Comparison of Magma Oxygen Fugacity and Zircon Hf Isotopes between Xianglushan Tungsten-Bearing Granite and Late Yanshanian Granites in Jiangxi Province, South China

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Abstract: Jiangxi Province (South China) is one of the world’s top tungsten (W) mineral provinces. In this paper, we present a new LA-ICP-MS zircon U-Pb age and Hf isotope data on the W ore-related Xianglushan granite in northern Jiangxi Province. The magmatic zircon grains (with high Th/U values) yielded an early Cretaceous weighted mean U-Pb age of 125 ± 1 Ma (MSWD = 2.5, 2σ). Zircon εHf(t) values of the Xianglushan granite are higher (−6.9 to −4.1, avg. −5.4 ± 0.7) than those of the W ore-related Xihuanshan granite in southern Jiangxi Province (−14.9 to −11.2, avg. −12.5 ± 0.9), implying different sources between the W ore-forming magmas in the northern and southern Jiangxi Province. Compiling published zircon geochemical data, the oxygen fugacity (fO2) of the late Yanshanian granitic magmas in Jiangxi Province (the Xianglushan, Ehu, Dahutang, and Xihuashan plutons) were calculated by different interpolation methods. As opposed to the W ore-barren Ehu granitic magma, the low fO2 of the Xianglushan granitic magma may have caused W enrichment and mineralization, whilst high fO2 may have led to the coexistence of Cu and W mineralization in the Dahutang pluton. Additionally, our study suggests that the absence of late Mesozoic Cu-Mo mineralization in the Zhejiang, Jiangxi, and Anhui Provinces (Zhe-Gan-Wan region) was probably related to low fO2 magmatism in the Cretaceous.

Keywords: Xianglushan (Jiangxi); tungsten ore formation; oxygen fugacity; zircon Hf isotopes; South China

1. Introduction

South China (especially Jiangxi Province) is the main tungsten (W)-producing province in China. The early-discovered W deposits are mainly distributed in southwest Jiangxi Province, such as the renowned Xihuashan, Piaotang, and Dajishan deposits [1–5]. Xianglushan deposit was discovered in the 1960s in the northern Jiangxi province, a region better known for its association with world class porphyry copper (Dexing copper deposit (DCP)) and large- to medium-sized polymetallic Cu deposits [6–12]. The recent discovery of several super-large W deposits, such as the Zhuxi and Dahutang deposits in northern Jiangxi Province, have renewed research interest on the W metallogeny in the region and its relationship with the coeval Cu mineralization. Although the main W mineralization in both northern and southern Jiangxi Province was related to the Yanshanian...
(Jurassic-Cretaceous) orogeny, there are obvious metallogenic differences between them. For instance, wolframite is the main W ore mineral in southern Jiangxi Province [5,10,13], while it is mainly scheelite in northern Jiangxi Province. Moreover, in northern Jiangxi Province, W mineralization coexists locally with Cu ± Mo and the reason for such differences is still unknown.

Advances in micro-analysis have resulted in the routine in-situ measurement of key geochemical and isotopic traits of zircon grains. Over the past few decades, there has been increasing interest in the use of zircon as a mineralization pathfinder for intrusion-related mineralization [14]. In this paper, zircon data from one ore-barren (Ehu) and two fertile granites (Dahutang and Xihuashan; Table A1) are compiled, and a new zircon U-Pb ages and Hf isotope data from the Xianglushan W bearing granite in northern Jiangxi Province are presented. We compared the age, oxygen fugacity ($f_{O_2}$), and possible magma source of the Xianglushan granite with those of the three other granite plutons and discussed the magmatic controls on W and W-Cu mineralization in the region. Our work also provides better understanding for the W mineralization during the Yanshanian period in Jiangxi Province.

2. Geological Background

2.1. Regional Geology

The South China Block (SCB) is composed of Yangtze and Cathaysia blocks separated along the Qin-Hang belt (Figure 1; [15,16]). Many previous studies proposed that the two blocks may have collided in the early Neoproterozoic, separated in the late Neoproterozoic, and then reassembled in the early Paleozoic (Caledonian) [3–7,15]. The SCB has since then experienced intensive and multiphase thermotectonic events [15,16], including those occurred in the Triassic (Indosinian) and Jurassic-Cretaceous (Yanshanian) [15,16]. Granites that formed during the Yanshanian orogeny are the most widespread, especially in the Cathaysia Block and the Qin-Hang belt. Moreover, there is a progressive coastward magmatic migration trend from the early to late Yanshanian orogeny [17–19].

![Figure 1](https://example.com/figure1.png)

Figure 1. (a) Sketched map of China. (b) Simplified geologic map, showing the distribution of Yanshanian granites in South China and its associated ore deposits (modified after [18,20]).
Neoproterozoic and late Mesozoic (Jurassic-Cretaceous; Yanshanian) granitoids are widespread in northern Jiangxi Province, and the latter occurs mainly as stocks intruding both the former and other Precambrian rocks [21,22]. In contrast, the Nanling Range extends across the northwestern Cathaysia Block [23] and encompasses southern Jiangxi Province, southern Hunan, and western Fujian Provinces. The Nanling Range includes a Neoproterozoic schist basement and Sinian–Silurian slate [18], which are covered by Upper Devonian to Middle Triassic shallow-marine carbonate rocks, mudstones, and sandstones, and then by Upper Triassic to Paleogene terrigenous clastic rocks and volcaniclastic rocks. Two world-class W ore belts were developed in the Nanling Range [8,10,13] and northern Jiangxi Province, respectively [10]. Southern Jiangxi Province is located in the eastern Nanling Range, including Xuehuading, Xianghualing, Qianlishan, and Xihuashan deposits. The northern Jiangxi Province contains the Dahutang W-Cu, Zhuxi W-Cu, and Xianglushan W deposits (Figure 1).

2.2. Petrology of Fertile/Barren Granites

The Xianglushan skarn W deposit in northwestern Jiangxi Province was discovered in 1958. The deposit has an ore reserve of 220 thousand tonnes (kt) at 0.641% WO₃. Local exposed sequences include the Cambrian Yangliugang Formation and upper member of the Huayansi Formation (Figure 2). These sequences mainly comprise well-bedded carbonaceous/cherty/muddy limestones and marl [24]. The Late Yanshanian biotite granite is the ore bearing rock, which is exposed in northeastern Xianglushan mining area, and dips gently to the southwest along the anticlinal limbs. Biotite granite is light-gray to white, and has quartz (55–60%), K-feldspar (~20%), plagioclase (10–15%), and biotite (5–10%) as its major constituents. Its accessory minerals include ilmenite, apatite, zircon, and titanite.

Figure 2. Simplified geologic map of the Xianglushan deposit (modified from [24,25]).
The Ehu pluton is located at about 30 km northeast of Jingdezhen and covers an area about 160 km². The pluton is located on the southeastern margin of the Yangtze plate (Figure 1). The Ehu granite intruded the low-grade meta-sedimentary rocks of the Shuangqiaoshan Group. It consists of massive medium-grained two-mica granites with an association of monzogranite-syenogranite. The rocks are mainly composed of K-feldspar (35–40%), quartz (30%), plagioclase (24%), biotite (5%), and muscovite. Most of the plagioclase grains are sericitized and biotite is partially replaced by chlorite. Accessory minerals include mainly zircon, apatite, epidote, and Fe-Ti oxides. Moreover, the Ehu granites are devoid of Cu (Au)-Mo or Sn-W mineralization [26].

The Shimensi W polymetallic deposit is the largest deposit in the Dahutang ore field with a reserve of 0.74 Mt WO₃, 403.6 kt Cu, and 28 kt Mo. Late Mesozoic granitic stocks and dikes are widely exposed in the Dahutang mining area and are considered to be W-Cu ore-related. These granites were emplaced into the Jiuling granodiorite batholith and Neoproterozoic Shuangqiaoshan Group, including porphyritic granite (dominant), fine-grained granite, and granite porphyry. The porphyritic granite has 30% quartz, 40–45% K-feldspar, 5–10% plagioclase, 10% biotite, and 5–10% muscovite, and accessory apatite, zircon, fluorite, ilmenite, scheelite, and wolframite. The fine-grained granite intruded mainly the porphyry granite and locally the Neoproterozoic granite. The rocks have 30% quartz, 45% K-feldspar, 10% plagioclase, 10% biotite, and 5–10% muscovite, and accessory zircon, fluorite, apatite, and ilmenite. Meanwhile, the granite porphyry dykes are distributed throughout the Shimensi deposit. They intruded both the porphyritic and fine-grained granites. Granite porphyry has 40% quartz, 40% feldspar, 5–10% plagioclase, 5% biotite, and 5–10% muscovite, as well as accessory zircon, apatite and fluorite. The three granites are interpreted as highly evolved S-type granites [5,27].

The Xihuashan pluton (outcrop size: 19.12 km²) is exposed in the Xihua Mountain and Dangping area, and intruded Cambrian sandstone and slate. The pluton is composed of medium-grained porphyritic/equigranular biotite granite and fine-grained two-mica granite, which are strongly peraluminous and belong to high-K S-type. The W-mineralized veins are spatially associated with the medium-grained biotite granite, which has plagioclase (~52%), quartz (~30%), alkali feldspar (~15%), biotite (~3%), and accessory minerals including zircon, apatite, monazite, xenotime, thorite, gadolinite, fluorite, and doverite [28].

3. Methods

3.1. Zircon Morphology and Texture

Zircon separation was conducted on a ~2 kg crushed rock sample (XLS01-1) at the Hongxing Geological Laboratory (Langfang, China). After heavy liquid and electromagnetic separation, zircon grains with better crystal shape and transparency were picked under the microscope. The internal structure of zircon grain was observed via cathodoluminescence (CL) imaging and transmitted-/reflected-light microscopy. All of the CL imaging were conducted at the Wuhan Sample Solution Analytical Technology Co. Ltd. (Wuhan, China). Zircon CL images were obtained using an Analytical Scanning Electron Microscope (JSM-IT100) connected to a GATAN MINICL system. The imaging condition was 10.0–13.0 kV accelerating voltage of electric field and 80–85 µA current of tungsten filament.

3.2. Zircon U-Pb Dating

LA-ICP-MS zircon U-Pb dating and trace element analysis were simultaneously conducted at the same laboratory as zircon CL imaging. The analyses were performed with a GeoLasPro laser ablation system that consists of a COMPeXPro 102 ArF excimer laser (193 nm wavelength and maximum 200 mJ energy) and a MicroLas optical system. Helium was used as a carrier gas, and argon as the make-up gas that mixed with helium via a T-connector before entering the ICP. A “wire” signal smoothing device was included in this laser ablation system [29,30]. The laser spot size and frequency were set to 32 µm and 5 Hz, respectively, and Plešovice zircon was used as the external standard.
obtained Plešovice (338.6 ± 1.1 Ma) ages are consistent with the value reported by [31]. The off-line selection and background-analyzed signal integration, trace element calibration, and time-drift correction were performed with the in-house (CUG, Wuhan, China) ICPMSDataCal software (Version 10.9) [30]. Common Pb correction was carried out using with the measured 204Pb contents [32]. Concordia diagrams and weighted mean calculations were plotted with the Isoplot/Ex_ver3 [33].

