

Article

U-Pb Geochronology, Geochemistry and Geological Significance of the Yongfeng Composite Granitic Pluton in Southern Jiangxi Province

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Abstract: The Yongfeng composite granitic pluton, located in the southern section of the Nanling area, is composed of the Yongfeng and Longshi biotite monzonitic granites. In order to reveal the genesis of this composite granitic pluton and its relationship with mineralization, this study conducted zircon U-Pb dating, whole-rock major and trace element analysis, and biotite electron probe analysis. The results show that the Yongfeng composite granitic pluton is rich in silicon and alkali, weakly peraluminous, and poor in calcium and iron. It shows the enrichment of light rare earth elements and a significant fractionation of light and heavy rare earth elements. It also shows the enrichment of large ion lithophile elements and depletion of Ba, K, P, Eu, and Ti relative to the primitive mantle. The contents of TFe_2O_3 , MgO, CaO, TiO_2 , and P_2O_5 are low and decrease with increasing SiO_2 content. The Yongfeng composite granitic pluton does not contain alkaline dark minerals. Its average zircon saturation temperature is 776 °C, average $\text{TFe}_2\text{O}_3/\text{MgO}$ is 4.81, and average $\text{Zr} + \text{Nb} + \text{Ce} + \text{Y}$ is 280.6 ppm, which correspond to a highly fractionated I-type granite. The Yongfeng and Longshi granites were respectively formed at 152.0 ± 1.0 Ma– 151.3 ± 1.1 Ma and 148.9 ± 1.2 Ma. They were formed in the extensional tectonic setting during the post-orogenic stage, under the control of the breakup or retreat of the backplate after the subduction of the Pacific Plate into the Nanling hinterland. The magmatic system of the Yongfeng composite granitic pluton is characterized by high fractionation, high content of F, high temperature, and low oxygen fugacity, which is conducive to mineralization of Sn, Mo, and fluorite.

Keywords: Yongfeng composite granitic pluton; highly fractionated granite; zircon U-Pb dating; granite petrogenesis; tectonic setting; southern Jiangxi Province



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1. Introduction

The Nanling region is an important mineral deposit area in China because it features a wide distribution of granites that are rich in non-ferrous and rare metal mineral resources, such as W, Sn, Li, Be, Nb, Ta, and U. In this region, mineralization is spatially related to the widespread intrusion of highly fractionated granites [1]. After undergoing high crystallization differentiation, granitic magma becomes enriched in volatile components, REEs, and rare metals in the residual melt-hydrothermal fluid system, providing the appropriate conditions for the formation of metal deposits [2–4].

The Yongfeng composite granitic pluton is located in Xingguo County, southern Jiangxi Province, east section of the Nanling Range. It consists of Yongfeng medium-coarse grained porphyritic biotite monzonitic granite and Longshi fine grained biotite monzonitic granite, exhibiting characteristics of highly fractionated granite. Multiple molybdenum deposits have been discovered at the contacting zone between the Yongfeng composite granitic pluton and its host rocks. The largest deposit is the Leigongzheng molybdenum

deposit [5]. In addition, a large-scale fluorite deposit (Longping fluorite deposit) has been found in the contact zone outside the Longshi granite [6]. Previous studies have generally believed that the Leigongzheng molybdenum deposit and the Longping fluorite deposit are closely related to the adjacent Yongfeng composite granitic pluton [7,8]. However, only a few studies have investigated the Yongfeng composite granitic pluton, and only Yang et al. [9] have suggested it as an A-type granite. Nevertheless, it exhibits distinct characteristics that differentiate it from typical A-type granites, and its genetic type remains to be further determined. In order to reveal the genesis of this composite granitic pluton and its relationship with mineralization, this study systematically conducted petrographic analysis, zircon U-Pb dating, whole-rock major and trace element analysis, and biotite electron probe analysis.

2. Geological Setting and Petrography

Southern Jiangxi province is located in the eastern part of the Nanling tectono-magmatic zone [10] (Figure 1b). The stratigraphy in the area comprises Pre-Carboniferous, Lower Paleozoic, Upper Paleozoic, Mesozoic, and Cenozoic age rocks (Figure 1a). Regional metamorphism generally occurred in the Carboniferous and Lower Paleozoic, forming epimetamorphic rocks, which are covered by Upper Paleozoic shallow marine carbonate and siliciclastic sedimentary rocks. Mesozoic volcanoclastic rocks and terrigenous red-bed sandstones are presented in faulted basins. The lithology of the Cenozoic is composed of loose mud and sand [11]. Southern Jiangxi province is mostly controlled by faults in EW, NNE, and SWW trends [12]. Granites are widespread in the region and mainly occur in Yanshanian [13] (Figure 1a).

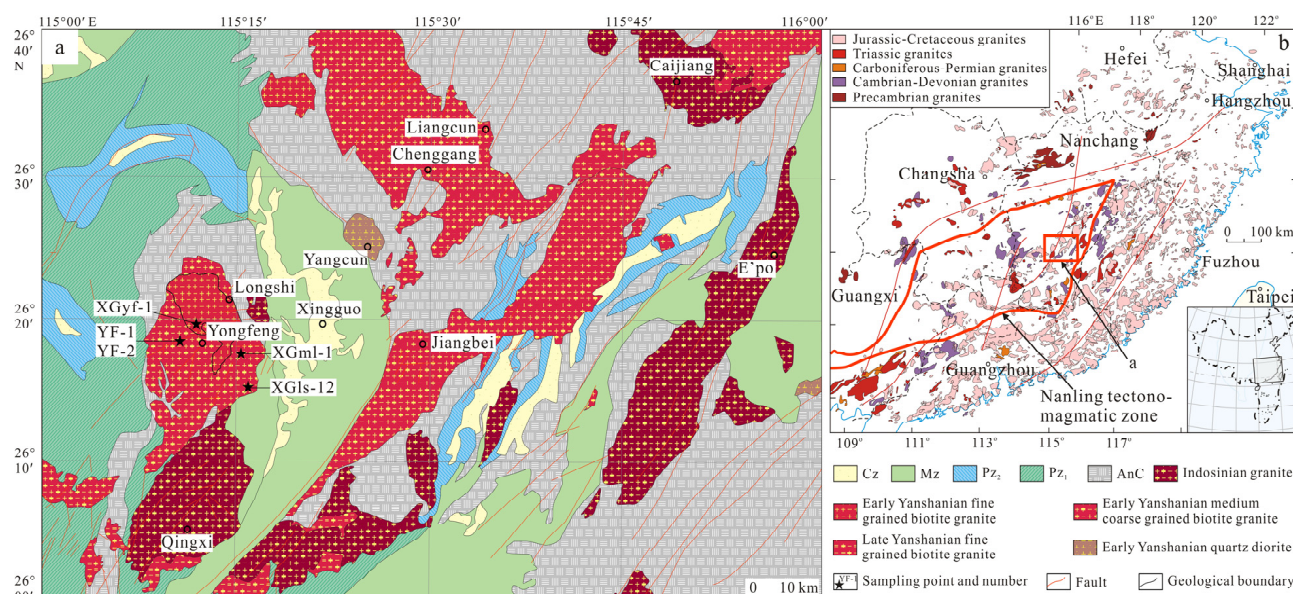


Figure 1. (a) Regional geological sketch of the Yongfeng composite granite pluton (modified according to [14]); (b) Distribution map of granite in South China (modified according to [15]).

The Yongfeng composite granitic pluton consists of Yongfeng, medium- to coarse-grained biotite porphyritic monzonite granite and Longshi fine-grained biotite monzonite granite, with an outcrop area of 350 km². The northern, eastern, and western parts of the composite granitic pluton are in contact with epimetamorphic rocks of the Laohutang formation and Bali formation, and the southern part intrudes the Qingxi granite (Figure 1a). The Yongfeng granite occurs along the margins of the composite granitic pluton, predominantly composed of reddish or grayish white medium-coarse grained porphyritic biotite monzonitic granite (Figure 2), occasionally with potash feldspar phenocrysts. The main minerals are alkali feldspar, plagioclase, and quartz, with a small amount of biotite and muscovite, and the accessory minerals are zircon, apatite, monazite, and rutile. Alka-

