (3) weakly stable during weathering; e.g., fluorite(–Y) and REE fluorcarbonate [7,24–27]. REE minerals are the main source of iRee deposits in the LC granite. Although feldspar, biotite, sphene, and apatite have low REE contents, weathering cycles may result in these minerals contributing to the deposit. Minerals in granites enriched in LREEs contribute to iLRee deposits when they are dissolved in the weathering crust. Allanite(–Y), fluorite(–Y), and REE fluorcarbonate are relatively enriched in HREEs, and are the main HREE source for iRee deposits. However, HREE minerals are not common in the LC granite. The QN granites, for example, are mainly enriched in LREEs, with relatively few exhibiting HREE enrichment, leading to QN deposits being rich in LREEs, but with a degree of HREE enrichment. The HREE minerals are scarce in MH granite, so the MH deposit is enriched with LREEs only.

5.3.2. Secondary Minerals

Rock-forming minerals such as feldspar and mica (biotite and muscovite) are altered to clay minerals during weathering and become carriers of Ree³⁺ [7,24–29,69]. Clay minerals such as those of the kaolin-group (kaolinite, dickite, nacrite, and halloysite), illite, and montmorillonite, which adsorb Ree³⁺, can also be considered as iRee ores. This study found that kaolinite, illite, and montmorillonite are the main clay minerals in the LC granite weathering profile, while halloysite also occurs in the NL weathering profile.

The REE adsorption capacity is influenced by surface structure, composition, and surface charge of clay minerals [31]. Illite and montmorillite occur in 2:1 clays, with higher adsorption capacities than kaolin-group minerals in 1:1 clays. The high adsorption capacity of montmorillonite is due to negative charges generated by isomorphism in the lattice, whereas kaolinite and halloysite have negative charges where –OH in the crystal lattice releases H⁺. The higher the pH, the higher the adsorption capacity [31,68,69]. The pH points of zero charge (pH_{pzc}) of kaolinite, illite, and montmorillonite are <3.7, ~2.5, and 7–9, respectively [70], so under natural pH conditions (4–7), kaolin-group minerals (especially kaolinite and halloysite) and illite are more capable of surface complexation of Ree³⁺ than montmorillonite [32,69]. In both the LC and NL areas, the kaolin-group represents the predominant clay minerals in the weathering profile, providing enrichment in Ree³⁺. In the appropriate pH range, the deposit's Ree³⁺ content, thus, depends on the amount of kaolin-group minerals in the weathering profile.

Horizon B of the granite weathering profile has the highest Ree³⁺ content, owing to its pH range of 4–6.8 and higher kaolinite and/or halloysite content. In the LC area, horizon B contains an average of 21–26% clay minerals [29], whereas in the NL area the clay-mineral content is up to 50% [24–26,32]. In the NL weathering profile, the content of kaolinite decreases but that of halloysite increases with depth, with both clay minerals contributing to the accumulation and fractionation of REEs at pH 5.5–6.3 [32]. The higher Ree³⁺ content of the NL weathering profile than that of the LC profile is, therefore, likely related to its higher kaolinite and halloysite contents.

5.3.3. Intensity of Granite Weathering

The Ree³⁺ content of the weathering profile is influenced by the intensity of granite weathering; the stronger the weathering, the more REE minerals are dissolved, and the more Ree³⁺ is released to the profile. The LC weathering profile has a lower REE content than the NL profile: 134–1111 ppm (mean 447 ppm; n = 77) and 168–2347 ppm (mean 572 ppm; n = 70), respectively, and the difference may be due to the relative intensities of weathering. In the NL area, the chemical index of alteration (CIA; $100 \times Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)$) of granite and the weathering profile are in the ranges of 45–60% and 65–95%, respectively, with the REE content increasing with CIA in the range 45–60%, but decreasing in the CIA range of 65–95% [27]. The CIA of LC granite and weathering profile are similar to the NL profile (Figure 12a, b).



40

60

Figure 12. Diagrams of LREE *versus* HREE (a) and CIA *versus* REE (b) of the LC granite and weathering profile.

2000

The intensity of weathering can also be reflected in the amounts and types of secondary minerals in the horizon. In natural chemical weathering, feldspar and mica (muscovite and biotite) are altered to clay through several stages, with each stage corresponding to a different clay mineral:

• Feldspar→kaolinite→gibbsite;

0

Muscovite→illite→montmorillonite→kaolinite→gibbsite;

1000

LREE

1500

• $Biotite \rightarrow chlorite \rightarrow vermiculite \rightarrow montmorillonite \rightarrow beidellite \rightarrow kaolinite \rightarrow gibbsite.$

Halloysite is in the kaolin group, and normally coexists with kaolinite in modern soils and sediments. The higher the intensity of weathering, the higher the content of clay minerals, such as those of the kaolin group (and possibly gibbsite). In NL granite weathering profile, halloysie is in common and play an important role in the carrier of Ree³⁺ [32,69]. But in the most of LC granite weathering profile, there is kaolinite only [28,29], which could be the reason why the concentration of Ree³⁺ in NL area are higher than LC area.

Weathering cycles are key to the secondary mineralization of Ree³⁺ in the weathering profile, with re-enrichment and re-fractionation and with Ree³⁺ being re-migrated and re-accumulated. As soil pH changes from acidic to alkalescent with increasing depth in the weathering profile, the Ree³⁺ concentration increases with the increasing adsorption capacity of clays. Previous studies have shown that a pH range of 5.4–6.8 is optimum for the accumulation of Ree³⁺ [32,70,71]. The HREEs of higher atomic mass are more soluble than LREEs in water, and accumulate at higher pH [32,70,71], with the depth of HREE enrichment, thus, being greater than that of LREE enrichment.

6. Conclusions

(1) REE minerals, including allanite, fluorapatite, and monazite, and HREE minerals such as xenotime, thorite, allanite(–Y), fluorite(–Y), and REE fluorcarbonate, make the greatest contribution to the REE content of the LC granite. The QN and MH granites are host rocks for Ree deposits with zircon U–Pb ages of ca. 217 Ma and 232 Ma, respectively, with these being the earliest times of REE mineral formation.

(2) The host rocks of the Ree deposits are strongly peraluminous with S-type granite affinities, suggesting they originated from partly melted crustal basement. Sr–Nd–Pb isotopic systematics and geochemical signatures of the LC granites indicate that they were derived from partial melting of the upper crust. Paleo-Tethyan continent–continent collision occurred during the early Indosinian, followed by post-collisional extension. Middle Indosinian magmatism was generated in a post-collisional tectonic setting related to early–middle Indosinian slab break-off.

(3) REE minerals such as allanite(–Y), fluorapatite, fluorite(–Y), and REE fluorcarbonate dissolved in the weathering crust are the main sources of Ree deposits. Dissolution of LREE and HREE minerals lead to LREE and HREE enrichment, respectively. Secondary minerals, such as kaolin-group minerals and illite (from altered feldspars and micas), are carriers of Ree³⁺, and its enrichment is influenced by the intensity of weathering; the stronger the weathering, the more REE minerals are dissolved

120

in the weathering profile. Weathering cycles are key to the secondary mineralization of Ree³⁺, and stable geological conditions over a narrow altitudinal range promote retention of Ree³⁺ in the weathering profile.

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