3.3. Zircon Hf Isotopic Analyses

In-situ Hf isotope analysis was conducted using a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Dreieich, Germany) coupled with a Geolas HD excimer ArF laser ablation system (Coherent, Göttingen, Germany) at the same laboratory as the zircon U-Pb dating. Analysis conditions include 44 µm spot size, 8 Hz laser repetition, and 5.3 J/cm² energy density, and other details are as described in Hu et al. [30]. Spot locations of the Hf isotopic analyses are shown in Figure 3. The analysis requires careful correction of isobaric interferences on 176Hf (e.g., 176Yb and 176Lu). It is observed that the mass fractionation of Yb (βYb) is not constant over time, and the βYb obtained from the solution introduction is unsuitable for the measurements [34]. The βYb miscalculation would affect the 176Hf/177Hf results. In this study, we used the βYb values directly obtained (real-time) from the zircon grains. Additionally, the 173Yb/171Yb and 179Hf/177Hf values were applied to estimate the mass bias of Yb (βYb) and Hf (βHf), which were normalized to 173Yb/171Yb (1.13268) and 179Hf/177Hf (0.73255) [35] with an exponential correction. Meanwhile, interference of 176Yb on 176Hf was corrected by measuring the interference-free 173Yb and utilizing 176Yb/173Yb (0.79639) [35] to calculate 176Yb/177Hf. Similarly, the relatively minor interference of 176Lu on 176Hf was corrected by measuring the interference-free 175Lu intensity and used 176Lu/175Lu (0.02656) to estimate 176Lu/177Hf. Since Yb and Lu have similar elemental behaviors, βYb was applied to calculate the mass fractionation of Lu. The off-line processing of analytical data (e.g., mass bias calibration, sample selection, and blank signal) were performed with the ICPMSDataCal software [30]. Our analyses yielded weighted mean 176Hf/177Hf ratios of 0.2820172 ± 0.0000060 for the GJ-1 zircon standard and 0.2823080 ± 0.0000035 for the 91500-zircon standard.

Figure 3. Representative zircon CL images of the Xianglushan biotite granite (sample XLS01-01). The yellow and red circles denote the Hf and U-Pb isotopic analysis spots, respectively.
3.4. Zircon Log fO2 Ratios, Ce and Eu Anomaly Estimation

Zircon has high closure temperature and is resistant to weathering or hydrothermal alteration. In general, Ce in magma has two valence states (Ce⁴⁺ and Ce³⁺). Compared to Ce³⁺, Ce⁴⁺ has the same ionic radius and valence state as Zr⁴⁺ in the zircon lattice. Therefore, Ce⁴⁺ (instead of Ce³⁺) is compatible in magmatic zircon, which thus show strong positive Ce anomaly in chondrite-normalized REE (Rare Earth element) pattern. Various zircon Ce-based oxygen fugacity (fO₂) indicators were developed to assess the magmatic redox conditions. In particular, Trail et al. [36] proposed an equation (Equation (1)) that can directly calculate the absolute value of oxygen fugacity. This equation has been widely adopted in many studies on the genesis of world-class porphyry Cu deposits:

\[
\ln\left(\frac{\text{Ce}}{\text{Ce}^*}\right)_D = (0.1156 \pm 0.0050) \times \ln(f_{O2}) + \frac{13.860 \pm 708}{T(K)} - 6.125 \pm 0.484
\]  

(1)

where \((\text{Ce}/\text{Ce}^*)_D\) is the zircon Ce anomaly estimated from the partition coefficients and \(T\) is the absolute zircon crystallization temperature.

Recent studies suggested [37,38] that substitution of Ti, Si⁴⁺, and Zr⁴⁺ in zircon lattice depends primarily on temperature. As a result, the titanium content can estimate zircon crystallization temperature, if the TiO₂ and SiO₂ activities in the melt at the time of crystallization are well constrained. Therefore, Equation (2) proposed by Ferry and Watson [37] was used to calculate the magma temperature at the time of zircon crystallization.

\[
\log(\text{ppm Ti-in-zircon}) = \left(5.711 \pm 0.072\right) - 4800 \pm 86\frac{T(K)}{T(K)} - \log\alpha_{SiO_2} + \log\alpha_{TiO_2}
\]  

(2)

Where \(\alpha_{SiO_2}\) and \(\alpha_{TiO_2}\) represent the Si and Ti activity, respectively.

Notably, the studies of natural samples and experiments by Trail et al. [36] suggested that Ce anomalies in the magma can be calculated by the following approximation:

\[
(\text{Ce}/\text{Ce}^*)_{\text{CHUR}} = \frac{D_{\text{Ce}}^{\text{melt}}}{\sqrt{D_{\text{La}}^{\text{melt}} \times D_{\text{Pr}}^{\text{melt}}}} = \frac{D_{\text{Ce}}^{\text{zirc/char}}}{\sqrt{D_{\text{La}}^{\text{zirc/char}} \times D_{\text{Pr}}^{\text{zirc/char}}}}
\]  

(3)

CHUR is the abbreviation of chondrite uniform reservoir, where \((\text{Ce}/\text{Ce}^*)_{\text{CHUR}}\) represents the Ce anomalies normalized to the chondritic uniform reservoir (CHUR; [39,40]). However, the measurement of \(\text{Ce}/\text{Ce}^* = \text{Ce}N/(\text{La}N \times \text{Pr}N)^{1/2}\) (subscript N indicates chondrite normalization) anomaly is difficult because La and Pr are very difficult to be measured precisely. Moreover, the two elements are susceptible to contamination by tiny melt and titanite inclusions that are common in zircon [38]. This has led some authors to use a ratio between Ce and a more abundant REE as a proxy for Ce enrichment or depletion (such as Ce/Nd; e.g., [40–42]). Loard et al. [43] argued that \(\text{Ce}/\text{Ce}^*\) can be estimated based on Equation (5), in which Sm and Nd were less affected by the inclusions and can be measured more precisely. Thus, determination of the Ce anomaly and fO₂ for the magmas using the Sm-Nd interpolation can yield more robust fO₂ values.

\[
Nd_N = \sqrt{\text{Ce}^* \times Sm_N}
\]  

(4)

\[
\text{Ce}^* \approx \frac{Nd_N^2}{Sm_N}
\]  

(5)

Furthermore, zircon \(\text{Eu}_{N}/\text{Eu}_{N}^*\) ratios can also evaluate the magmatic oxygen fugacity, because Eu⁴⁺ cannot substitute into zircon due to its cationic size and charge [42]. However, the redox effect on zircon \(\text{Eu}_{N}/\text{Eu}_{N}^*\) ratios is complicated by the strong partitioning of Eu⁴⁺ into other minerals, notably plagioclase [36,38,40]. Plagioclase crystallization can deplete the melt in Eu relative to Sm and Gd.
Hence, zircon Eu anomalies are not only influenced by redox, but also by the plagioclase abundance. In view of this, Eu anomaly is not used to assess the $f_{O_2}$ of granitic magmas in this study.

4. Results

4.1. Zircon U-Pb Age

Zircon grains separated from XLS01-1 sample are colorless, euhedral transparent, and about 50 to 150 µm long. Most zircon grains have fine oscillatory zoning and some are sector-zoned (Figure 3). A total of 39 zircon grains from the sample were analyzed (Table 1) and their U and Th contents and Th/U ratios are of 255 to 8210 ppm, 244 to 1268 ppm, and 0.15 to 1.12, respectively (Table 1), resembling typical magmatic zircons ($Th/U > 0.1$, [12]). U-Pb ages of the zircon grains are highly consistent (122 to 129 Ma), which yielded a weighted-mean age of 125 ± 1 Ma ($n = 40$, MSWD = 2.5; Figure 4), representing the crystallization age of the biotite granite XLS01-1.

Figure 4. (a) Zircon U-Pb concordia and (b) weighted mean age diagrams for the Xianglushan biotite granite.
Table 1. Zircon U-Pb isotopic compositions and ages of the Xianglushan biotite granite ("PLE" represent the "Plesovice zircon").