line feldspar mainly consists of microcline and perthite, with a semi-idiomorphic plate shape. The length ranges from 0.2 mm to 8.0 mm, with a content of 35 vol%. Tartan twinning and striped structure can be observed (Figure 3a,b). Plagioclase occurs in the form of semi-idiomorphic plate, and polysynthetic twin can be observed, with a length of 0.2–7.0 mm and a content of 32 vol%. The alkali feldspar and plagioclase have undergone strong sericitization alteration (Figure 3a,b). Quartz has a xenomorphic-granular shape, with a diameter of 0.2–5.0 mm and a content of 30 vol%. In the hand specimen, biotite appears as a clump-like aggregate, and under the microscope, it appears scaly, with a length of 0.2–10 mm and a content of 2 vol%. Muscovite also appears scaly (Figure 3a,d), with a length of 0.2–0.6 mm and a content of 1 vol%. The biotite and muscovite have undergone strong chloritization alteration. The Longshi granite is located in the middle of the composite granitic pluton and intrudes the Yongfeng granite. The edges of the granite are heavily weathered. The lithology of the Longshi granite is similar to that of the Yongfeng granite, with only differences in mineral grain size, content, and the phenocrysts content. The lithology of the Longshi pluton is fine-grained biotite monzonitic granite, occasionally with feldspar phenocrysts. The main minerals include potassium feldspar (~20 vol%), plagioclase feldspar (~30 vol%), and quartz (~40 vol%), followed by biotite (~8 vol%) and muscovite (~2 vol%). Potassium feldspar occurs in semi-idiomorphic plate form with grain sizes of 0.2–1.5 mm, with occasional occurrences of striped feldspar and microcline. Plagioclase feldspar occurs in semi-idiomorphic plate form with grain sizes of 0.2–2.0 mm, showing the development of polysynthetic twins. Quartz occurs in granular form with grain sizes of 0.1–2.5 mm. Biotite occurs in scaly form, with a length of 0.1–1 mm. Muscovite occurs in scaly shape, with a length of 0.1–0.6 mm. The accessory minerals mainly include apatite, xenotime, zircon, and a small amount of metallic minerals. The alteration mainly includes K-feldsparization, silicification, sericitization, chloritization, epidotization, and carbonatization (Figure 3d).

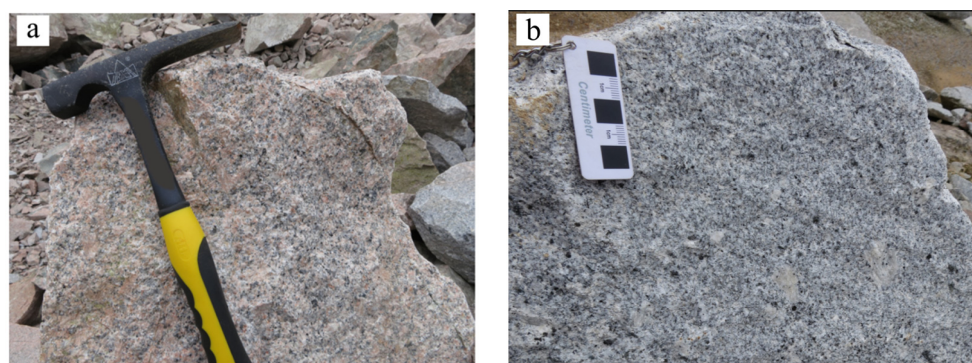


Figure 2. Field photos of the Yongfeng composite granitic pluton. (a) reddish medium-coarse grained porphyritic biotite monzonitic granite; (b) grayish white medium-coarse grained porphyritic biotite monzonitic granite.

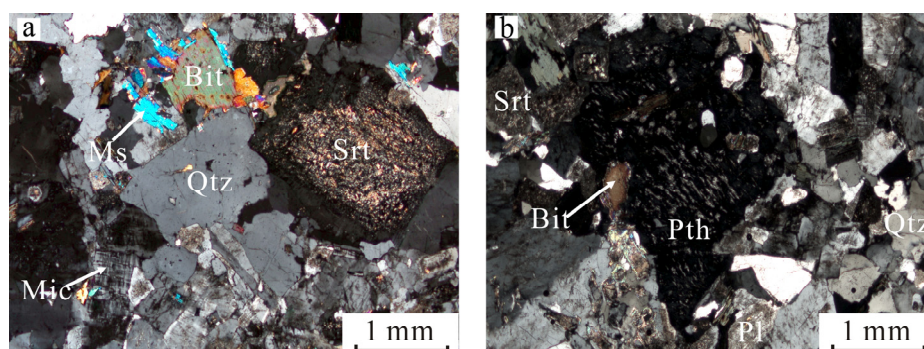


Figure 3. Cont.

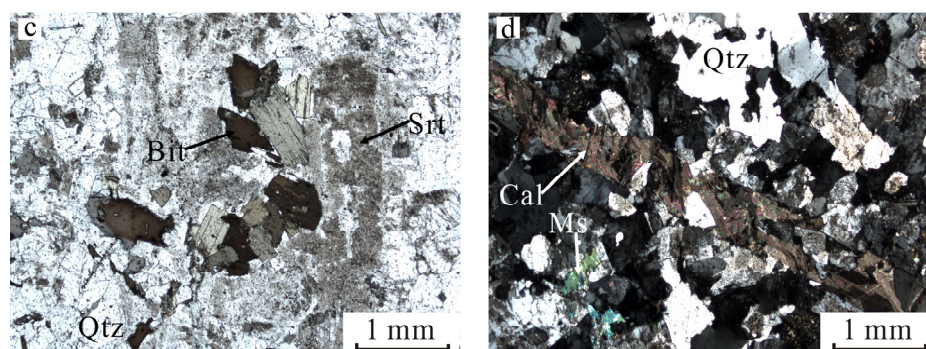


Figure 3. Typical petrographic photos of the Yongfeng composite granitic pluton (a,b,d) are orthogonal-polarization micrographs and (c) is a single-polarization micrograph. (Bt-biotite, Cal-calcite, Ms-muscovite, Pth-striped feldspar, Srt-sericite, Qtz-quartz, Pl-plagioclase).

3. Sample Information and Analysis Methods

The sample information is provided in Supplementary Table S1 and Figure 1a. All samples were subjected to zircon U-Pb dating. Samples YF-1 and YF-2 were analyzed for whole-rock major and trace elements, zircon trace elements, and biotite composition.

3.1. Zircon U-Pb Dating and Trace Elements

The zircon grains were separated from five samples (YF-1, YF-2, XGml-1, XGls-12, XGyf-1) using heavy liquid and magnetic techniques. Representative zircons were hand-picked and mounted in epoxy resin and then polished and coated with carbon. The internal morphology was examined using cathodoluminescence (CL) prior to U-Pb analyses. Zircon U-Pb dating and trace element analysis were completed in the MC-ICP-MS laboratory of the Institute of Mineral Resources, Chinese Academy of Geological Sciences, using a Bruker M90 ICP-MS equipped with a RESOLUTION S-155 193 nm laser. The $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ ratios were calculated using the ICP-MS Data Cal 8.0 program and corrected using zircon GJ-1 as external calibration. These correction factors were then applied to each sample to correct for both instrumental mass bias and depth-dependent elemental and isotopic fractionation. Common Pb content was evaluated using the method described by Andersen [16]. The concordia diagrams were plotted using ISOPLOT (version 3.0). The errors quoted in the tables and figures are at the 1σ level. Instrument operation and data processing methods are described in Hou et al. [17]. Zircon trace elements were quantified using SRM610 as the external standard.

3.2. Major and Trace Element Analysis

Whole-rock samples were trimmed to remove weathered surfaces, cleaned with deionized water, crushed, and then powdered through a 200-mesh screen using a tungsten carbide ball mill. Major elements were analyzed using an X-ray fluorescence (XRF) spectrometer (PW4400) at the National Geological Experimental Testing Center. The detection method is based on GB/T 14506.28-2010. Trace elements were determined using an inductively coupled plasma mass spectrometer (PE300D) at the National Geological Experimental Testing Center. The detection method is based on GB/T 14506.30-2010. The error of the analysis results is less than 5%.

3.3. Electron Probe Microanalysis (EPMA)

Biotite without alteration or with weak alteration was selected for compositional analysis. Biotite composition analysis was performed on a JXA-8230 electron probe analyzer, which is housed at the MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences. The working conditions were as follows: 15 kV voltage, 20 nA current, 5 μm beam spot. Fe^{3+} and Fe^{2+} were obtained according to the calculation method of Lin et al. [18]. The structural formula of biotite was calculated on the basis of 22 oxygen atoms.

