

# Late Mesozoic oxidized magma for porphyry Ag mineralization: A comparative study from mineralized and barren granite porphyries in the Lengshuikeng Ag-(Pb-Zn) deposit, South China



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## ABSTRACT

The Lengshuikeng Ag-(Pb-Zn) deposit (LSKD) is one of the largest independent porphyry silver deposits in China. Its silver mineralization is related to the Late Mesozoic granite porphyry, but the oxidizing hydrous conditions of the associated magma are still unclear. This study focuses on the associated granite porphyry (GP) and barren K-feldspar granite porphyry (KFGP) to constrain their oxidizing hydrous conditions. New zircon U-Pb dating shows the GP emplaced at  $155.8 \pm 1.9$  Ma and  $158.5 \pm 2.3$  Ma for GP, and the KFGP emplaced at  $136.6 \pm 1.9$  Ma. Both granites are peraluminous with A/CNK ratios of 1.09–3.01 (mean = 1.48), similar to that of typical S-type granites. They are enriched in light rare earth elements (LREE), with large  $(La/Yb)_N$  (7.0–19.1 for the GP and 1.8–34.3 for the KFGP) and negative Eu anomalies (0.29–0.67 for the GP and 0.02–0.05 for the KFGP). The GP has  $\epsilon_{\text{Nd}}(t)$  values ranging from  $-10.0$  to  $-9.7$  with  $T_{\text{DM2}}$  ages of 1688–1915 Ma, while the KFGP has higher  $\epsilon_{\text{Nd}}(t)$  values ranging from  $-7.5$  to  $-7.6$  with younger  $T_{\text{DM2}}$  ages of 1538–1548 Ma. The initial Pb isotopic ratios for  $(^{206}\text{Pb}/^{204}\text{Pb})_i$ ,  $(^{207}\text{Pb}/^{204}\text{Pb})_i$  and  $(^{208}\text{Pb}/^{204}\text{Pb})_i$  are 17.647–17.952, 15.555–15.604 and 37.851–38.541, respectively. Our new chemical and isotopic data suggest that both granites were dominantly derived from dehydration melting of the Proterozoic meta-sedimentary rocks, with more dehydration fluids for the GP and relatively more mantle contribution to the KFGP. Both granites underwent fractional crystallization of plagioclase, K-feldspar and ilmenite/magnetite followed by minor assimilation of the upper crust. Comparative study on the relative water content, oxidation state and melting temperature of magma have shown relatively moderate oxidation state and water content in the associated magma probably played more important roles in porphyry silver mineralization than other factors in porphyry Cu deposit. This study helps deepen the understanding of silver mineralization.

## 1. Introduction

Silver often occurs with other metals, such as Cu and Au, in hydrothermal deposits. The styles of silver hydrothermal mineralization can vary from veins, skarn, greisen to porphyry type. Increasing giant independent silver deposits as a general porphyry type or a special epithermal type (unified as porphyry type below), such as Pachuca (45,000 t Ag) and Fresnillo (16,050 t Ag) in Mexico and El Indio (3100 t Ag) in Chile, have attracted great attention due to their high grades and large tonnages (Simmons et al., 2005). The porphyry Ag ore bodies are usually far away from the central granite porphyry. This leads to the difficulty to identify ore-related granite porphyry and insufficient research on their mineralization fertility. Most researchers

suggest the silver mineralization is related to magmatic-hydrothermal activities of intermediate-felsic magma (e.g. Megaw et al., 1988). The metal and sulfur of porphyry copper mineralization have been thought to be magmatic origin (Cline and Bodnar, 1991; Hedenquist and Lowenstern, 1994; Candela and Piccoli, 2005; Halter et al., 2005; Williams-Jones and Heinrich, 2005; Zajacz et al., 2008), but the nature of silver-mineralization-related magma remains unclear.