| Composition (ppm) | Isotopic Ratio | Isotopic Age (Ma) |
|-------------------|----------------|-------------------|
|                   | Th   | U    | Th/U  | 206Pb/238U | 206Pb/238U | 207Pb/235U | 206Pb/238U | 207Pb/235U | 206Pb/238U | 207Pb/235U | 206Pb/238U |
| Samples           | Ratio| 1σ  | Ratio| 1σ   | Age   | 1σ   | Age   | 1σ   | Age   | 1σ   | Age   |
| 1                 | 595  | 704  | 0.85 | 0.1436 | 0.0074 | 0.0203 | 0.0003 | 136  | 6.6   | 129  | 2.1   |
| 2                 | 589  | 790  | 0.75 | 0.1396 | 0.0059 | 0.0198 | 0.0002 | 133  | 5.2   | 126  | 1.5   |
| 3                 | 841  | 925  | 0.91 | 0.1309 | 0.0054 | 0.0200 | 0.0003 | 125  | 4.8   | 128  | 1.8   |
| 4                 | 780  | 953  | 0.82 | 0.1339 | 0.0048 | 0.0195 | 0.0002 | 128  | 4.3   | 124  | 1.5   |
| 5                 | 599  | 2267 | 0.26 | 0.1286 | 0.0041 | 0.0195 | 0.0003 | 123  | 3.7   | 124  | 2.2   |
| 6                 | 388  | 619  | 0.63 | 0.1305 | 0.0059 | 0.0201 | 0.0002 | 125  | 5.3   | 128  | 1.5   |
| 7                 | 681  | 733  | 0.93 | 0.1333 | 0.0046 | 0.0193 | 0.0003 | 127  | 4.1   | 123  | 1.6   |
| 8                 | 633  | 631  | 1.00 | 0.1386 | 0.0059 | 0.0197 | 0.0002 | 132  | 5.3   | 126  | 1.5   |
| 9                 | 602  | 848  | 0.71 | 0.1483 | 0.0047 | 0.0200 | 0.0003 | 140  | 4.1   | 127  | 1.8   |
| 10                | 541  | 590  | 0.92 | 0.1244 | 0.0079 | 0.0191 | 0.0003 | 119  | 7.2   | 122  | 1.7   |
| 11                | 547  | 703  | 0.78 | 0.1352 | 0.0052 | 0.0197 | 0.0002 | 129  | 4.6   | 126  | 1.5   |
| 12                | 652  | 833  | 0.78 | 0.1325 | 0.0051 | 0.0193 | 0.0003 | 126  | 4.6   | 123  | 1.6   |
| 13                | 1016 | 910  | 1.12 | 0.1243 | 0.0052 | 0.0192 | 0.0002 | 119  | 4.7   | 122  | 1.4   |
| 14                | 400  | 691  | 0.58 | 0.1249 | 0.0054 | 0.0191 | 0.0002 | 120  | 4.8   | 122  | 1.4   |
| 15                | 1191 | 1784 | 0.67 | 0.1271 | 0.0039 | 0.0193 | 0.0003 | 122  | 3.5   | 123  | 1.8   |
| 16                | 546  | 940  | 0.58 | 0.1350 | 0.0055 | 0.0203 | 0.0003 | 129  | 5.0   | 129  | 1.8   |
| 17                | 381  | 615  | 0.62 | 0.1357 | 0.0062 | 0.0202 | 0.0003 | 129  | 5.5   | 129  | 1.8   |
| 18                | 586  | 670  | 0.87 | 0.1420 | 0.0068 | 0.0192 | 0.0003 | 135  | 6.1   | 123  | 2.0   |
| 19                | 1049 | 1057 | 0.99 | 0.1243 | 0.0047 | 0.0192 | 0.0002 | 119  | 4.3   | 122  | 1.3   |
| 20                | 855  | 996  | 0.86 | 0.1273 | 0.0047 | 0.0191 | 0.0002 | 122  | 4.2   | 122  | 1.4   |
| 21                | 592  | 589  | 1.01 | 0.1329 | 0.0061 | 0.0191 | 0.0002 | 127  | 5.4   | 122  | 1.5   |
| 22                | 730  | 775  | 0.94 | 0.1348 | 0.0054 | 0.0199 | 0.0003 | 128  | 4.8   | 127  | 1.7   |
| 23                | 692  | 937  | 0.74 | 0.1325 | 0.0048 | 0.0202 | 0.0003 | 126  | 4.3   | 129  | 2.1   |
| 24                | 504  | 675  | 0.75 | 0.1266 | 0.0049 | 0.0195 | 0.0002 | 121  | 4.4   | 124  | 1.4   |
| 25                | 543  | 699  | 0.78 | 0.1345 | 0.0055 | 0.0197 | 0.0002 | 128  | 5.0   | 126  | 1.3   |
| 26                | 484  | 575  | 0.84 | 0.1389 | 0.0070 | 0.0194 | 0.0002 | 132  | 6.2   | 124  | 1.3   |
| 27                | 1007 | 3696 | 0.27 | 0.1384 | 0.0036 | 0.0195 | 0.0003 | 132  | 3.2   | 125  | 1.7   |
| 28                | 537  | 764  | 0.70 | 0.1289 | 0.0053 | 0.0193 | 0.0002 | 123  | 4.8   | 123  | 1.3   |
| 29                | 793  | 1211 | 0.65 | 0.1393 | 0.0052 | 0.0192 | 0.0002 | 132  | 4.6   | 123  | 1.6   |
|    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|
| 30 | 336| 747| 0.45| 0.1280| 0.0044| 0.0197| 0.0002| 122| 3.9| 126| 1.3|
| 31 | 534| 764| 0.70| 0.1252| 0.0046| 0.0197| 0.0002| 120| 4.1| 126| 1.3|
| 32 | 962|1299| 0.74| 0.1461| 0.0049| 0.0197| 0.0002| 138| 4.4| 126| 1.5|
| 33 | 244| 613| 0.40| 0.1418| 0.0054| 0.0198| 0.0003| 135| 4.8| 126| 1.6|
| 34 | 249| 255| 0.98| 0.1383| 0.0078| 0.0198| 0.0003| 132| 6.9| 127| 2.1|
| 35 | 618| 770| 0.80| 0.1451| 0.0058| 0.0198| 0.0002| 138| 5.2| 127| 1.4|
| 36 | 332| 646| 0.51| 0.1400| 0.0054| 0.0199| 0.0003| 133| 4.9| 127| 1.6|
| 37 |1268|8210| 0.15| 0.1440| 0.0033| 0.0201| 0.0002| 137| 2.9| 128| 1.4|
| 38 | 842| 964| 0.87| 0.1395| 0.0048| 0.0201| 0.0002| 133| 4.2| 128| 1.3|
| 39 | 717|1013| 0.71| 0.1433| 0.0046| 0.0202| 0.0002| 136| 4.1| 129| 1.3|
| 40 |1147|1244| 0.92| 0.1439| 0.0049| 0.0202| 0.0002| 136| 4.3| 129| 1.5|
| PLE| 140| 929| 0.15| 0.3962| 0.0117| 0.0543| 0.0005| 339| 8.5| 341| 3.2|
| PLE| 137| 928| 0.15| 0.3964| 0.0127| 0.0538| 0.0005| 339| 9.2| 338| 3.4|
| PLE| 140| 921| 0.15| 0.4072| 0.0098| 0.0542| 0.0005| 347| 7.1| 340| 2.9|
| PLE| 48.1| 491| 0.10| 0.4102| 0.0123| 0.0549| 0.0005| 349| 8.9| 345| 3.3|
| PLE| 79.3| 795| 0.10| 0.3852| 0.0109| 0.0537| 0.0006| 331| 8.0| 337| 3.4|
| PLE| 77.4| 786| 0.10| 0.3778| 0.0113| 0.0532| 0.0006| 325| 8.3| 334| 3.7|
| PLE| 145| 917| 0.16| 0.4043| 0.0100| 0.0540| 0.0004| 345| 7.3| 339| 2.7|
4.2. Zircon Hf Isotopes

Zircon Hf-isotopic data of the Xianglushan biotite granite (XLS01-1) were listed in Table 2. These zircon crystals have $^{176}\text{Hf} / ^{177}\text{Hf}$ ratios mainly range from 0.282513 to 0.282594. The zircon $\varepsilon_{\text{Hf}}(t)$ values of the Xianglushan biotite granite are characterized by a narrow initial range ($-6.9$ to $-4.1$; avg. $-5.4 \pm 0.7$). In addition, the Hf-isotopic data show the younger two-stage model ages (TDM2) of 1085 to 1215 Ma (avg. 1143 ± 30 Ma; Figure 5 and Table 2).

Figure 5. (a) $\varepsilon_{\text{Hf}}(t)$ vs. U-Pb age diagram and histograms of (b) $\varepsilon_{\text{Hf}}(t)$ value; (c) Two-stage model ages (TDM2).
Table 2. Zircon Hf isotopes of the Xianglushan biotite granite.

| Samples  | 176Hf/177Hf | 1σ | 176Lu/177Hf | 1σ | 177Yb/177Hf | 1σ | εHf(0)  | εHf(t)  | TDM2 (Ma) |
|----------|-------------|----|-------------|----|-------------|----|----------|----------|-----------|
| XLS01-01 | 0.282568    | 0.000011 | 0.001965    | 0.00005 | 0.057096    | 0.001344 | -7.6736743 | -5.0 | 1127      |
| XLS01-02 | 0.282544    | 0.000009 | 0.002183    | 0.000058 | 0.067082    | 0.001738 | -8.5223757 | -5.9 | 1168      |
| XLS01-03 | 0.282552    | 0.000008 | 0.002332    | 0.000072 | 0.071557    | 0.001866 | -8.2394752 | -5.6 | 1155      |
| XLS01-04 | 0.282559    | 0.00001 | 0.002042    | 0.000053 | 0.060775    | 0.001423 | -7.9919373 | -5.4 | 1143      |
| XLS01-06 | 0.282561    | 0.000009 | 0.001585    | 0.000022 | 0.04803     | 0.000642 | -7.9212122 | -5.3 | 1137      |
| XLS01-08 | 0.282576    | 0.00001 | 0.001691    | 0.000019 | 0.051412    | 0.000514 | -7.3907739 | -4.7 | 1113      |
| XLS01-09 | 0.282577    | 0.000011 | 0.002001    | 0.000031 | 0.061653    | 0.000679 | -7.3554114 | -4.7 | 1112      |
| XLS01-10 | 0.282538    | 0.000008 | 0.002075    | 0.000072 | 0.061922    | 0.00193 | -8.734551 | -6.1 | 1178      |
| XLS01-12 | 0.28254    | 0.000009 | 0.001714    | 0.000055 | 0.051492    | 0.001585 | -8.6638259 | -6.0 | 1173      |
| XLS01-14 | 0.282563    | 0.000009 | 0.001555    | 0.000049 | 0.046709    | 0.001414 | -7.8504871 | -5.2 | 1134      |
| XLS01-15 | 0.282535    | 0.000009 | 0.002769    | 0.000056 | 0.084887    | 0.001648 | -8.8406386 | -6.3 | 1185      |
| XLS01-18 | 0.282573    | 0.000009 | 0.00172     | 0.000016 | 0.05109     | 0.000402 | -7.4968161 | -4.8 | 1118      |
| XLS01-22 | 0.282542    | 0.000009 | 0.002125    | 0.000085 | 0.064811    | 0.002413 | -8.5931008 | -6.0 | 1171      |
| XLS01-24 | 0.282573    | 0.000013 | 0.001833    | 0.000029 | 0.055654    | 0.000636 | -7.4968161 | -4.9 | 1118      |
| XLS01-25 | 0.282572    | 0.000011 | 0.001906    | 0.000043 | 0.057709    | 0.000925 | -7.5322241 | -4.9 | 1120      |
| XLS01-26 | 0.282574    | 0.000009 | 0.00135     | 0.000022 | 0.040415    | 0.00073 | -7.461499 | -4.8 | 1115      |
| XLS-05  | 0.282576    | 0.000016 | 0.001841    | 0.000027 | 0.061811    | 0.000767 | -7.3964216 | -4.8 | 1114      |
| XLS-11  | 0.282545    | 0.000011 | 0.001343    | 0.00009 | 0.045204    | 0.000274 | -8.4776856 | -5.8 | 1163      |
| XLS-12  | 0.282594    | 0.000017 | 0.002001    | 0.00009 | 0.067159    | 0.000373 | -6.7633205 | -4.1 | 1085      |
| XLS-14  | 0.282513    | 0.000015 | 0.000950    | 0.000016 | 0.032482    | 0.000642 | -9.620265 | -6.9 | 1215      |
| XLS-16  | 0.282556    | 0.000015 | 0.001317    | 0.000013 | 0.043197    | 0.000308 | -8.1122868 | -5.4 | 1145      |
| XLS-18  | 0.282526    | 0.000017 | 0.001107    | 0.000007 | 0.036130    | 0.000360 | -9.1530133 | -6.4 | 1193      |
| XLS-30  | 0.282585    | 0.000017 | 0.001688    | 0.000014 | 0.058506    | 0.000515 | -7.074418 | -4.4 | 1098      |
| XLS-31  | 0.282555    | 0.000019 | 0.002039    | 0.000012 | 0.068353    | 0.000525 | -8.1272592 | -5.5 | 1149      |
| XLS-32  | 0.282559    | 0.000014 | 0.001587    | 0.000027 | 0.033373    | 0.000873 | -7.9958257 | -5.3 | 1141      |
| XLS-33  | 0.282553    | 0.000014 | 0.000614    | 0.000002 | 0.020463    | 0.000999 | -8.2042643 | -5.5 | 1147      |
| XLS-35  | 0.282555    | 0.000015 | 0.001045    | 0.000007 | 0.034642    | 0.000237 | -8.148415 | -5.4 | 1146      |

Note: εHf(t) = 10,000 × [(178Hf/177Hf) S − (178Hf/177Hf) CHUR × (e^(-λt) − 1)] / [(178Hf/177Hf) CHUR × (e^(-λt) − 1)] − 1. (176Lu/177Hf) CHUR = 0.0332, (176Hf/177Hf) CHUR = 0.28325 [44–46]. Two-stage model age (TDM2) calculation after [46], and we used Lu/Hf = 0.042 (S-type granites with > 74 wt.% SiO2).
Similarly, the zircon $\varepsilon_{\text{Hf}}(t)$ and TDM2 are of $-10$ to $-2.4$ (avg. $-6.2 \pm 1.8$) and $1042$ to $1394$ Ma (avg. $1221 \pm 86$ Ma) for the Dahutang ore-related granite [8]. Comparatively, the Xihuashan W ore-related granite has lower zircon $\varepsilon_{\text{Hf}}(t)$ values ($-14.9$ to $-11.4$, avg. $-12.5 \pm 0.9$; [47,48]), which plot above the CHUR evolutionary line in the $\varepsilon_{\text{Hf}}(t)$ vs. U-Pb age diagram (Figure 5a, b). Moreover, the Xihuanshan granite shows the older TDM2, ranging from $1473$ to $1634$ Ma (avg. $1525 \pm 43$ Ma; Figure 5c; Table A2).