4. Results

4.1. Zircon Trace Element Geochemistry

The results of trace elements of zircons from samples YF-1 and YF-2 are shown in Supplementary Table S2. The content of total rare-earth elements (Σ REE) in zircons from sample YF-1 was 518.25–1679.63 ppm, with an average of 921.04 ppm. The content of light rare-earth elements (LREEs) was 6.53–102.18 ppm, with an average of 27.36 ppm. The content of heavy rare-earth elements (HREEs) was 504.49–577.45 ppm, with an average of 893.69 ppm. The LREE/HREE ratio was 0.01–0.07, with an average of 0.03, indicating HREE enrichment and LREE depletion. Chondrite-normalized REE patterns of zircons invariably showed a left-leaning trend (Figure 4). Eu presented a significant negative anomaly ($\text{Eu}/\text{Eu}^* = 0.04\text{--}0.61$, mean of 0.16), whereas Ce presented a significant positive anomaly ($\text{Ce}/\text{Ce}^* = 1.10\text{--}593.83$, mean of 73.65). The content of Σ REE in zircons from sample YF-2 was 508.96–1434.22 ppm, with an average of 991.67 ppm. The content of LREEs was 9.72–234.52 ppm, with an average of 37.80 ppm. The content of HREEs was 499.05–1414.01 ppm, with an average of 953.87 ppm. The LREE/HREE ratio was 0.01–0.32, with an average of 0.04. The zircons in sample YF-2 were also enriched in HREE and depleted in LREE. Chondrite-normalized REE patterns of zircons from sample YF-2 also invariably showed a left-leaning trend (Figure 4). Eu presented a significant negative anomaly ($\text{Eu}/\text{Eu}^* = 0.04\text{--}0.43$, mean of 0.13) and Ce presented a significant positive anomaly ($\text{Ce}/\text{Ce}^* = 1.30\text{--}147.88$, average of 18.97). The chondrite-normalized REE patterns of zircons from the Yongfeng complex pluton are similar to the chondrite-normalized REE patterns of typical magmatic zircons (Figure 4), indicating that the zircons are magmatic zircon.

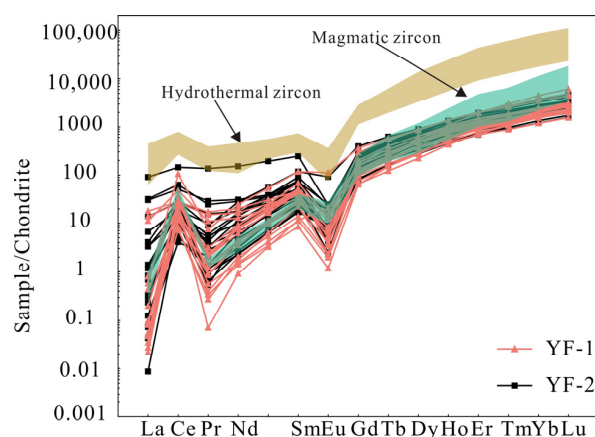


Figure 4. Chondrite-normalized REE patterns for the zircons from the Yongfeng composite granitic pluton (REE data for magmatic and hydrothermal zircons from [19]; the chondrite normalization values are from [20]).

4.2. Zircon U-Pb Age

Zircon cathodoluminescence (CL) images of five samples are shown in Figure 5 and U-Pb dating results are shown in Supplementary Table S3 and Figure 6.

The zircons from sample YF-1 were generally euhedral, measuring up to 80–170 μm , with a length/width ratio of 2:1. Most zircons were colorless or light brown and transparent to subtransparent. They exhibited clear oscillatory zoning in CL images and some of them had inherited cores. The Th content in the zircons was 90.15–666.90 ppm, U content was 146.74–2316.61 ppm, and Th/U ratio was 0.08–1.67, with an average of 0.59. The Th/U ratio of sample point 8 was 0.09, but there was a distinct oscillatory zoning, indicating that it should also be the product of magmatic crystallization. A total of 20 analytical data points were extracted from sample YF-1, and one of the data points was discarded because the concordance was below 90%. Six zircons had older apparent ages, and the other 13 zircons showed relatively consistent apparent age, with a weighted mean age of 151.5 ± 1.2 Ma (MSWD = 1.18, $n = 13$, 1σ) (Figure 6a).



Figure 5. The cathodoluminescence (CL) images of zircons from the Yongfeng composite granitic pluton (the white circle is the analysis location).

The zircons from sample YF-2 were also generally euhedral, measuring up to 80–160 μm with a length/width ratio of 2:1. Most zircons were colorless or light brown and transparent to subtransparent. They exhibited clear oscillatory zoning in CL images and some of them had inherited cores. The Th content in the zircons was 77.49–426.99 ppm, U content was 115.16–874.41 ppm, and Th/U ratio was 0.25–1.05, with an average of 0.59, which are typical of magmatic zircon [21]. A total of 21 analytical data points were obtained, and three of those data points were discarded because the concordance was below 90%. Six zircons showed older apparent ages, and the other 12 zircons showed relatively consistent apparent ages, with a weighted mean age of (151.3 ± 1.1) Ma (MSWD = 0.51, $n = 12$, 1σ) (Figure 6b).

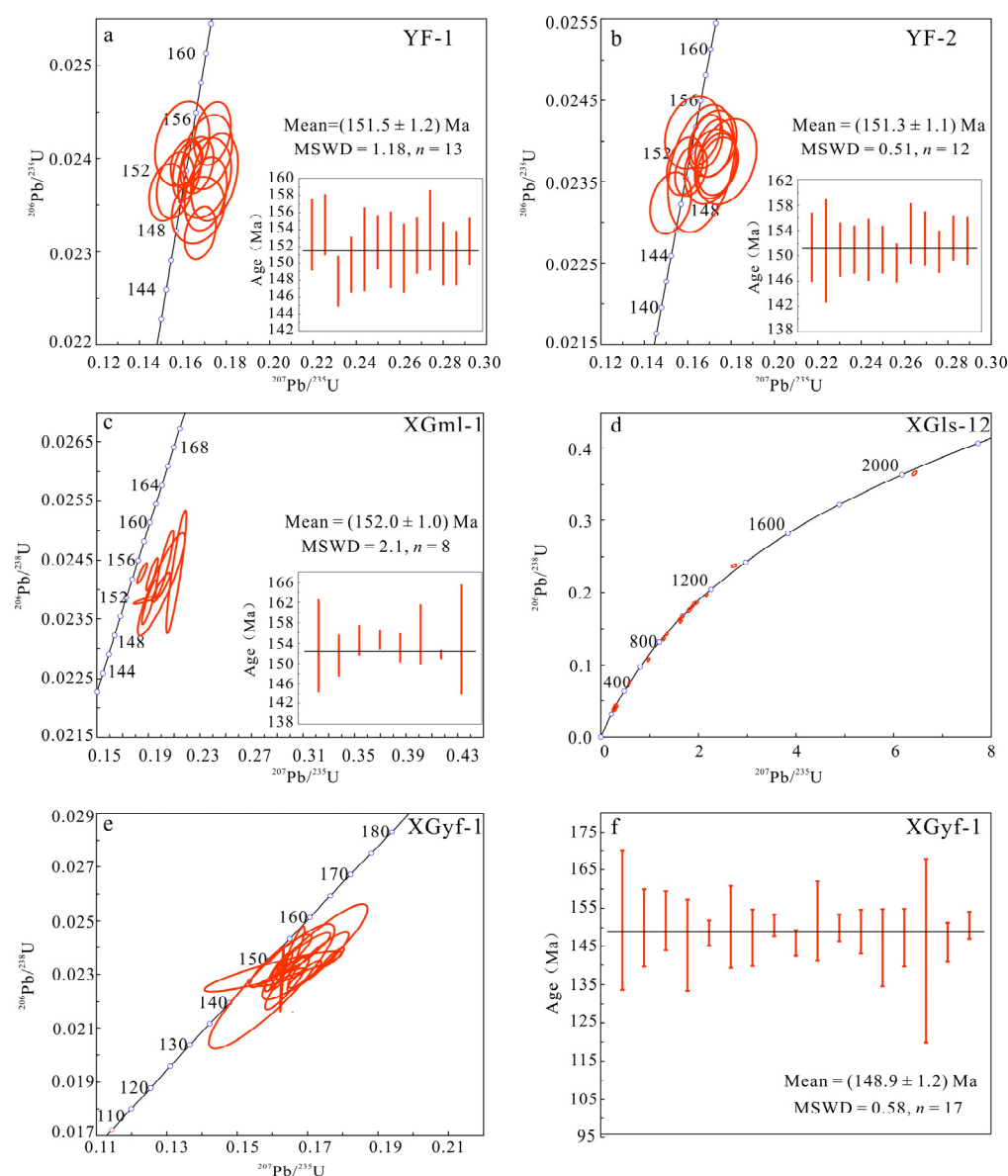


Figure 6. The zircon U-Pb age concordance diagram and weighted average age diagram of the Yongfeng composite granitic pluton (a) YF-1, (b) YF-2, (c) XGml-1; The zircon U-Pb age concordance diagram of (d) XGls-12 and (e) XGyf-1; (f) The weighted average age diagram of XGyf-1.