Previous studies have shown granites related to porphyry Cu deposit generally have relatively high  $f\text{O}_2$  ( $f\text{O}_2 > \Delta\text{FMQ} + 2$  or  $\Delta\text{NNO} + 1$ ) and water contents as the precondition for the formation of copper-rich metallogenetic magma (Mungall, 2002; Jugo, 2009; Richards, 2003, 2009; Griffin et al., 2013; Hou et al., 2015, 2017; Sun et al., 2017). Similar to copper, silver is an incompatible chalcophile element, and its

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behavior is also strongly controlled by sulfides. The speciation of sulfur is controlled by oxygen fugacity. Hence, it is speculated that a relatively high oxygen fugacity is a necessary condition for making a silver deposit. In addition, more water content in magma source will promote the differentiation of magma and the formation of ore-forming fluid (Richards, 2011; Wang et al., 2014b,c). However, the  $f_{\text{O}_2}$  and water content of the granite porphyry related to porphyry Ag deposit has not been well constrained.

The Lengshuikeng Ag-(Pb-Zn) deposit (LSKD), with an ore reserves of ~43 Mt and average grades of 204.53 g/t Ag, 2.11% Pb and 2.61% Zn, is one of the largest independent porphyry silver deposits in China (Wang et al., 2014a). Based on the alteration zoning characteristics, consistency of mineralization and magmatic crystallization chronology, the silver mineralization is closely related to the granite porphyry occurred in the LSKD (Wang et al., 2014a; Meng et al., 2007, 2012). This study focuses on the mineralized granite porphyry and barren granite in the LSKD, and compares their magma sources, formation, evolution, oxygen fugacity, and water content, to clarify the controlling factors on silver mineralization. This study also helps us deepen the current understanding of silver mineralization.

## 2. Regional geology

The Lengshuikeng Ag-Pb-Zn deposit locates in the north part of the Wuyi metallogenic belt (Ye, 1987; Liu et al., 1994; Yang et al., 2004; Meng et al., 2007; Wang et al., 2010), and on the southern side of the Gan-Hang Tectonic Belt (GHTB), which is the northeastern boundary between the Yangtze and Cathaysia blocks (Fig. 1, Li et al. 2011; Wong et al. 2011). In the North Wuyi Area (NWA), the Dongxiang, Tianhuashan, Huanggangshan, and Lizikeng (Tongboshan) Basins distribute

along the regional EW-trending basement uplift, represented by a prominent series of NNE-trending volcanic basins (Fig. 1b). Many ore deposits developed within these volcanic basins, such as the Lengshuikeng Ag-Pb-Zn deposit, Xiongjashan Mo deposit, Shengmikeng Pb-Zn deposit, Jiaotang Pb-Zn deposit and Jinzhuping Mo deposit (Fig. 1; Luo et al., 2009; Su et al., 2013), all of which are related to the Late Mesozoic magmatism (Liu et al., 1994; Meng et al., 2007; Wang et al., 2010; Yang et al., 2004; Ye, 1987).

The NWA has undergone a long and complex geodynamic evolution from Proterozoic to Mesozoic (Yu et al., 2009), including the Neoproterozoic continental amalgamation between the Yangtze and Cathaysia blocks (WX, Li et al., 2008); the Kwangian tectonothermal events that are synchronous with the Early Paleozoic orogeny in South China (ZX, Li et al., 2010; Yu et al., 2012); and the Indosinian (Late Permian to Triassic) and Yanshanian (Jurassic to Cretaceous) tectonothermal events (Lu et al., 2007; Mei, 1998; Yu et al., 2012; Wang et al., 2013b). Pre-Sinian basement rocks, Sinian to Middle Triassic marine sedimentary strata, Mesozoic–Cenozoic terrestrial sequence and volcanic rocks comprise the stratigraphic system in the NWA. Several unconformities between different structural layers exist within the system. The lower member of the basement is a set of metamorphic rocks formed between Late Archean and Early Proterozoic, whereas the upper part of the basement consists of Late Meso-Neoproterozoic metamorphic strata that were originally marine volcanic-sedimentary formations (Zhao, 1999). The lower members of the covering strata include the Lower Sinian to Lower Paleozoic continuous sedimentary rocks with low-grade metamorphic flyschoid formations. The upper member of the covering rocks consists of Devonian–Middle Triassic strata. The Late Triassic–Cretaceous strata are widely and continuously distributed in the NWA. They are dominated by continental sedimentary and volcanic