4.3. Temperature-Redox Conditions

Calculated Ti-in-zircon temperatures of the W-related granites from the three deposits and the Ehu ore-barren granite are listed in Table A1. The activities of TiO$_2$ and SiO$_2$ were estimated to be 0.7 and 1, respectively. The Ti-in-zircon temperatures are $666$ to $786$ °C (avg. $699 \pm 32$ °C) for the Xianglushan biotite granite, $709$ to $848$ °C (avg. $745 \pm 35$ °C) for the Dahutang granite, $654$ to $890$ °C (avg. $727 \pm 51$ °C) for the Xihuashan granite, and $654$ to $890$ °C (avg. $727 \pm 33$ °C) for the Ehu granite.

The log $f_O_2$ values for the W-related and barren granites were listed in Table A1 and illustrated in Figures 6 and 7. It is noted that the log $f_O_2$ values were calculated by the La-Pr and Nd-Sm interpolation methods, respectively. As shown in Figure 6a, most data from the Xianglushan granite are located below those of the Ehu ore-barren granite. Log $f_O_2$ values range from FMQ $-12.01$ to $4.76$ (avg. $-7.97 \pm 3.73$) for the bearing granite, and from FMQ $-10.13$ to $+7.59$ (avg. $-2.36 \pm 4.32$) for the barren one (Figure 6b). Although the results are broadly consistent with the previous redox estimates for these zircons [37], our results indicate a slightly oxidizing environment. It is also noted that the log $f_O_2$ range of Ehu granite in Figure 6c is narrower than that in Figure 6a. The results estimated by Equation (3) range from FMQ $-13.00$ to $+3.61$ (avg. $-7.16 \pm 4.5$) for the ore-bearing granite, and from FMQ $-6.01$ to $+5.54$ (avg. $-1.93 \pm 2.46$) for the barren granite (Table A1; Figure 6d).

Figure 6. log $f_O_2$-related binary diagrams of zircon grains from the Xianglushan and Ehu granites (a) log $f_O_2$ vs. temp diagram, where log $f_O_2$ was calculated with the method of Trail et al. [37], and CeN* by
As shown in Figure 7, although the Dahutang granite zircon data are partially overlapped with those from the Xihuanshan and Xianglushan granites, zircon grains from the Dahutang ore-bearing granite still have the highest log\(\text{O}_2\) values regardless of the calculation method. The La-Pr interpolation approach yielded log\(\text{O}_2\) values of FMQ \(-9.34\) to \(+4.76\) (avg. \(-0.37 \pm 3.63\)) for the Dahutang granite, FMQ \(-11.70\) to \(+3.33\) (avg. \(-2.80 \pm 4.33\)) for the Xihuashan granite, and FMQ \(-12.01\) to \(+4.76\) (avg. \(-7.97 \pm 3.73\)) for the Xianglushan granite (Figure 7a,b). In contrast, the Sm-Nd interpolation method obtained a narrower log\(\text{O}_2\) range (Figure 7c,d), and higher values (albeit some overlapping) for the Dahutang (FMQ \(-7.33\) to \(+5.90\); avg. \(-0.79 \pm 3.27\)) and Xihuashan (FMQ \(-10.29\) to \(+4.97\); avg. \(-1.92 \pm 3.67\)) granites than the Xianglushan granite (FMQ \(-13.00\) to \(+3.61\); avg. \(-7.16 \pm 4.54\)) (Figure 7; Table A1). Notably, unlike the La-Pr interpolation, the Sm-Nd fitting method does not require accurate measurement of La or Pr and is thus considered to be more robust. Meanwhile, some studies [25] further suggested that zircon REEs have a concave-downward (rather than linear) chondrite-normalized pattern. Hence, neither of the two methods can accurately determine Ce* and would result in under-/over-estimation of the true Ce*. 

Figure 7. log\(\text{O}_2\)-related binary diagrams of zircon grains from the Xianglushan, Dhutang and Xihuashan granites. (a) log\(\text{O}_2\) vs. temp diagram, where log\(\text{O}_2\) value was calculated with the method of Trail et al. [34], and Ce* with the La-Pr interpolation method; (b) Histogram of oxygen fugacity; (c) log\(\text{O}_2\) vs. temp diagram, where log\(\text{O}_2\) value was calculated with the method of Trail et al. [34], and Ce* with the Sm-Nd fitting method; (d) Histogram of oxygen fugacity. Data are listed in Table A1.
5. Discussion

5.1. Timing of Magmatism and its Related W Mineralization

LA-ICP-MS zircon U-Pb dating suggests that the Xianglushan granite was formed at 125 ± 1 Ma, coeval to the W mineralization (scheelite Sm-Nd age: 121 ± 11 Ma [23]). Moreover, the molybdenite Re-Os age and 40Ar-39Ar dating of muscovite are also consistent with the U-Pb zircon age of 125 ± 1 Ma for the biotite granite. On the basis of the LA-ICP-MS zircon U-Pb, molybdenite Re-Os, and muscovite 40Ar-39Ar ages [9,23], it is concluded that W mineralization at the Xianglushan deposit is genetically associated with the biotite granite. Magmatism and mineralization in the Xianglushan deposit occurred during the Early Cretaceous. Additionally, published age data indicate two late Mesozoic (Yanshanian) magmatic event in Jiangxi Province (Table 3; Figure 8): The first Late Jurassic-Early Cretaceous events occurred mainly at 160–140 Ma, e.g., the emplacement of ore-related granite (porphyries) at the Zhuxi W-Cu (148–152 Ma) and Xihuashan W deposits (158–161 Ma) [13]. The second event occurred mainly at 135–120 Ma, e.g., the Xianglushan granite (ca. 125 Ma; this study). It is noteworthy that both magmatic events were reported at the Dahutang W deposit (Table 3), and both events may have been ore-related [49,50]. In summary, the Yanshanian magmatism and its related W mineralization in southern Jiangxi Province occurred in a relatively confined period of time, while the magmatism and related W-Cu-(Mo) mineralization in northern Jiangxi Province are characterized by occurring as multi-phases at a wider age span.

![Figure 8. Histogram of granite ages in Jiangxi Province. Age data are listed in Table 3.](image)

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Table 3. Yanshanian granites and related W deposits in Jiangxi Province selected for this study.

| Area                  | Deposit                  | Lithology                                      | Age (Ma) | Method              | Ref. | Mineralization age (Ma) | Method          | Ref. |
|-----------------------|--------------------------|------------------------------------------------|----------|---------------------|------|-------------------------|-----------------|------|
|                       | Northern Jiangxi Province | Dahutang W-Cu deposit                          |          |                     |      |                         |                 |      |
|                       |                          | Porphyritic muscovite granite                  | 144 ± 1  | Zircon LA-ICP-MS U–Pb | [47] | 141 ± 4                 | Molybdenite Re–Os | [1]  |
|                       |                          | W-rich granite porphyry                         | 135 ± 1  | Zircon LA-ICP-MS U–Pb | [47] | 142 ± 9                 | Scheelite Sm–Nd  | [48] |
|                       |                          | Porphyritic two-mica granite                    | 144 ± 1  | Zircon LA-ICP-MS U–Pb | [47] |                         |                 |      |
|                       |                          | Porphyry two-mica granite                       | 130 ± 1  | Zircon LA-ICP-MS U–Pb | [47] |                         |                 |      |
|                       |                          | Porphyritic biotite granite                     | 138 Ma   | Zircon LA-ICP-MS U–Pb | [49] | 144 ± 1                 | Molybdenite Re–Os | [1]  |
|                       |                          | Granite porphyry                               | 135 Ma   | Zircon LA-ICP-MS U–Pb | [49] | 150 ± 1                 | Molybdenite Re–Os | [49] |
|                       |                          | Porphyritic biotite granite                     | 147 ± 1  | Zircon LA-ICP-MS U–Pb | [9]  | 139 ± 1                 | Molybdenite Re–Os | [20] |
|                       |                          | Porphyritic biotite granite                     | 148 ± 2  | Zircon LA-ICP-MS U–Pb | [9]  | 144 ± 1                 | Molybdenite Re–Os | [48] |
|                       |                          | Granule biotite granite                         | 145 ± 1  | Zircon LA-ICP-MS U–Pb | [9]  |                         |                 |      |
|                       |                          | Granite biotite granite                         | 146 ± 1  | Zircon LA-ICP-MS U–Pb | [9]  |                         |                 |      |
|                       |                          | Granite porphyry                               | 143 ± 1  | Zircon LA-ICP-MS U–Pb | [9]  |                         |                 |      |
|                       |                          | Granite porphyry                               | 143 ± 1  | Zircon LA-ICP-MS U–Pb | [9]  |                         |                 |      |
|                       |                          | Muscovite granite                              | 147 ± 1  | Zircon LA-ICP-MS U–Pb | [50] |                         |                 |      |
|                       |                          | altered granite                                | 149 ± 2  | Zircon LA-ICP-MS U–Pb | [51] |                         |                 |      |
|                       | Zhuxi W-Cu deposit       | Altered granite porphyry                        | 148 ± 3  | Zircon LA-ICP-MS U–Pb | [51] |                         |                 |      |
|                       |                          | Granite porphyry                               | 151 ± 2  | Zircon LA-ICP-MS U–Pb | [51] |                         |                 |      |
|                       |                          | Granite porphyry                               | 150 ± 2  | Zircon LA-ICP-MS U–Pb | [51] |                         |                 |      |
|                       | Yangchuling W deposit    | Granite porphyry                               | 146 ± 3  | Zircon LA-ICP-MS U–Pb | [52] |                         |                 |      |
|                       | Xianglushan W deposit    | biotite granite                                | 120 ± 1  | Zircon LA-ICP-MS U–Pb | [53] | 121 ± 11                |                  | [54] |
|                       |                         | Porphyr medium-grained biotite granite          | 159 ± 1  | Zircon SIMS U–Pb     | [13] | 158 ± 1                 |                 |      |
|                       |                         | Garnet-bearing fine-grained biotite granite     | 161 ± 3  | Zircon SIMS U–Pb     | [13] | 153 ± 2                 |                 |      |
|                       | Dangping W deposit       | Garnet-bearing fine-grained porphyry biotite granite | 159 ± 2  | Zircon SIMS U–Pb     | [13] |                         |                 |      |
|                       |                          | Fine-grained porphyry biotite granite           | 158 ± 2  | Zircon SIMS U–Pb     | [13] |                         |                 |      |
|                       |                          | Porphyritic granite                            | 159 ± 3  | Zircon LA-ICP-MS U–Pb | [55] |                         |                 |      |
|                       |                          | Porphyr biotite granite                         | 155 ± 2  | Zircon LA-ICP-MS U–Pb | [55] |                         |                 |      |
|                       |                          | Medium-fine-grained porphyry granite            | 157 ± 2  | Zircon LA-ICP-MS U–Pb | [55] |                         |                 |      |
|                       |                          | biotite granite                                | 158 ± 2  | Zircon LA-ICP-MS U–Pb | [55] |                         |                 |      |
5.2. $\varepsilon_{Hf}(t)$ Variation and Ore Material Source

Previous studies demonstrated that the W mineralization is closely related with Cu-(Mo) mineralization in northern Jiangxi Province, which is uncommon worldwide outside of South China [2,23,47]. Tungsten is an a lithophile element due to a valence of +6 in nature. Currently, over 20 W-bearing minerals (notably wolframite and scheelite) have been identified in nature [2,10,47,55,56]. The increase of oxygen content between the core and the mantle leads to the separation of tungsten from the core and its entry into the mantle [47,57]. Meanwhile, tungsten is an incompatible element and tends to accumulate in the crust during the crust mantle process and evolution. O’Neill et al. [57] reported that partition coefficients for W between silicate and Fe-rich metal will be highly increased under reduced condition. Unlike W, the oxidized magma is beneficial for Cu-(Au)-Mo mineralization through controlling the valence of sulfur. Thus, W and Cu tend to be enriched in the crust and mantle, respectively [10,12,18].