The zircons from sample XGml-1 were generally long columnar and xenomorphic-subhedral, measuring up to 100–210 μm with a length/width ratio of 2:1–4:1. The internal morphology of the zircons was complex, with clear oscillatory zoning in some, and unclear or no oscillatory zoning in others. A few zircons had inherited cores, while oscillatory zoning was invisible. Some zircons were black, indicating a high content of U. The Th content of the zircons was 29.32–1061.16 ppm, U content was 52.46–1475.35 ppm, and Th/U ratio was 0.02–1.73, with an average of 0.76. The Th/U ratio of sample point 9 was 0.02, and its oscillatory zoning was not prominent, suggesting that this zircon was a metamorphic zircon [22]. A total of 20 analytical data points were obtained from sample XGml-1, and four of the data points were discarded because their concordance was below 90%. Eight zircons showed older apparent ages, and the other eight zircons showed relatively consistent apparent ages, with a weighted mean age of 152.0 ± 1.0 Ma (MSWD = 2.1, $n = 8$, 1σ) (Figure 6c).

The zircons from sample XGls-12 were morphologically diverse and xenomorphic-subhedral, measuring up to 50–200 μm with a length/width ratio of 2:1. The internal

morphology of the zircons was complex, with clear oscillatory zoning in some, but unclear or no oscillatory zoning in others. A few zircons had inherited cores, while oscillatory zoning was invisible. Some zircons were black in color, indicating a high U content. The Th content in zircons was 9.51–2478.66 ppm, U content was 133.76–2759.93 ppm, and Th/U ratio was 0.05–1.32, with an average of 0.55. The Th/U ratios of sample points 1 and 2 were less than 0.1, and their oscillatory zonings were not prominent, indicating they were metamorphic zircon [22]. A total of 20 analytical data points were obtained from sample XGls-12, and two of the data points were discarded because their concordance was below 90%. The weighted mean age could not be determined because the apparent ages were highly scattered (Figure 6d).

The zircons from sample XGyf-1 were short columnar, long columnar, and round, measuring up to 50–230 μm with a length/width ratio of 2:1–5:1. The internal morphology of the zircons is complex, with clear oscillatory zoning in some, but unclear or no oscillatory zoning in others. A zircon had an inherited core. The Th content in zircons was 47.01–6213.76 ppm, U content was 116.37–7576.37 ppm, and the Th/U ratio was 0.07–1.37, with an average of 0.58. The Th/U ratio of point 6 was 0.07, and its oscillatory zoning was not prominent, indicating it was metamorphic zircon [22]. A total of 20 analytical data points were obtained, and three of the data points were discarded because their concordance was below 90%. The data points were distributed on or near the concordance curve, with a weighted mean age of (148.9 ± 1.2) Ma (MSWD = 0.58, $n = 17$, 1σ) (Figure 6f).

4.3. Element Geochemistry of Granite

The results of major elements, trace elements, and rare-earth elements for samples YF-1 and YF-2 are presented in Supplementary Table S4.

As shown in Supplementary Table S4, the major elemental composition of the Yongfeng composite granitic pluton can be characterized as follows: (1) High SiO_2 . The contents of SiO_2 in YF-1 and YF-2 were 72.48%–73.28% (average of 72.87%) and 72.41%–73.21% (average of 72.76%), respectively. The average content of SiO_2 in the Longshi granite was 74.30% [8]. (2) High K_2O . The contents of K_2O in YF-1 and YF-2 were 4.99%–5.53% (average of 5.35%) and 5.25%–5.53% (average of 5.35%), respectively. The $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios in YF-1 and YF-2 were 1.45–1.70 (average of 1.57) and 1.68–1.79 (average of 1.72), respectively. The content of K_2O in the Longshi granite was 5.15%–6.06%, with an average of 5.60%. The $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio was 1.71–2.13, with an average of 2.00. In the SiO_2 – K_2O diagram (Figure 7c), most samples of the Yongfeng composite granitic pluton are distributed within the range of shoshonite. (3) High alkali. The contents of $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ in YF-1 and YF-2 were 8.39%–9.14% (average of 8.76%) and 8.37%–8.62% (average of 8.48%), respectively. The alkali aluminum index (AKI) values of YF-1 and YF-2 were 0.80–0.91 (average of 0.86) and 0.79–0.80 (average of 0.80), respectively. The content of $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ in the Longshi granite was 8.09%–8.96%, with an average of 8.40%. Its AKI was 0.76–0.87, with an average value of 0.80. In the ANOR–Q' diagram (Figure 7a), the samples of the Yongfeng composite granitic pluton were distributed within the range of alkaline-granite and syenogranite. In the SiO_2 – $(\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO})$ diagram (Figure 7b), the samples of the Yongfeng composite granitic pluton were distributed within the range of alkaline-calcic and calc-alkalic. (4) Slightly peraluminous. The A/CNK values of YF-1 and YF-2 were 0.95–1.04 (average of 1.00) and 1.06–1.07 (average of 1.06), respectively. The A/CNK value of the Longshi granite was slightly higher, ranging from 1.05 to 1.25, with an average of 1.20. In the A/CNK–A/NK diagram (Figure 7d), the samples of the Yongfeng composite granitic pluton were located in the ranges of metaluminous and peraluminous. (5) High degree of fractionation. The differentiation index ($\text{DI} = \text{quartz} + \text{orthoclase} + \text{albite} + \text{nepheline} + \text{leucite} + \text{kalsilite}$) values of YF-1 and YF-2 were 88.40–91.80 (average of 90.39) and 88.55–89.38 (average of 89.13), respectively. The average DI of Longshi granite was 93.43. The contents of TFe_2O_3 , MgO , CaO , TiO_2 , and P_2O_5 were low in both the Yongfeng granite and Longshi granite, and gradually decreased with increasing SiO_2 content (Figure 8). These results indicate that the magma experienced a high degree of fractionation. In addition, the sample points of

the Longshi granite were close to the end of evolution line (Figure 8), indicating a higher degree of crystallization differentiation compared to the Yongfeng granite.

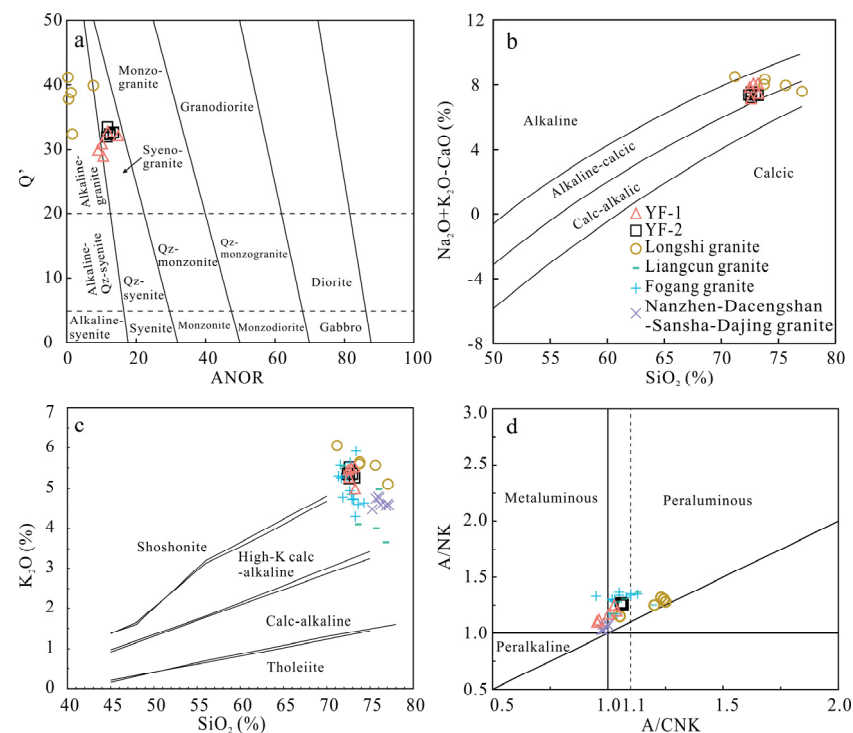


Figure 7. ANOR–Q' diagram (a), SiO_2 – ($\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO}$) diagram (b), SiO_2 – K_2O diagram (c), and A/CNK–A/NK diagram (d) of the Yongfeng composite granitic pluton. The data of the Longshi granite, Liangcun granite, Fogang granite, and Nanzhen-Daliangshan-Sansha-Dajing granite are respectively cited from [9,23–25].