In this study, W-bearing granites from both the northern and southern Jiangxi Province have negative $\varepsilon_{Hf}(t)$ values ($-14.9$ to $-2.4$). Moreover, the Hf two-stage model age vary from 1085 to 1634 Ma and the Hf two-stage model of the individual granite is relatively uniform in age, indicating that these granites may have mainly crustal source [47]. Meanwhile, the $\varepsilon_{Hf}(t)$ values of ore-related granites in northern Jiangxi Province are clearly higher than those in southern Jiangxi Province. As shown in Figure 5c, compared to the ore-related granites in southern Jiangxi Province, those in northern Jiangxi Province have the younger TDM2 age which indicates the major source difference between the northern and southern magmas. This may have caused by partial melting of different metamorphic substrates [12,24,56]. According to the whole-rock geochemical data, granites in southern Jiangxi Province have higher SiO$_2$, but lower Al$_2$O$_3$, TiO$_2$, and MgO, and significantly lower P$_2$O$_5$ contents. The A/CNK-A/NK diagram suggests that W ore-related granites from both southern and northern Jiangxi Province are peraluminous. In addition, the ore-bearing granites in southern Jiangxi Province have higher SiO$_2$, but lower Al$_2$O$_3$, TiO$_2$, and MgO, and significantly lower P$_2$O$_5$ contents. The A/CNK-A/NK diagram suggests that W ore-related granites from both southern and northern Jiangxi Province are peraluminous. In addition, the ore-bearing granites in southern Jiangxi Province have higher Rb/Sr, but lower Zr/Hf, LREE/HREE and Eu/Eu* than their northern Jiangxi counterparts. By comparing the granite whole-rock $\varepsilon^{57}$Sr/$\varepsilon^{87}$Sr and $\varepsilon_{Nd}(t)$ values from northern Jiangxi Province and those of the Neoproterozoic Shuangqiaoshan Group, Su and Jiang [48] proposed that the former may have partly originated from the latter, which contains much higher contents of W (avg. 9.13 ppm) and Cu (avg. 38.1 ppm) than the average continental crust (W: 1 ppm, Cu: 27 ppm; [47]). Comparatively, both the ore-related granites and wall-rock sequences in southern Jiangxi Province have high W background contents [47,48], which may have contributed some ore-forming materials for the (super)-large W mineralization in the region. Notably, differences in Sr/Sr, Nd and Hf isotopes of granites in north and south do indicate probable differences in the source [8,47]. But the geochemical characteristics as lower Zr/Hf, Eu/Eu, Al$_2$O$_3$, TiO$_2$, and MgO or higher SiO$_2$ and Rb/Sr might be most probably related to differences in the fractionation of these magmas [13,43,58], that is, this probably indicates that granites from the south are more evolved that those from the north.

5.3. Oxygen Fugacity Variation and Implications

Pirajno [59] proposed that the fO$_2$ dependency of mineralization increases in the Sn-W-Mo-Cu-Mo-Cu-Au sequence, while the Fe dependency increases in the Mo-Sn-W-Cu-Mo-Cu-Au sequence. Nevertheless, the relationship between fO$_2$ and W mineralization is still not fully understood [18]. Some workers believed that low fO$_2$ is beneficial to W mineralization, whereas many others suggested that fO$_2$ plays little role in the W mineralization. Although W mineralization shows little dependence on magma fO$_2$ in view of geochemical affinity [60], large-scale W mineralization is always closely associated with reduced granites [18,47]. In our study, no matter which calculation method is used, the fO$_2$ of the Xianglushan granite is always lower than that of the ore-barren Ehu granite. This suggests that lower fO$_2$ may have been beneficial for W mineralization in northern Jiangxi, e.g., at Xianglushan. It may be explained by that low fO$_2$ facilitates W enrichment in silicate melts during source melting and magmatic differentiation. However, as shown in Figure 7, Dahutang granite has the highest fO$_2$, and could be interpreted as having different magma sources. Based on the Hf isotope evidence, the Dahutang ore-bearing granite in northern Jiangxi Province was probably sourced from
arc-type materials (of the Shuangqiao Group), which commonly have high log\(f_O^2\) values (NNO +1 to +3). Copper mineralization is generally associated with oxidized magmas [60–63] and can explain the coexistence of Cu and W mineralization in the northern Jiangxi Province.

Magma oxygen fugacity has been widely accepted as the most important control of Cu-Mo-Au mineralization (e.g., [5,8,47,64]). Many recent studies showed that high \(f_O^2\) granitic magma is the key for Cu mineralization in northeastern Jiangxi Province. For example, the ore-related granites in the Dexing and Tongcun PCDs have likely high \(f_O^2\) [11]. Meanwhile, Qiu et al. [26,62] suggested that the low magma \(f_O^2\) found in several Mo ore-related and ore-barren porphyries in western Zhejiang Province may have contributed to the Cretaceous Cu-Mo mineralization gap in the Zhe-Gan-Wan region. This hypothesis is supported by our study, as shown in Figure 9 and Table 4. Nd-Sm interpolation approach yielded log\(f_O^2\) values of FMQ \(-10.29\) to \(+11.87\) (avg. \(+3.54 \pm 4.02\)) for the Late Jurassic granites (145–170 Ma) FMQ \(-13.00\) to \(-5.55\) (avg. \(-3.69 \pm 4.70\)) for the Early Cretaceous granites (120–145 Ma). It shows that \(f_O^2\) gradually decreased from Jurassic to Cretaceous (Figure 9).

| Sample          | n  | FMQ Value | Mean      | Min | Max   |
|-----------------|----|-----------|-----------|-----|-------|
| Late Jurassic   | 171| 3.54 ± 4.02| -10.29    | 11.87 |
| Early Cretaceous| 112| -3.69 ± 4.70| -13       | 5.55  |

**Table 4.** Statistics of oxygen fugacity data for Yanshanian granites in Jiangxi Province.

![Figure 9](image_url) Log\(f_O^2\) values vs. U-Pb age plot for the Yanshanian granites in Jiangxi Province (\(P < 0.01\) and \(R = 0.72\)).

### 5.4. Tectonic Implications

Although the origin of strong oxidation has been still argued, a broad consensus has been reached that high oxidization is associated with subduction zone [18,36,40]. Sun et al. [18,59] proposed that subduction zone can release fluids to elevate oxygen fugacity. The closer distances from subduction zone are, the more fluids contribute and the higher oxygen fugacities are. For
example, many hydrous (3–5 wt % water) arc magmas have high $f_{O_2}$, ranging from NNO + 1 to NNO + 3 [18,60]. This phenomenon likely because of high amounts of dehydration-released fluid containing a lot of oxidized materials (i.e., Fe$^{3+}$, Mn$^{4+}$, S$^{6+}$, and C$^{4+}$) in subduction zones [18,60]. Additionally, the tectonic evolution of South China in late Mesozoic remains controversial for a long time [7,25,59]. A variety of tectonic models have been presented to address the Late Mesozoic large-scale magmatism and mineralization in South China, with most models invoking subduction of the paleo-Pacific plate [2,4,62]. Based on the drifting direction of the Pacific plate before 125 Ma [18,59] and the age distribution of magmatic rocks and mineralization zonation in the Late Jurassic to the Early Cretaceous in southern China like that in the South America. Sun et al. [59] proposed that the paleo-Pacific plate was subducting from NE to SW during ca. 180–125 Ma, and from SE to NW after 125 Ma in South China. This model may explain the differences in oxygen fugacity between the Late Jurassic and the Early Cretaceous granites in South China. According to this model, the Late Jurassic granites (such as Dexing granodiorite porphyry) are input more oxidized materials from the subduction than that of Early Cretaceous (such as Xianglushan biotite granite). Hence, it is observed that $f_{O_2}$ of granites gradually decreased from Jurassic to Cretaceous (Figure 9). Furthermore, Dahutang granite is closer from subduction zone than that of Xihuashan granite and Dahutang granite has the higher oxygen fugacity than that of Xihuashan granite.

5.5. Implications for Zircon as an Indicator

Zircons are widely distributed in igneous rocks and have stable geochemical properties. They faithfully record the information of zircon crystallization (i.e., $f_{O_2}$). Moreover, with the development of analytical technology, researchers have obtained a lot of REE (rare earth element) as well as zircon age data. Ce and Eu are variable valence elements, whose valence state are affected by the redox conditions of magma. Unlike $Ce_{\text{A}}/Ce_{\text{B}}$, $Eu_{\text{A}}/Eu_{\text{B}}$ in zircon is generally affected by the crystallization of plagioclase [18,40]. Hence, most researchers use Ce anomalies of zircon/melt distribution coefficients (Di) to estimate the oxygen fugacity. A series of oxygen fugacity barometers have been developed based on Ce anomalies to indicate the redox conditions of magma since 2002 [37,43,64]. However, these methods produced a wide range of $Ce_{\text{A}}/Ce_{\text{B}}$ ($f_{O_2}$) values which vary by up to 3 orders of magnitude for a single rock in some studies [43]. In this study, all zircon Ce$^{3+}$/Ce$^{4+}$ ratios from selected granites also show a wide range (Figures 6 and 7). The cause of this phenomenon has not been well understood [40,43]. One possibility is that some tiny inclusions (i.e., monazite, apatite, and titanite) frequently can be detected in zircon. Meanwhile, as shown in Figure 6, no matter which calculation method is used, the $f_{O_2}$ of the Xianglushan granite is always lower than that of the ore-barren Ehu granite. Therefore, it is suggested that zircon $f_{O_2}$ may be still used as an indicator to discriminate ore-bearing and barren granites in areas of W mineralization.

6. Conclusions

1. LA-ICP-MS zircon U-Pb dating of the Xianglushan biotite granite yielded an Early Cretaceous age (125 ± 1 Ma). Age compilation indicates that the magmatism and W-Cu-(Mo) mineralization in northern Jiangxi Province are characterized by being multiphase, while the magmatism and W mineralization in southern Jiangxi Province occurred mainly in the Middle to Late Jurassic (165–150 Ma).

2. The ore-related granites in northern Jiangxi Province have a younger TDM2 age and clearly higher $\varepsilon$Hf(t) values than those in southern Jiangxi Province, which seem to indicate a major source difference between the northern and southern granitic magmas in Jiangxi Province.

3. Compared with the coeval ore-barren Ehu granites, the low $f_{O_2}$ of the ore-related Xianglushan granite may have caused the W enrichment and mineralization, whilst the high $f_{O_2}$ of the Dahutang granite may have facilitated the coexistence of Cu and W mineralization. Zircon $f_{O_2}$ may be still used as an indicator to discriminate ore-bearing and barren granites in some cases.

4. Variation of oxygen fugacity among different granites may support a model that the Paleo-Pacific plate was subducting southwestwardly, as proposed in some previous studies.
Author Contributions: X.-Y.L. conceived and designed the experiments; X.-Y.L. and J.-R.Z. performed the experiments; J.-R.Z. and X.-Y.L. analyzed the data; X.-Y.L. wrote the paper, assisted by all other authors; and C.-K.L. revised the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Crystallization temperatures, Ce anomalies, and magma oxygen fugacity of zircon grains from the Xianglushan, Dahutang, and Xihuashan granites.

| Spot No. | δCe a | δCe b | δEu | T (°C) | Age (Ma) | logfO2 a | FMQ a | logfO2 b | FMQ b |
|----------|------|------|-----|-------|---------|---------|------|---------|------|
| Xianglushan | | | | | | | | | |
| 1 | 3 | 3 | 0.09 | 694 | 129 | −27.23 | −9.29 | −26.07 | −8.14 |
| 2 | 2 | 2 | 0.08 | 710 | 126 | −27.69 | −10.22 | −26.62 | −9.16 |
| 3 | 3 | 4 | 0.09 | 696 | 128 | −26.38 | −8.51 | −25.21 | −7.33 |
| 4 | 4 | 7 | 0.08 | 676 | 124 | −26.82 | −8.36 | −24.39 | −5.93 |
| 5 | 2 | 2 | 0.10 | 676 | 128 | −29.28 | −10.83 | −28.48 | −10.02 |
| 6 | 21 | 50 | 0.16 | 675 | 126 | −20.36 | −1.88 | −17.04 | 1.44 |
| 7 | 4 | 4 | 0.11 | 681 | 127 | −26.09 | −7.76 | −25.91 | −7.59 |
| 8 | 4 | 10 | 0.09 | 736 | 122 | −22.92 | −6.15 | −19.74 | −2.97 |
| 9 | 15 | 45 | 0.12 | 719 | 126 | −19.27 | −2.04 | −15.06 | 2.17 |
| 10 | 2 | 3 | 0.07 | 719 | 123 | −26.27 | −9.05 | −25.21 | −7.99 |
| 11 | 43 | 89 | 0.09 | 675 | 122 | −17.60 | 0.88 | −14.87 | 3.62 |
| 12 | 2 | 4 | 0.08 | 718 | 123 | −26.20 | −8.94 | −24.37 | −7.12 |
| 13 | 1 | 2 | 0.07 | 666 | 129 | −30.79 | −12.01 | −29.78 | −11.00 |
| 14 | 3 | 3 | 0.08 | 672 | 129 | −28.37 | −9.78 | −27.62 | −9.03 |
| 15 | 4 | 6 | 0.08 | 693 | 122 | −25.88 | −7.92 | −23.84 | −5.87 |
| 16 | 13 | 48 | 0.12 | 692 | 127 | −21.08 | −3.08 | −16.28 | 1.71 |
| 17 | 5 | 8 | 0.10 | 684 | 129 | −25.55 | −7.34 | −23.33 | −5.11 |
| 18 | 2 | 1 | 0.09 | 728 | 124 | −27.27 | −10.30 | −27.52 | −10.55 |
| 19 | 2 | 3 | 0.11 | 786 | 124 | −23.41 | −7.93 | −22.25 | −6.78 |
| 20 | 5 | 7 | 0.10 | 682 | 123 | −25.60 | −7.31 | −23.81 | −5.52 |
| 21 | 2 | 2 | 0.05 | 674 | 124 | −29.96 | −11.45 | −29.19 | −10.68 |
| 22 | 1 | 1 | 0.10 | 703 | 123 | −28.87 | −11.20 | −30.20 | −12.53 |
| 23 | 2 | 2 | 0.10 | 704 | 122 | −27.56 | −9.93 | −27.52 | −9.89 |
| 24 | 1 | 1 | 0.09 | 712 | 123 | −28.88 | −11.48 | −29.69 | −12.28 |
| 25 | 2 | 2 | 0.10 | 688 | 122 | −28.42 | −10.31 | −28.44 | −10.32 |
| 26 | 1 | 1 | 0.15 | 714 | 122 | −28.11 | −10.75 | −29.59 | −12.24 |
| 27 | 1 | 1 | 0.10 | 685 | 126 | −29.69 | −11.50 | −31.19 | −13.00 |
| 28 | 2 | 2 | 0.07 | 707 | 125 | −27.84 | −10.29 | −27.37 | −9.81 |
| 29 | 2 | 2 | 0.10 | 741 | 123 | −25.60 | −8.97 | −25.60 | −8.97 |
| 30 | 2 | 2 | 0.08 | 655 | 126 | −30.37 | −11.24 | −30.37 | −11.24 |
| 31 | 9 | 16 | 0.08 | 765 | 126 | −18.75 | −2.75 | −16.58 | 0.58 |
| 32 | 3 | 3 | 0.06 | 655 | 126 | −28.79 | −9.69 | −28.79 | −9.69 |
| 33 | 2 | 1 | 0.08 | 688 | 126 | −28.42 | −10.32 | −31.03 | −12.92 |
| 34 | 56 | 7 | 0.09 | 793 | 127 | −10.55 | 4.76 | −18.38 | −3.06 |
| 35 | 2 | 2 | 0.11 | 708 | 127 | −27.33 | −9.80 | −27.33 | −9.80 |
| 36 | 13 | 39 | 0.08 | 712 | 127 | −20.08 | −2.65 | −15.94 | 1.48 |
| 37 | 2 | 4 | 0.06 | 760 | 128 | −24.66 | −8.53 | −22.05 | −5.92 |
| 38 | 7 | 10 | 0.11 | 683 | 128 | −24.01 | −5.74 | −22.67 | −4.40 |
### Minerals

| Sample | Size | 280 | 120 | 208 | 256 |
|--------|------|-----|-----|-----|-----|
| XHS-19-15C | 77  | 35  | 0.18 | 678  | 150.7 |
| XHS-19-12R  | 5   | 13  | 0.18 | 738  | 156.3 |
| XHS-19-1C  | 29  | 9   | 0.23 | 744  | 155.6 |
| XHS-21-3C  | 11  | 18  | 0.10 | 755  | 156.0 |
| XHS-19-5R  | 2   | 4   | 0.14 | 701  | 160.8 |
| XHS-19-3R  | 12  | 37  | 0.17 | 739  | 162.2 |
| XHS-19-1R  | 2   | 4   | 0.15 | 737  | 160.7 |
| XHS-21-2R  | 2   | 3   | 0.07 | 800  | 156.0 |
| XHS-19-16  | 2   | 2   | 0.13 | 709  | 160.7 |
| XHS-19-13  | 4   | 18  | 0.33 | 812  | 160.7 |
| XHS-19-14 | 21  | 14  | 0.33 | 780  | 165.9 |
| XHS-19-15C | 77  | 35  | 0.18 | 678  | 150.7 |
| XHS-19-15R  | 63  | 29  | 0.26 | 700  | 161.4 |
| XHS-19-16 | 2   | 2   | 0.13 | 709  | 151.5 |
| XHS-21-1R  | 4   | 9   | 0.15 | 829  | 154.9 |
| XHS-21-2R  | 2   | 3   | 0.07 | 800  | 156.0 |
| XHS-21-C  | 11  | 18  | 0.10 | 755  | 156.0 |

### Dahutang

| Sample | Size | 280 | 120 | 208 | 256 |
|--------|------|-----|-----|-----|-----|
| D27-10 | 26  | 41  | 0.31 | 762  | 142  |
| D27-11 | 27  | 16  | 0.33 | 841  | 151  |
| D27-12 | 55  | 43  | 0.32 | 770  | 146  |
| D27-17 | 4   | 5   | 0.09 | 731  | 142  |
| D27-20 | 45  | 29  | 0.46 | 719  | 148  |
| D27-21 | 9   | 13  | 0.08 | 746  | 144  |
| D27-23 | 13  | 13  | 0.27 | 758  | 150  |
| D27-24 | 12  | 14  | 0.38 | 746  | 145  |
| D27-27 | 30  | 20  | 0.30 | 790  | 141  |
| D27-32 | 19  | 13  | 0.33 | 793  | 150  |
| D27-33 | 3   | 3   | 0.10 | 723  | 139  |
| D27-34 | 15  | 9   | 0.25 | 807  | 152  |
| D27-38 | 61  | 26  | 0.37 | 736  | 140  |
| D27-44 | 9   | 3   | 0.14 | 794  | 136  |
| D32-1  | 25  | 22  | 0.37 | 744  | 143  |
| D32-21 | 20  | 24  | 0.10 | 816  | 147  |
| D32-24 | 11  | 11  | 0.14 | 789  | 139  |
| D32-25 | 2   | 4   | 0.05 | 759  | 148  |
| D32-34 | 10  | 7   | 0.10 | 720  | 145  |
| D32-35 | 59  | 55  | 0.22 | 757  | 144  |
| D32-41 | 75  | 102 | 0.48 | 745  | 154  |
| D32-43 | 25  | 23  | 0.25 | 739  | 147  |
| D32-48 | 28  | 24  | 0.26 | 774  | 146  |
| D32-58 | 9   | 21  | 0.23 | 775  | 153  |
| D32-60 | 13  | 16  | 0.43 | 755  | 142  |
| D32-61 | 9   | 3   | 0.16 | 848  | 154  |
| D32-62 | 50  | 22  | 0.56 | 709  | 155  |

### Xihuashan

| Sample | Size | 280 | 120 | 208 | 256 |
|--------|------|-----|-----|-----|-----|
| XHS-19-1C | 29  | 9   | 0.23 | 744  | 155.6 |
| XHS-19-1R | 2   | 4   | 0.15 | 737  | 160.7 |
| XHS-19-2C | 19  | 25  | 0.11 | 769  | 154.4 |
| XHS-19-2R | 54  | 90  | 0.16 | 724  | 152.6 |
| XHS-19-3C | 2   | 2   | 0.11 | 669  | 152.8 |
| XHS-19-3R | 12  | 37  | 0.17 | 739  | 162.2 |
| XHS-19-4C | 2   | 3   | 0.13 | 757  | 160.7 |
| XHS-19-4R | 8   | 6   | 0.06 | 711  | 160.1 |
| XHS-19-5C | 18  | 8   | 0.29 | 774  | 156.2 |
| XHS-19-5R | 2   | 4   | 0.14 | 701  | 160.8 |
| XHS-19-7 | 22  | 36  | 0.21 | 720  | 162.1 |
| XHS-19-8R | 6   | 5   | 0.04 | 701  | 151.8 |
| XHS-19-9C | 38  | 27  | 0.24 | 695  | 150.2 |
| XHS-19-11C | 7 | 10 | 0.17 | 762  | 156.7 |
| XHS-19-12R | 5 | 13 | 0.18 | 738  | 156.3 |
| XHS-19-13 | 4 | 9 | 0.07 | 890  | 156.8 |
| XHS-19-14 | 21 | 14 | 0.33 | 780  | 165.9 |
| XHS-19-15C | 77 | 35 | 0.18 | 678  | 150.7 |
| XHS-19-15R | 63 | 29 | 0.26 | 700  | 161.4 |
| XHS-19-16 | 2 | 2 | 0.13 | 709  | 151.5 |
| XHS-21-1R | 4 | 9 | 0.15 | 829  | 154.9 |
| XHS-21-2R | 2 | 3 | 0.07 | 800  | 156.0 |
| XHS-21-3C | 11 | 18 | 0.10 | 755  | 156.0 |
| Sample  | ID   | UK  | US  | Italian  | V   |
|---------|------|-----|-----|----------|----|
| XHS-21-3R | 4    | 9   | 0.08 | 680     | 156 |
| XHS-21-4C | 13   | 29  | 0.05 | 655     | 156 |
| XHS-21-4R | 12   | 14  | 0.10 | 684     | 156 |
| XHS-21-5C | 38   | 27  | 0.28 | 694     | 156 |
| XHS-21-5R | 57   | 56  | 0.06 | 687     | 156 |
| XHS-21-6C | 18   | 63  | 0.04 | 667     | 156 |
| XHS-21-6R | 34   | 69  | 0.10 | 654     | 156 |
| XHS-21-7C | 9    | 12  | 0.26 | 779     | 156 |
| XHS-21-8R | 4    | 10  | 0.06 | 715     | 156 |
| XHS-21-9C | 50   | 33  | 0.19 | 748     | 156 |
| XHS-21-9R | 47   | 35  | 0.21 | 723     | 156 |