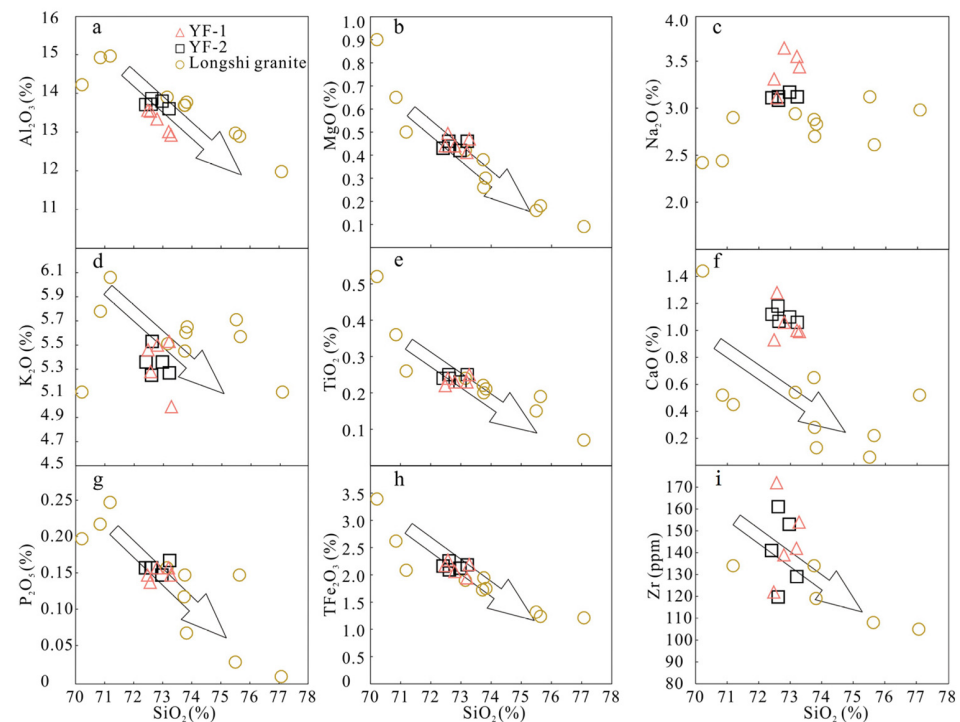


Figure 8. SiO_2 vs. Al_2O_3 (a), MgO (b), Na_2O (c), K_2O (d), TiO_2 (e), CaO (f), P_2O_5 (g), TFe_2O_3 (h), and Zr (i) variation diagrams of the Yongfeng composite granitic pluton. The data of the Longshi granite is cited from [9].

The Σ REE, LREE, and HREE contents of YF-1 were 186.85–211.23 ppm (average of 199.49 ppm), 170.42–188.95 ppm (average of 181.27 ppm), and 16.43–22.28 ppm (average value of 18.23 ppm), respectively. The LREE/HREE ratio was 8.48–10.98, with an average of 10.03. The $(\text{La}/\text{Yb})_{\text{N}}$ value was 10.33–15.55, with an average of 13.97. The fractionation of LREEs and HREEs was distinct, showing a rightward inclination in the chondrite-normalized REE diagram (Figure 9a). Meanwhile, Eu presented a significant negative anomaly ($\text{Eu}/\text{Eu}^* = 0.25\text{--}0.28$, average of 0.27). The primitive mantle-normalized trace element spider diagram (Figure 9b) shows the enrichment of large ion lithophile elements (LILEs) such as Rb, Th, U, and Pb, and depletion of Ba, K, P, Eu, and Ti. The Σ REE, LREE, and HREE contents of YF-2 were 199.72–227.30 ppm (average of 209.40 ppm), 182.56–203.42 ppm (average of 190.55 ppm), and 17.16–23.88 ppm (average of 18.84 ppm), respectively. The LREE/HREE ratio was 8.52–11.00, with an average of 10.23. The $(\text{La}/\text{Yb})_{\text{N}}$ value was 10.55–16.28, with an average of 14.21. The chondrite-normalized REE diagram also shows a rightward trend (Figure 9a). Eu presented a significant negative anomaly ($\text{Eu}/\text{Eu}^* = 0.23\text{--}0.27$, average of 0.26). The primitive mantle-normalized trace element spider diagram (Figure 9b) also shows the enrichment of LILEs such as Rb, Th, U, and Pb, and the depletion of Ba, K, P, Eu, and Ti. In the chondrite-normalized REE diagram (Figure 9a), the distribution curves of the Longshi granite were generally flat, with less fractionation of LREE and HREE, and stronger negative Eu anomaly, indicating a higher degree of differentiation.

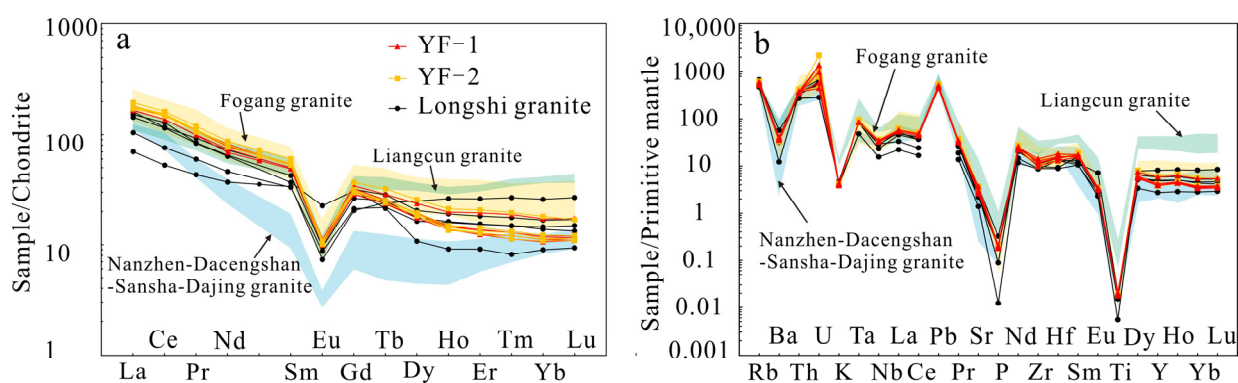


Figure 9. Chondrite-normalized REE patterns (a) and primitive-mantle-normalized trace element spider diagram (b) of the Yongfeng composite granitic pluton (chondrite and primitive mantle normalizing values from [20]). The data of the Longshi granite, Liangcun granite, Fogang granite, and Nan-zhen-Daliangshan-Sansha-Dajing granite are respectively cited from [9,23–25].

In general, the Yongfeng granite and the Longshi granite exhibit similar geochemical characteristics, suggesting that they are products of the same magmatic system. The Longshi granite shows a higher degree of crystallization differentiation than the Yongfeng granite. Overall, the element geochemical characteristics of the Yongfeng composite granitic pluton are similar to those of highly fractionated I-type granites, such as the Liangcun granite, Fogang granite, and Nanzhen-Dacengshan-Sansha-Dajing granites (Figures 7 and 9).

4.4. Element Geochemistry of Biotite

The SiO_2 , FeO , TiO_2 , and MgO contents of biotite were 34.05%–35.16% (average of 34.63%), 21.43%–23.91% (average of 22.63%), 1.97%–3.44% (average of 2.68%), and 4.91%–5.93% (average of 5.24%), respectively, indicating that biotite is enriched in Fe and Ti. The $\text{Fe}/(\text{Fe} + \text{Mg})$ and $\text{Mg}/(\text{Mg} + \text{Fe})$ ratios of biotite were 0.68–0.72 (average of 0.71) and 0.28–0.32 (average of 0.29), indicating that biotite is enriched in Fe but depleted in Mg. The classification diagram of biotite (Figure 10b) shows that biotite belongs to ferruginous biotite. In the $10 \times \text{TiO}_2 - \text{FeO} - \text{MgO}$ diagram (Figure 10a), most sample points are located in the area of primary magmatic biotites.

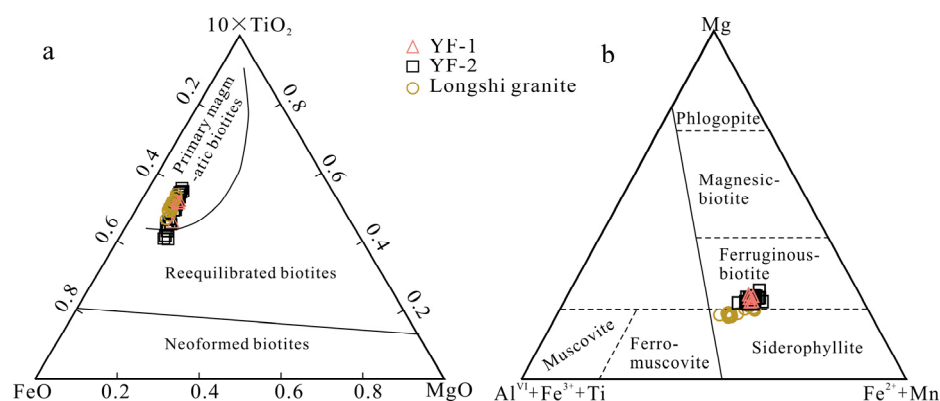


Figure 10. (a) $(10 \times \text{TiO}_2)$ – FeO – MgO diagram, base map according to [26]; (b) Mg – $(\text{Al}^{\text{VI}} + \text{Fe}^{3+} + \text{Ti})$ – $(\text{Fe}^{2+} + \text{Mn})$ diagram, base map according to [27] of the biotite from the Yongfeng composite granitic pluton. The data of the Longshi granite is cited from [8].

5. Discussion

5.1. Rock-Forming Age

Liu and Li [28] reported that the zircon U-Pb ages of the Yongfeng granite are (160.0 ± 1.1) Ma and (155 ± 2.2) Ma. Qiu [29] reported that the U-Pb zircon age of the Longshi granite is (142.9 ± 0.8) Ma. Yang et al. [9] reported that the zircon U-Pb ages of the Yongfeng granite are (155.8 ± 2.0) Ma and (154.7 ± 0.75) Ma, while those of the Longshi granite are (154.0 ± 2.2) Ma and (156.9 ± 1.8) Ma. In this study, the zircon U-Pb ages of the Yongfeng granite and Longshi granite were determined to be 152.0 ± 1.0 Ma– 151.3 ± 1.1 Ma and 148.9 ± 1.2 Ma, respectively. Regionally, the rock formation ages of the Liangcun, Jiangbei, and Donggu granites are 158–147 Ma, 156–153 Ma, and 152 ± 2 Ma, respectively [30–33], indicating the occurrence of large-scale magmatism during the late Jurassic in southern Jiangxi province. The above evidence proves that the Yongfeng composite granitic pluton formed in the late Jurassic.

Inherited zircons were observed in samples (Figure 5) and they could be divided into four groups according to their ages: (1) 164–239 Ma. This group of inherited zircons may indicate the presence of Mesozoic magmatism in the study area. For example, the rock-forming age of the Qingxi granite is 229.3 ± 0.8 Ma [34]. (2) 275–462 Ma. This group of inherited zircons may indicate the presence of Paleozoic magmatism in the study area. For example, the rock-forming ages of the Hanfang, Dabu, and Danqian granites are 438.0 ± 1.7 Ma, 434.1 ± 2.0 Ma, and 427.3 ± 1.8 Ma, respectively [23]. (3) 656–990 Ma. Magmatism in the Cathaysian block was relatively weak during the Neoproterozoic and mainly distributed in the northern Wuyi area, which is located in the east of the Cathaysian block [35]. The Yongfeng composite granitic pluton is located in the southern part of the Wuyi area, where the magmatism is weak during Neoproterozoic, while the northern part of the Wuyi area has strong magmatism during Neoproterozoic [35]. This group of inherited zircons may indicate that some rocks from northern Wuyi area entered magma. (4) 1035–2661 Ma. The age of the basement of the Cathaysian block is mainly early middle Proterozoic [36]. The presence of inherited zircons from this period suggests that early middle Proterozoic basement rocks from the Cathaysian block may have been mixed with magma.

5.2. Rock-Forming Physicochemical Conditions

5.2.1. Temperature

The zircon saturation temperature (T_{Zr}) and zircon Ti temperature (T_{Ti}) can be used to estimate the crystallization temperature of granitic magma [37–39]. In this study, the T_{Zr} of samples YF-1 and YF-2 were calculated using the method of Miller et al. [38]. The T_{Zr} of sample YF-1 was 763–792 °C, with an average of 774 °C. The T_{Zr} of sample YF-2 was 764–789 °C, with an average of 777 °C (Supplementary Table S4).

The presence of alkali-rich melt and inherited zircon can lead to overestimation of the calculated zircon saturation temperature [38,40]. The samples of the Yongfeng granite are alkali-rich and have inherited zircons. Therefore, the crystallization temperature was lower than the zircon saturation temperature of the Yongfeng granite. In addition, the T_{Ti} of samples YF-1 and YF-2 was calculated using the method of Ferry and Watson [37]. Except for the low T_{Ti} (631 °C, 679 °C) and high T_{Ti} (907 °C), the normal T_{Ti} ranged from 707 °C to 868 °C, with an average of 773 °C (Supplementary Table S2), which is consistent with T_{Zr} .

5.2.2. Oxygen Fugacity

Oxygen fugacity is one of the crucial factors influencing metal mineralization, as it controls the migration and enrichment of metallic elements. Trail et al. [41] proposed a method for calculating the absolute oxygen fugacity. However, natural zircon has very low La and Pr content and often contains LREE-rich mineral inclusions. This will lead to inaccurate calculations of the absolute oxygen fugacity [42]. These interferences can be avoided by using the Geo-fO₂ software developed by Li et al. [42]. In this study, the oxygen fugacity of magma was calculated using this software. The results are listed in Supplementary Table S2. Because the ages of some zircons are much older than the rock formation age of the Yongfeng granite, the calculation results may not represent the true oxygen fugacity. After removing these points, the Ce^{4+}/Ce^{3+} ratio was 1.93–121.23, with an average of 21.49, which is much lower than the Ce^{4+}/Ce^{3+} value of zircon in the porphyry Cu, Mo deposit metallogenic granite (>300, [43,44]), but similar to the Ce^{4+}/Ce^{3+} value of zircon in the Sn deposit metallogenic granite [45]. The absolute oxygen fugacity ($lgf(O_2)$) ranged from −24.47 to −10.23, with an average value of −16.64. On the whole, the range of oxygen fugacity presented significant variations with generally low values.

In addition, the absolute oxygen fugacity of magma can be estimated according to the empirical formula of biotite: $lgf(O_2) = 10.9 - 27,000/T$ [46]. Using this formula, this study calculated the absolute oxygen fugacity of magma was −20.56–−17.48, with an average of −18.80 (Supplementary Table S5), which also indicates low oxygen fugacity.

5.3. Genetic Type

The determination of the genetic type of granite is an important and basic problem in the study of granite [47]. Previous researchers have proposed several criteria from multiple perspectives [48–53]. However, for granite that has experienced strong evolution, as its mineral and chemical compositions are close to hypoeutectic granite, established indicators are usually inapplicable for accurately determining the genesis type [48,54].

Yang et al. [9] considered the Yongfeng composite granitic pluton to be an A-type granite, but the geochemical characteristics clearly differ from those of A-type granites. For example, the TFe_2O_3/MgO ratio < 10, $Zr + Nb + Ce + Y$ content < 350 ppm and the zircon saturation temperature was lower than 800 °C. Samples YF-1 and YF-2 also exhibit mineralogical and geochemical characteristics distinctly different from those of A-type granites: (1) They do not contain alkaline dark minerals. (2) The Yongfeng composite granitic pluton is depleted in high field strength elements (HFSEs) such as Zr, Nb, Y, REE, and Ga. (3) The TFe_2O_3/MgO is low. The TFe_2O_3/MgO of YF-1 and YF-2 were 4.63–4.93 (4.73 on average) and 4.74–5.05 (4.89 on average), respectively, which are smaller than that of typical A-type granites (>10, [52]). (4) The $Zr + Nb + Ce + Y$ value is low. The $Zr + Nb + Ce + Y$ values of YF-1 and YF-2 were 248.60–319.10 ppm (average of 279.92 ppm) and 256.70–297.30 ppm (average of 281.28 ppm), which are smaller than that of typical A-type granites (>350 ppm, [52]). On the $(Zr + Nb + Ce + Y) - (TFe_2O_3/MgO)$ diagram (Figure 11a) and $(Zr + Nb + Ce + Y) - (K_2O + Na_2O)/CaO$ diagram (Figure 11b), wherein the vast majority of sample points are located in the range of fractionated felsic granite. (5) The crystallization temperature of magma is low. The average zircon saturation temperatures of YF-1 and YF-2 were 774 °C and 777 °C, respectively. The crystallization temperature is lower than that of A-type granite (>800 °C, [55]), but close to that of highly fractionated I-type granite (764 °C, [55]).