**Ehu**

| Sample  | ID   | UK  | US  | Italian  | V   |
|---------|------|-----|-----|----------|----|
| D019-07 | 25   | 22  | 0.05 | 769     | 131.1 |
| D019-10 | 21   | 9   | 0.06 | 782     | 132.7 |
| D019-11 | 30   | 19  | 0.05 | 774     | 131.7 |
| D019-14 | 24   | 11  | 0.03 | 768     | 133.2 |
| D019-15 | 7    | 10  | 0.02 | 830     | 132.7 |
| D019-17 | 24   | 15  | 0.04 | 752     | 131.6 |
| D019-18 | 25   | 7   | 0.08 | 790     | 130.4 |
| D019-19 | b.d. | 10  | 0.03 | 724     | 134.3 |
| D019-20 | 15   | 8   | 0.07 | 772     | 131.1 |
| D019-21 | b.d. | 14  | 0.03 | 754     | 133.5 |
| D019-22 | b.d. | 20  | 0.06 | 770     | 132.5 |
| D019-23 | 39   | 16  | 0.07 | 763     | 132.2 |
| D019-24 | 10   | 17  | 0.05 | 759     | 131.9 |
| D019-33 | b.d. | 12  | 0.03 | 701     | 131.3 |
| D019-34 | 17   | 9   | 0.03 | 745     | 131.9 |
| D019-35 | 20   | 15  | 0.03 | 741     | 132.7 |
| D019-41 | 6    | 21  | 0.04 | 743     | 134   |
| D019-43 | b.d. | 22  | 0.04 | 772     | 131.2 |
| D019-44 | 2    | 5   | 0.04 | 744     | 131.3 |
| D019-45 | b.d. | 14  | 0.04 | 740     | 133.4 |
| D019-46 | 2    | 8   | 0.04 | 724     | 131.2 |
| D019-47 | 1    | 4   | 0.05 | 834     | 131.3 |
| D019-48 | b.d. | 13  | 0.02 | 739     | 130   |
| D019-49 | b.d. | 24  | 0.02 | 758     | 132.3 |
| D019-50 | 20   | 7   | 0.07 | 731     | 132.2 |
| D019-51 | 7    | 5   | 0.06 | 739     | 131   |
| D019-55 | b.d. | 12  | 0.04 | 690     | 132.6 |
| D019-60 | 11   | 4   | 0.04 | 792     | 135.8 |
| D019-62 | 3    | 7   | 0.06 | 745     | 138.7 |
| D019-63 | 2    | 8   | 0.05 | 777     | 131.8 |
| D019-83 | 27   | 18  | 0.05 | 726     | 135.7 |
| D019-86 | 3    | 6   | 0.03 | 771     | 131.5 |
| D019-87 | 5    | 6   | 0.06 | 823     | 125.2 |
| D019-91 | 8    | 9   | 0.04 | 789     | 128.5 |
| D019-92 | 203  | 118 | 0.04 | 708     | 131.2 |

**Tongcun**

| Sample  | ID   | UK  | US  | Italian  | V   |
|---------|------|-----|-----|----------|----|
| CB-13-6-01 | 95  | 61  | 0.02 | 688     | 132.2 |
| CB-13-6-02 | 80  | 243 | 0.06 | 735     | 133.8 |
| D019-102 | b.d. | 13  | 0.05 | 786     | 132.5 |
| D019-111 | 1    | 3   | 0.03 | 782     | 135.1 |

**Notes:**
- UK and US are weights in mg.
- Italian is the Italian percentage.
- V is the contamination factor.
| Sample   | No. | Type | Mass | Oxidation | Charge | NO   | Charge |
|----------|-----|------|------|-----------|--------|------|--------|
| CB-13-6-06 | 76  | 142  | 615  | 165       | -19.17 | 1.26 | -16.82 |
| CB-13-6-16 | 51  | 254  | 623  | 158       | -20.15 | 0.01 | -14.11 |
| CB-13-6-18 | 33  | 24   | 721  | 160       | -16.09 | 1.07 | -17.30 |
| CB-13-6-19 | 25  | 31   | 686  | 158       | -19.02 | -0.86 | -18.16 |
| CB-13-6-20 | 88  | 52   | 715  | 155       | -12.68 | 4.65 | -14.71 |
| CB-13-6-29 | 34  | 245  | 613  | 167       | -22.33 | -1.82 | -14.90 |
| CB-13-6-30 | 44  | 25   | 790  | 160       | -11.55 | 3.83 | -13.75 |
| TC-P1-5-02 | 69  | 84   | 720  | 164       | -13.37 | 3.82 | -12.60 |
| TC-P1-5-03 | 50  | 166  | 599  | 161       | -21.80 | -0.79 | -17.32 |
| TC-P1-5-04 | 47  | 157  | 634  | 172       | -19.73 | 0.06 | -15.21 |
| TC-P1-5-06 | 37  | 173  | 612  | 155       | -22.05 | -1.51 | -16.27 |
| TC-P1-5-07 | 50  | 115  | 781  | 174       | -11.53 | 4.07 | -8.39  |
| TC-P1-5-12 | 45  | 218  | 624  | 166       | -20.53 | -0.40 | -14.62 |
| TC-P1-5-14 | 55  | 132  | 654  | 157       | -17.93 | 1.21 | -14.63 |
| TC-P1-5-16 | 65  | 72   | 682  | 162       | -15.64 | 2.64 | -15.25 |
| TC-P1-5-20 | 80  | 50   | 746  | 157       | -11.45 | 5.04 | -13.24 |
| TC-P1-5-21 | 116 | 233  | 632  | 166       | -16.49 | 3.37 | -13.86 |
| TC-P1-5-23 | 91  | 239  | 631  | 160       | -17.48 | 2.42 | -13.83 |
| TC-P1-5-24 | 152 | 413  | 611  | 167       | -16.83 | 3.75 | -13.07 |
| TC-P1-5-27 | 47  | 88   | 615  | 158       | -20.95 | -0.51 | -18.64 |
| TC-P1-29-01 | 28  | 117  | 610  | 163       | -23.28 | -2.67 | -17.89 |
| TC-P1-29-04 | 88  | 281  | 655  | 163       | -16.11 | 3.00 | -11.73 |
| TC-P1-29-07 | 67  | 75   | 684  | 165       | -15.43 | 2.80 | -15.02 |
| TC-P1-29-13 | 106 | 1083 | 635  | 163       | -16.63 | 3.14 | -7.88  |
| TC-P1-29-15 | 27  | 80   | 670  | 166       | -19.62 | -0.97 | -15.55 |
| TC-P1-29-16 | 46  | 117  | 623  | 165       | -20.57 | -0.41 | -17.02 |
| TC-P1-29-17 | 93  | 218  | 637  | 167       | -16.98 | 2.71 | -13.80 |
| TC-P1-29-20 | 22  | 241  | 613  | 171       | -23.89 | -3.39 | -14.97 |
| TC-P1-29-27 | 38  | 222  | 670  | 167       | -18.41 | 0.23 | -11.73 |
| TC-P1-29-29 | 57  | 321  | 636  | 165       | -18.90 | 0.83 | -12.40 |