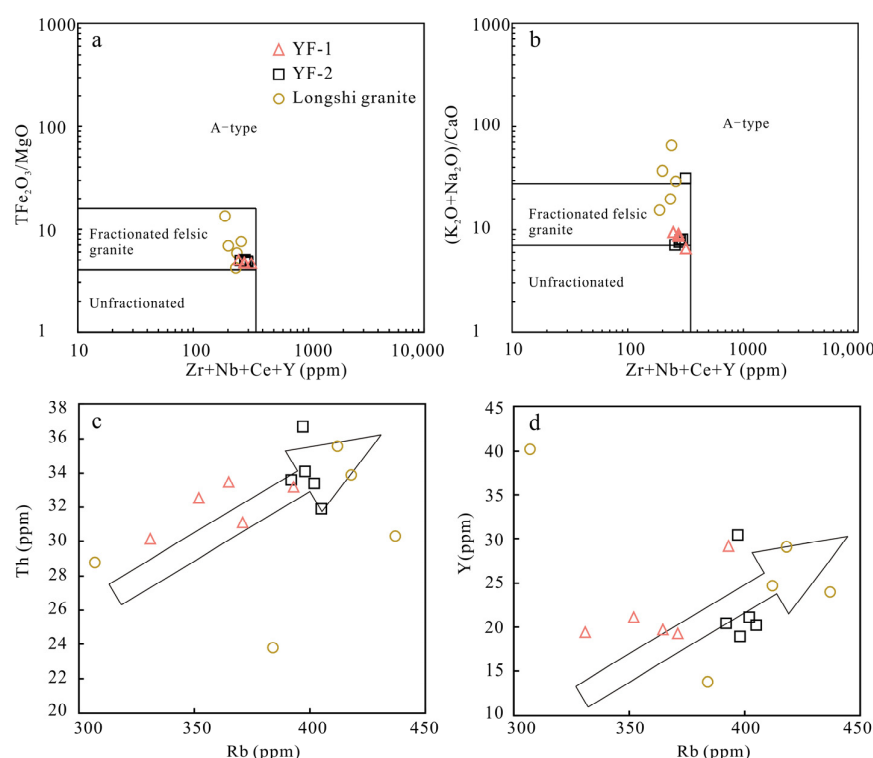


Figure 11. (a) $(Zr + Nb + Ce + Y) - (TFe_2O_3/MgO)$ diagram, base map according to [52]; (b) $(Zr + Nb + Ce + Y) - (K_2O + Na_2O)/CaO$ diagram, base map according to [52]; (c) Rb–Th diagram; (d) Rb–Y diagram of the Yongfeng composite granitic pluton. The data of Longshi granite is cited from [9].

The aluminum saturation index (A/CNK) of the Yongfeng composite granitic pluton varied widely. Some samples reached the level of peraluminous granite, similar to S-type granite formed by the partial melting of metasedimentary rocks [56]. Mineralogically, the Yongfeng composite granitic pluton does not contain aluminum-rich minerals, except for a small amount of muscovite. Furthermore, all samples showed decreases in P_2O_5 with increasing SiO_2 (Figure 8g), and increases in Th and Y with increasing Rb (Figure 11c,d). This feature is consistent with I-type granite, while opposite to S-type granite [54]. The Yongfeng composite granitic pluton has high SiO_2 , high DI, and significant negative Eu anomaly. These characteristics indicate that the Yongfeng composite granitic pluton has experienced a high degree of fractionation. Wu et al. [47] believe that the most feasible method for determining the genetic type of highly fractionated granite is to compare the genetic type of contemporaneous paragenetic granite. The petrological and geochemical characteristics of the Yongfeng composite granitic pluton are similar to those of highly fractionated I-type granites that formed in the Nanling area during the late Jurassic, such as the Liangcun granite, Fogang granite, and Nanzhen–Dacengshan–Sansha–Dajing granites [23–25]. In conclusion, the Yongfeng composite granitic pluton is a highly fractionated I-type granite, rather than an A-type granite as previously believed.

5.4. Petrogenesis

The $\epsilon Hf(t)$ value of the Yongfeng composite granitic pluton ranged from -27.71 to -9.92 . The corresponding two stage model age was 1.83–2.93 Ga, which is within the Paleoproterozoic [9]. The zircon U–Pb age was homogeneous whereas the $\epsilon Hf(t)$ value varied widely, indicating that magma came from different sources [57]. Although the $\epsilon Hf(t)$ value of the Yongfeng composite granitic pluton was negative, it varied widely. This evidence indicates that the magmatic source is mainly composed of Paleoproterozoic basement rocks, and there may be a small amount of mantle magma. Regionally, the $\epsilon Hf(t)$ value of the adjacent Liangcun granite ranged from -12.96 to -7.4 , and the corresponding two-stage model age was 1.67–2.0 Ga. Its magmatic source is estimated to

contain 25% mantle magma [23]. The $\epsilon_{\text{Hf}}(t)$ and $\delta^{18}\text{O}$ values of the zircons from the biotite granite in the Longyuanba composite granitic pluton indicated that the magmatic source is dominated by crust-derived sediments, with a small proportion of mantle magma [58]. No petrographic evidence of crust-mantle mixing was found in the Yongfeng composite granitic pluton. Intermediate-basic intrusive rocks and alkaline rock-syenite in the Nanling area occurred during late Jurassic, such as the Chencun diorite, Wushi diorite-hornblende gabbro, Nankunshan alkaline granite, Ejinao alkaline syenite, Qinghu quartz monzonite, Luorong-Mashan granitoid complex, Huashan-Guposhan granite, and syenite-granitoid in southern Jiangxi [59–63]. Moreover, mafic mineral inclusions are found in the Fogang, Guposhan, and Dadongshan granites [64,65]. This evidence indicates that crust-mantle mixing was widespread in the Nanling area during the late Jurassic.

The Rb/Sr and Rb/Nb ratios of the Yongfeng composite granitic pluton are significantly higher than those of the global upper crust (0.32 and 4.5, respectively [66]), indicating the possible occurrence of continental crust rocks with high maturity in the magmatic source. In the (Rb/Sr) – (Rb/Ba) diagram (Figure 12a), a positive correlation was observed between Rb/Sr and Rb/Ba. Except for one sample point being located in the region of clay-poor sources, other sample points were located in the region of clay-rich sources. This indicates that the magmatic source corresponds to the partial melting of argillaceous rocks. It is enriched in LREEs and features a significant negative Eu anomaly, indicating that its magma originates from the melting of crustal rocks. In the $(\text{Al}_2\text{O}_3 + \text{TFeO} + \text{MgO} + \text{TiO}_2) - \text{Al}_2\text{O}_3/(\text{TFeO} + \text{MgO} + \text{TiO}_2)$ diagram (Figure 12b), most sample points of the Yongfeng composite granitic pluton are located in the area corresponding to the partial melting of amphibolite and mafic argillaceous rocks. This indicates the presence of magma derived from the partial melting of basaltic rocks and metamorphosed argillaceous rocks [67]. Therefore, the magmatic source of the Yongfeng composite granitic pluton is suggested to be the mixing of basaltic magma and ancient metamorphic argillaceous magma.

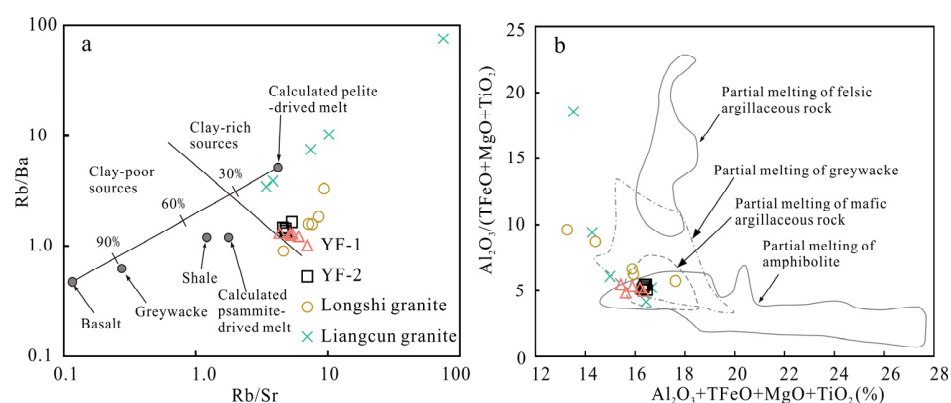


Figure 12. (Rb/Sr) – (Rb/Ba) diagram. (a) base map according to [68]) and $(\text{Al}_2\text{O}_3 + \text{TFeO} + \text{MgO} + \text{TiO}_2) - \text{Al}_2\text{O}_3/(\text{TFeO} + \text{MgO} + \text{TiO}_2)$; (b) base map according to [69]) of the Yongfeng composite granitic pluton. The data of the Longshi granite and Liangcun granite are respectively cited from [9,23].

As mentioned earlier, the Yongfeng composite granitic pluton has the following characteristics: high SiO_2 and DI; low TFe_2O_3 , MgO , CaO , TiO_2 , and P_2O_5 , which gradually decrease with increasing SiO_2 ; depletion of trace elements such as Ba, P, Ti, and Nb; and significant negative Eu anomaly. These features indicate that the Yongfeng composite granitic pluton experienced a high degree of crystallization differentiation. The strong depletion of Ba, Eu, and enrichment of Rb are mainly caused by the crystallization differentiation of K-feldspar and plagioclase. The variation of REEs is controlled by the crystallization differentiation of zircon and monazite. The depletion of Ti is caused by the crystallization differentiation of Ti-rich minerals, such as ilmenite and rutile. In addition, the distribution coefficients of Nb and Ta in rutile are high [70]. Therefore, the crystallization differentiation

of rutile is an important reason for the Nb depletion in the Yongfeng composite granitic pluton. From the Yongfeng granite to the Longshi granite, the SiO_2 content, DI, Rb/Sr, and Rb/Ba values increased, whereas the contents of CaO, MgO, and TFe_2O_3 decreased, and the depletion of Sr, Ti, P, and Eu intensified; nevertheless, their Hf isotope compositions were similar. These features indicate that the Yongfeng granite and Longshi granite formed through the same magmatic system under different degrees of crystallization differentiation. The degree of crystallization differentiation of the Longshi granite is higher than that of the Yongfeng granite.