**Dexing**

| Sample   | No. | Type | Mass | Oxidation | Charge | NO   | Charge |
|----------|-----|------|------|-----------|--------|------|--------|
| FJW1-37-1 | 228 | 181  | 682  | 166       | -10.95 | 7.34 | -11.83 |
| FJW1-37-2 | 101 | 66   | 644  | 174       | -16.23 | 3.22 | -17.81 |
| FJW1-37-2 | 82  | 119  | 678  | 168       | -15.00 | 3.39 | -13.59 |
| FJW1-37-3 | 280 | 195  | 671  | 170       | -10.81 | 7.81 | -12.17 |
| FJW1-37-4 | 92  | 79   | 679  | 167       | -14.52 | 3.86 | -15.08 |
| FJW1-37-5 | 347 | 167  | 670  | 173       | -10.02 | 8.61 | -12.78 |
| FJW1-37-7 | 221 | 665  | 665  | 164       | b.d.   | b.d. | b.d.   |
| FJW1-37-8 | 64  | 91   | 687  | 165       | -15.41 | 2.71 | -14.09 |
| FJW1-37-9 | 126 | 155  | 676  | 169       | -13.53 | 4.94 | -12.74 |
| FJW1-37-11 | 91  | 197  | 669  | 168       | -15.13 | 3.54 | -12.21 |
| FJW1-37-13 | 290 | 175  | 657  | 167       | -11.47 | 7.57 | -13.37 |
| FJW1-37-14 | 192 | 668  | 671  | 171       | b.d.   | b.d. | b.d.   |
| FJW1-37-15 | 207 | 664  | 664  | 166       | b.d.   | b.d. | b.d.   |
| FJW1-37-16 | 269 | 249  | 652  | 167       | -12.05 | 7.15 | -12.34 |
| FJW1-37-17 | 223 | 156  | 690  | 166       | -10.53 | 7.50 | -11.89 |
| FJW1-37-23 | 150 | 693  | 665  | 166       | b.d.   | b.d. | b.d.   |
| FJW1-37-24 | 251 | 665  | 665  | 166       | b.d.   | b.d. | b.d.   |
| FJW1-37-25 | 164 | 681  | 681  | 169       | b.d.   | b.d. | b.d.   |
| FJW1-37-26 | 173 | 683  | 683  | 169       | b.d.   | b.d. | b.d.   |
| FJW1-37-28 | 328 | 184  | 678  | 166       | -9.77  | 8.62 | -11.95 |
| FJW1-37-29 | 156 | 670  | 670  | 164       | b.d.   | b.d. | b.d.   |
| FJW1-37-30 | 399 | 252  | 677  | 165       | -9.09  | 9.34 | -10.81 |
| Sample Code | Cl (ppm) | Na (ppm) | Si (ppm) | Mg (ppm) | Fe2O3 (%) | FeO (%) |
|------------|----------|----------|----------|----------|------------|---------|
| FJW1-37-2.11 | 100 | 150 | 662 | 173 | -15.18 | 3.70 | -13.66 | 5.23 |
| FJW1-37-2.12 | b.d. | 149 | 676 | 168 | b.d. | b.d. | -12.91 | 5.57 |
| FJW1-37-2.13 | 217 | 289 | 684 | 166 | -11.00 | 7.22 | -9.93 | 8.29 |
| FJW1-37-2.14 | 384 | 224 | 677 | 170 | -9.28 | 9.16 | -11.30 | 7.14 |
| FJW1-37-2.15 | 145 | 152 | 670 | 169 | -13.34 | 5.32 | -13.16 | 5.50 |
| FJW1-37-2.16 | 78 | 158 | 685 | 163 | -14.80 | 3.39 | -12.13 | 6.06 |
| TC44-1 | 180 | 107 | 690 | 170 | -11.37 | 6.67 | -13.31 | 4.73 |
| TC44-4 | b.d. | 63 | 676 | 178 | b.d. | b.d. | -16.13 | 2.34 |
| TC44-6 | 221 | 96 | 674 | 171 | -11.48 | 7.03 | -14.62 | 3.88 |
| TC3-1 | 150 | 143 | 710 | 170 | -10.94 | 6.53 | -11.12 | 6.35 |
| TC3-2 | 86 | 94 | 701 | 160 | -13.54 | 4.19 | -13.19 | 4.54 |
| TC3-3 | 81 | 121 | 674 | 170 | -15.26 | 3.25 | -13.74 | 4.77 |
| TC3-4 | 28 | 125 | 812 | 173 | -12.27 | 2.60 | -6.69 | 8.18 |
| TC3-5 | 260 | 112 | 669 | 172 | -11.18 | 7.50 | -14.36 | 4.32 |
| TC3-6 | 33 | 63 | 665 | 171 | -19.15 | -0.36 | -16.73 | 2.06 |
| TC43-1 | 259 | 184 | 657 | 176 | -11.90 | 7.14 | -13.19 | 5.85 |
| TC43-2 | 265 | 274 | 684 | 167 | -10.24 | 7.98 | -10.11 | 8.11 |
| TC43-3 | 322 | 162 | 700 | 176 | -8.59 | 9.15 | -11.18 | 6.56 |
| TC43-4 | 362 | 192 | 690 | 173 | -8.76 | 9.30 | -11.16 | 6.90 |
| TC44-8 | 431 | 186 | 661 | 170 | -9.74 | 9.18 | -12.90 | 6.02 |
| TC44-9 | b.d. | 179 | 657 | 169 | b.d. | b.d. | -13.32 | 5.74 |
| TC44-10 | b.d. | 177 | 686 | 173 | b.d. | b.d. | -11.68 | 6.49 |
| TC44-13 | b.d. | 213 | 627 | 170 | b.d. | b.d. | -14.49 | 5.52 |
| TC44-14 | b.d. | 207 | 658 | 166 | b.d. | b.d. | -12.69 | 6.32 |
| TC44-15 | 330 | 211 | 670 | 175 | -10.22 | 8.42 | -11.90 | 6.74 |
| TC44-16 | 240 | 201 | 659 | 173 | -12.05 | 6.92 | -12.72 | 6.25 |
| TC44-17 | b.d. | 106 | 677 | 178 | b.d. | b.d. | -14.13 | 4.31 |
| TC44-19 | 206 | 175 | 666 | 167 | -12.25 | 6.53 | -12.87 | 5.91 |
| TC3-9 | 354 | 165 | 655 | 171 | -10.85 | 8.26 | -13.74 | 5.37 |
| TC3-10 | b.d. | 225 | 672 | 171 | b.d. | b.d. | -11.56 | 7.03 |
| TC3-12 | 392 | 198 | 676 | 176 | -9.24 | 9.23 | -11.81 | 6.66 |
| TC3-13 | 264 | 346 | 688 | 173 | -10.03 | 8.07 | -9.00 | 9.09 |
| TC3-14 | 397 | 180 | 665 | 175 | -9.85 | 8.96 | -12.83 | 5.98 |
| TC3-15 | b.d. | 226 | 659 | 169 | b.d. | b.d. | -12.31 | 6.68 |
| TC3-16 | 422 | 252 | 685 | 162 | -8.46 | 9.74 | -10.40 | 7.80 |
| TC3-17 | 357 | 192 | 674 | 158 | -9.72 | 8.81 | -12.05 | 6.48 |
| TC3-18 | 43 | 110 | 671 | 172 | -17.82 | 0.79 | -14.28 | 4.32 |
| TC3-19 | b.d. | 184 | 691 | 168 | b.d. | b.d. | -11.25 | 6.77 |
| TC3-20 | 243 | 204 | 674 | 160 | -11.17 | 7.37 | -11.83 | 6.71 |
| TC3-21 | 175 | 210 | 667 | 169 | -12.80 | 5.94 | -12.11 | 6.63 |
| TC3-22 | 383 | 164 | 680 | 172 | -9.07 | 9.26 | -12.26 | 6.07 |
| TC3-23 | 258 | 179 | 666 | 164 | -11.37 | 7.39 | -12.75 | 6.01 |
| TC3-24 | 371 | 171 | 666 | 162 | -10.02 | 8.75 | -12.94 | 5.83 |
| TC3-25 | b.d. | 126 | 686 | 167 | b.d. | b.d. | -12.92 | 5.24 |
| TC3-26 | 429 | 151 | 698 | 161 | -7.66 | 10.16 | -11.59 | 6.22 |
| TC3-27 | 389 | 142 | 668 | 166 | -9.73 | 8.98 | -13.53 | 5.18 |
| TC3-28 | b.d. | 290 | 654 | 179 | b.d. | b.d. | -11.68 | 7.47 |
| TC3-29 | 230 | 67 | 681 | 167 | -10.93 | 7.38 | -15.58 | 2.73 |
| TC3-30 | 439 | 251 | 674 | 178 | -8.90 | 9.61 | -11.00 | 7.51 |
| TC3-32 | 30 | 124 | 685 | 175 | -18.42 | -0.23 | -13.04 | 5.15 |
| TC3-33 | b.d. | 221 | 673 | 169 | b.d. | b.d. | -11.56 | 6.99 |
| TC3-34 | 386 | 201 | 683 | 172 | -8.87 | 9.37 | -11.33 | 6.91 |
| TC43-6 | 391 | 194 | 687 | 173 | -8.60 | 9.53 | -11.23 | 6.90 |
| TC43-7 | 314 | 138 | 660 | 174 | -10.99 | 7.96 | -14.09 | 4.86 |
| Spot  | 176Yb/177Hf | 176Lu/177Hf | 176Hf/177Hf | εHf(t) | TDM2(Ma) |
|-------|----------|------------|-------------|--------|---------|
| Dahutang |          |            |              |        |         |
| 1     | 0.0029405| 0.0000436  | 0.2824949    | −6.5   | 1042    |
| 2     | 0.0118261| 0.0002274  | 0.2824995    | −6.4   | 1078    |
| 3     | 0.0069998| 0.0001264  | 0.2825899    | −3.1   | 1143    |
| 4     | 0.0250298| 0.0005874  | 0.2825216    | −5.6   | 1166    |
| 5     | 0.0182471| 0.0003612  | 0.2824659    | −7.6   | 1194    |
| 6     | 0.0328127| 0.0006971  | 0.2825122    | −5.9   | 1195    |
| 7     | 0.0013712| 0.0000202  | 0.2824347    | −8.6   | 1210    |
| 8     | 0.0056955| 0.0000978  | 0.282509     | −4.5   | 1219    |
| 9     | 0.0160187| 0.0003447  | 0.282492     | −6.6   | 1229    |
| 10    | 0.0205019| 0.0004278  | 0.2824932    | −6.6   | 1236    |

Notes: (1) Temperatures were calculated with the Ti-in-zircon thermometer [37]. (2) Oxygen fugacities were calculated by the method proposed by [43]. (3) Trace elements data from [5] for Dahutang complex, Qiu et al. [26] for Ehu granite and Yang et al. [28] for Xihuashan granite. b.d. = below the detection limit. “a” and “b” mean the values are calculated by the La-Pr and Nd-Sm interpolation methods respectively.

Table A2. Zircon Hf isotope data of the Dahutang and Xihuashan granites.
|   | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---------|---------|---------|---------|---------|---------|---------|
| 11 | 0.0593198 | 0.0012226 | 0.2826147 | -2.4 | 1241 |
| 12 | 0.0240443 | 0.0004526 | 0.2825063 | -6.1 | 1242 |
| 13 | 0.0373943 | 0.0008386 | 0.2824021 | -10 | 1250 |
| 14 | 0.0358791 | 0.0008128 | 0.2825389 | -5.2 | 1286 |
| 15 | 0.0435529 | 0.0008814 | 0.2824529 | -8.2 | 1310 |
| 16 | 0.0209965 | 0.0004417 | 0.2824873 | -7 | 1336 |
| 17 | 0.0240384 | 0.0004984 | 0.282521 | -5.8 | 1394 |

Xihuashan

|   | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---------|---------|---------|---------|---------|---------|---------|
| XHS-19-1 | 0.02924 | 0.00102 | 0.282296 | -13.5 | 1473 |
| XHS-19-2 | 0.011224 | 0.00045 | 0.282298 | -13.4 | 1475 |
| XHS-19-3 | 0.06476 | 0.00209 | 0.28231 | -13.1 | 1480 |
| XHS-19-4 | 0.03147 | 0.00108 | 0.282346 | -11.7 | 1481 |
| XHS-19-5 | 0.03242 | 0.00121 | 0.282274 | -14.3 | 1482 |
| XHS-19-6 | 0.02409 | 0.00085 | 0.282323 | -12.5 | 1487 |
| XHS-19-7 | 0.02377 | 0.00084 | 0.282271 | -14.3 | 1488 |
| XHS-19-9 | 0.02463 | 0.00087 | 0.282345 | -11.7 | 1490 |
| XHS-19-10 | 0.05415 | 0.00187 | 0.282352 | -11.6 | 1490 |
| XHS-19-11 | 0.03011 | 0.001 | 0.282257 | -14.9 | 1498 |
| XHS-19-13 | 0.03034 | 0.00106 | 0.282333 | -12.2 | 1501 |
| XHS-19-14 | 0.03688 | 0.00137 | 0.28234 | -12 | 1502 |
| XHS-19-16 | 0.04093 | 0.00155 | 0.282306 | -13.2 | 1504 |
| XHS-19-17 | 0.03498 | 0.00118 | 0.282287 | -13.8 | 1505 |
| XHS-19-18 | 0.03031 | 0.00106 | 0.282306 | -13.1 | 1509 |
| XHS-19-19 | 0.02442 | 0.0009 | 0.282344 | -11.8 | 1512 |
| XHS-19-20 | 0.02868 | 0.00107 | 0.282349 | -11.6 | 1515 |
| XHS-9-8 | 0.13465 | 0.00438 | 0.282339 | -12.3 | 1520 |
| XHS-9-10 | 0.05669 | 0.00197 | 0.282323 | -12.6 | 1524 |
| XHS-9-15 | 0.13349 | 0.00445 | 0.28232 | -13 | 1530 |
| XHS-9-17 | 0.07194 | 0.00274 | 0.282331 | -12.4 | 1547 |
| XHS-9-18 | 0.07813 | 0.00286 | 0.282343 | -12 | 1552 |
| XHS-9-19 | 0.04143 | 0.00151 | 0.282356 | -11.4 | 1553 |
| XHS-9-20 | 0.21745 | 0.00776 | 0.282351 | -12.2 | 1556 |
| XHS-10-4 | 0.02976 | 0.00103 | 0.282353 | -11.5 | 1564 |
| XHS-10-5 | 0.12769 | 0.00443 | 0.282347 | -12 | 1570 |
| XHS-10-6 | 0.02777 | 0.00105 | 0.282335 | -12.1 | 1585 |
| XHS-10-10 | 0.10121 | 0.00369 | 0.282358 | -11.6 | 1607 |
| XHS-10-18 | 0.07579 | 0.00283 | 0.282341 | -12.1 | 1610 |
| XHS-10-19 | 0.13134 | 0.00474 | 0.282355 | -11.8 | 1634 |

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