5.5. Tectonic Implication

The early Yanshanian granites in the Nanling area are distributed in EW and NE directions. Ling et al. [71] believe that the formation of the early Yanshanian granite with the EW distribution may be related to the revival and extension of the existing EW distribution of the Indosinian structure under the influence of the subduction of the Pacific Plate, while the formation of the early Yanshanian granite with the NE distribution is mainly related to the intracontinental fault extension caused by the subduction of the Pacific Plate. In addition, alkaline granites, bimodal volcanic rocks, alkaline basalt, and basic-acid complexes developed in the Nanling area during the early Yanshanian [60,72–74]. The above evidence indicates that the Nanling area has been in an extension–thinning tectonic setting since the Middle Jurassic.

The composition of trace elements in igneous rocks varies significantly under different tectonic settings. Therefore, the tectonic background of igneous rock can be restored according to differences in trace element compositions [75]. In the Yb–Ta diagram (Figure 13a), the sample points are located in the range of syn-collision granite and within plate granite. In the $(\text{Yb} + \text{Nb}) - \text{Rb}$ and $(\text{Rb}/30) - \text{Hf} - (\text{Ta} \times 3)$ diagrams (Figure 13b,c), the sample points are located in the range of syn-collision granite and post-collision granite. In the $\text{SiO}_2 - \lg[\text{CaO}/(\text{K}_2\text{O} + \text{Na}_2\text{O})]$ diagram (Figure 13d), the sample points are located in the area of extrusion and extension. Based on the geochronology, geochemistry, and tectonic setting discrimination diagrams, the Yongfeng composite granitic pluton is suggested to have formed under the extensional setting during the post-collision stage, which was controlled by the breakup or retreat of the backplate after the subduction of the Pacific Plate into the Nanling hinterland [1].

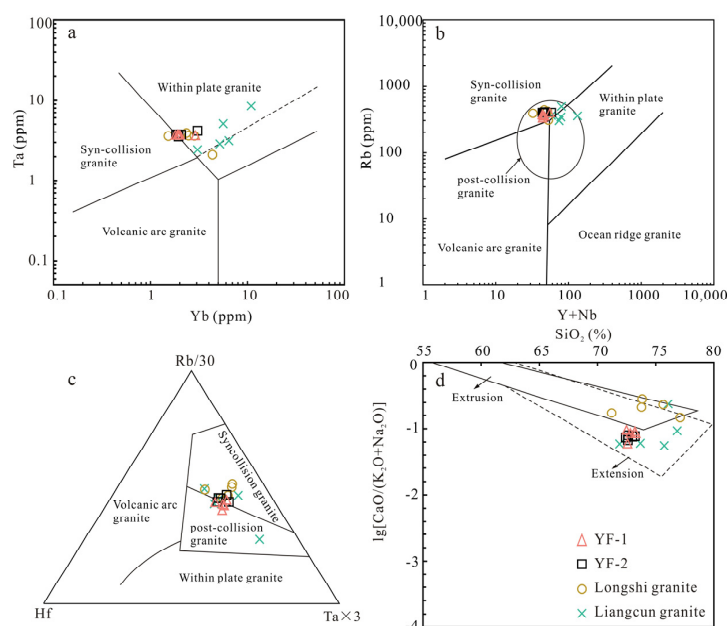


Figure 13. Tectonic setting discrimination diagrams of the Yongfeng composite granitic pluton and Liangcun granite (a–d), with base map according to [75–78], respectively. The data of the Longshi granite and Liangcun granite are respectively cited from [9,23]).

5.6. Relationship between Magmatism and Mineralization

The Leigongzhang molybdenum deposit is a medium-sized quartz vein type molybdenum deposit, which is different from the porphyry molybdenum deposit and quartz vein molybdenum polymetal deposit in the Nanling area. Previous studies suggest that it has a close spatiotemporal relationship with the Yongfeng composite granitic pluton [7,79]. Mineral deposits closely associated with granite are influenced by factors such as magmatic source, oxygen fugacity, degree of fractionation, and volatile content [80,81]. During the intrusive process, high oxygen fugacity magmas not only assimilate sulfides, but also suppress the separation of metals as magma sulfide melts (such as MoS_2), thereby retaining them in large quantities in the exsolved liquid phase [82] which is favorable for mineralization. However, the oxygen fugacity of the Yongfeng granite is low compared to that of porphyry type molybdenum mineralization granite. Oxygen fugacity is not the only factor controlling the formation of the Leigongzhang molybdenum deposit. Granite related to Mo deposits has undergone a high degree of crystallization differentiation and has a high content of F [80,83]. A high content of F in magma can promote the enrichment of metal elements such as Sn, Mo, and W during magma intrusion and fractionation processes. For example, the magmatic systems of the Zhuxiling Mo-W deposit and the Shizhuyuan W-Sn-Mo-Bi polymetallic deposit have a high content of F [84,85]. The biotite in Longshi granite has a high content of F (>1%) [8], which is similar to biotite in granite related to fluorite mineralization in the region [86]. Furthermore, a large fluorite deposit is developed in the outer contact zone of Longshi granite. This evidence indicates that the Longshi granite has a high content of F, which is conducive to molybdenum mineralization.

The Sn deposit is related to the crystallization differentiation of reducing magma [87]. Most Sn deposits in the South China region are associated with low oxygen fugacity granite, such as the Guposhan granite and the Qitianling granite [45]. Additionally, the temperature of magma also plays a role in controlling Sn enrichment. Stemprok [88] notes that higher temperatures during magma crystallization lead to higher SnO_2 content. The magmatic systems of the Gejiu Sn deposit and the Xitian W-Sn deposit also exhibit high temperature characteristics [89,90]. The magmatic system of the Yongfeng composite granitic pluton has the characteristics of high temperature, low oxygen fugacity, and high content of F, similar to the magmatic system of a typical Sn deposit. In addition, the Yongfeng composite granitic pluton shows high Sn anomaly on the Sn element anomaly map [91]. In summary, the Yongfeng composite granitic pluton has significant Sn, Mo, and fluorite mineralization potential.

6. Conclusions

- (1) The Yongfeng composite granitic pluton is rich in silicon, potassium, and alkali, weakly peraluminous, poor in calcium and iron, and has a high content of ΣREE , with the enrichment of LREEs and significant fractionation of LREEs and HREEs. It is also enriched in LILEs such as Rb, Th, U, and Pb, and strongly depleted in elements such as Ba, K, P, Eu, and Ti, showing a clear negative Eu anomaly.
- (2) The Yongfeng composite granitic pluton does not contain alkaline dark minerals, and has low contents of TFe_2O_3 , MgO, CaO, TiO_2 , and P_2O_5 , which decrease with increasing SiO_2 content. The negative Eu anomaly is significant and the Rb/Sr ratio is high. This evidence indicates the crystallization differentiation of minerals such as plagioclase, potassium feldspar, biotite, zircon, monazite, and ilmenite/rutile during magma evolution. The average zircon saturation temperature is 776 °C, the average $\text{TFe}_2\text{O}_3/\text{MgO}$ ratio is 4.81, and the average Zr + Nb + Ce + Y content is 280.6 ppm, indicating that it is a highly fractionated I-type granite.
- (3) The crystallization age of the Yongfeng granite and the Longshi granite are 152.0 ± 1.0 Ma– 151.3 ± 1.1 Ma and 148.9 ± 1.2 Ma, respectively. They are products of large-scale magmatic activity in the Nanling region during the Late Jurassic. Further, they formed in the extensional tectonic setting during the post-orogenic stage,

under the control of the breakup or retreat of the backplate after the subduction of the Pacific Plate into the Nanling hinterland.

- (4) The magmatic system of the Yongfeng composite granitic pluton is characterized by high fractionation, high F content, high temperature, and low oxygen fugacity, which is conducive to the large-scale mineralization of Sn, Mo, and fluorite.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13111457/s1>, Table S1: List of samples information; Table S2: Results of trace elements in zircons from samples YF-1 and YF-2 (ppm); Table S3: LA-ICP-MS U-Pb zircon data of the Yongfeng composite pluton; Table S4: Major (wt%), trace, and rare earth (ppm) element data of the Yongfeng granite; Table S5: The chemical composition of biotite from the Yongfeng granite [92].

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