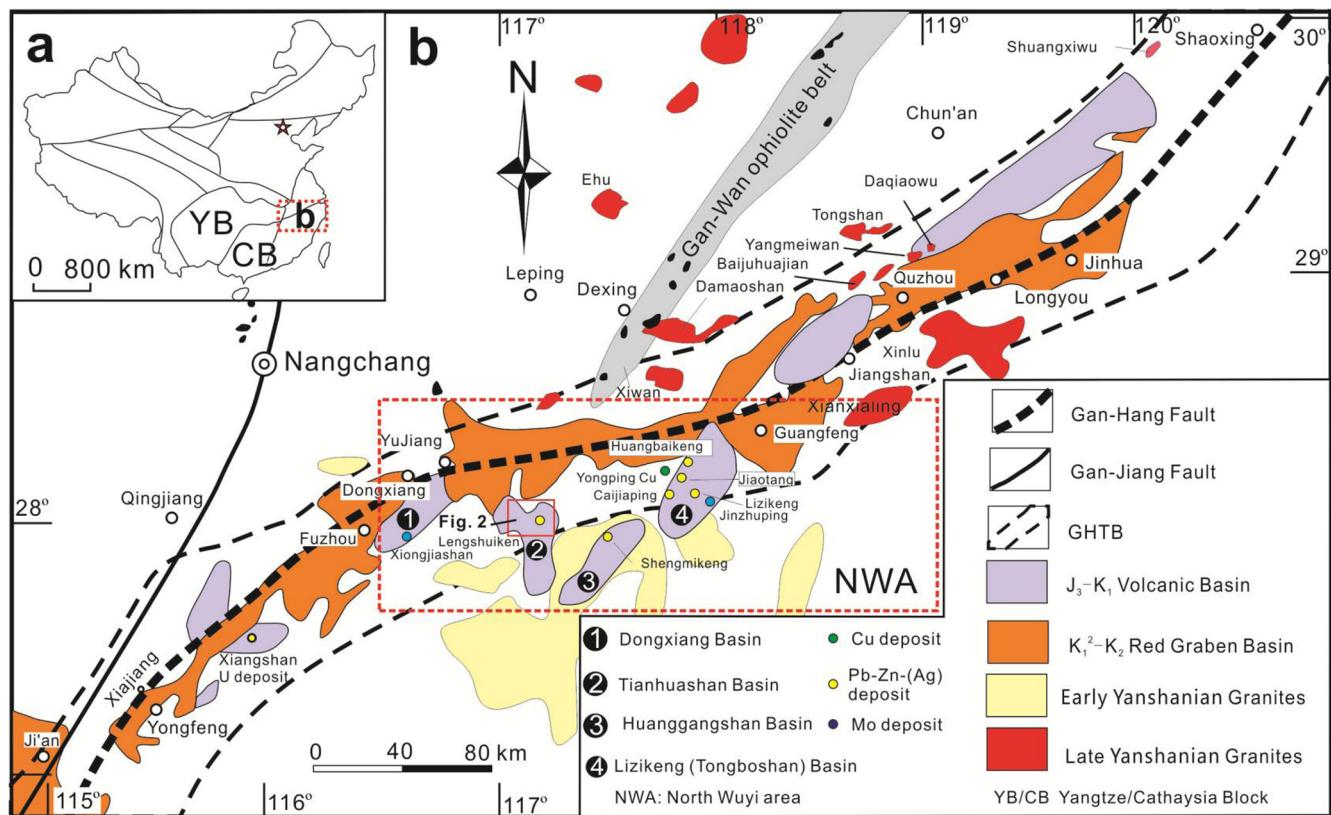
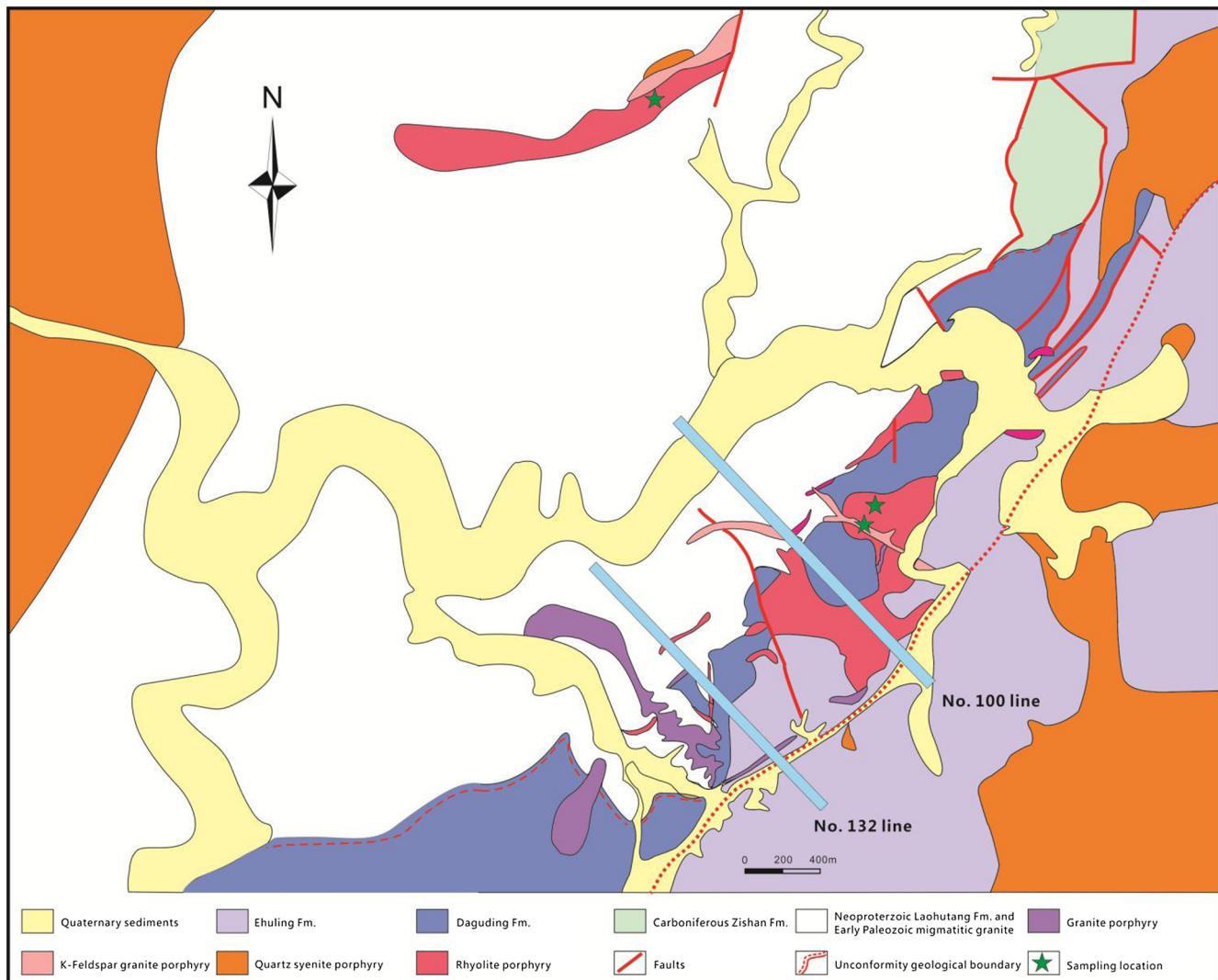


Fig. 1. (a) Simplified map of China; (b) Geological map of the Gan-Hang tectonic belt (GHTB), and volcanic basins in the North Wuyi Area (NWA), South China (modified from Qi et al., 2016).



**Fig. 2.** Geological map of the Lengshuikeng Ag-(Pb-Zn) deposit (LSKD).

rocks, substantially varying in longitudinal and landscape orientations (JXBGMR (Bureau of Geology and Mineral Resources of Jiangxi Province), 1984; JXBGMR (Department of Geology and Mineral Resources of Jiangxi Province), 1997; Liu et al., 1994; Mei, 1998; Xie et al., 2006).

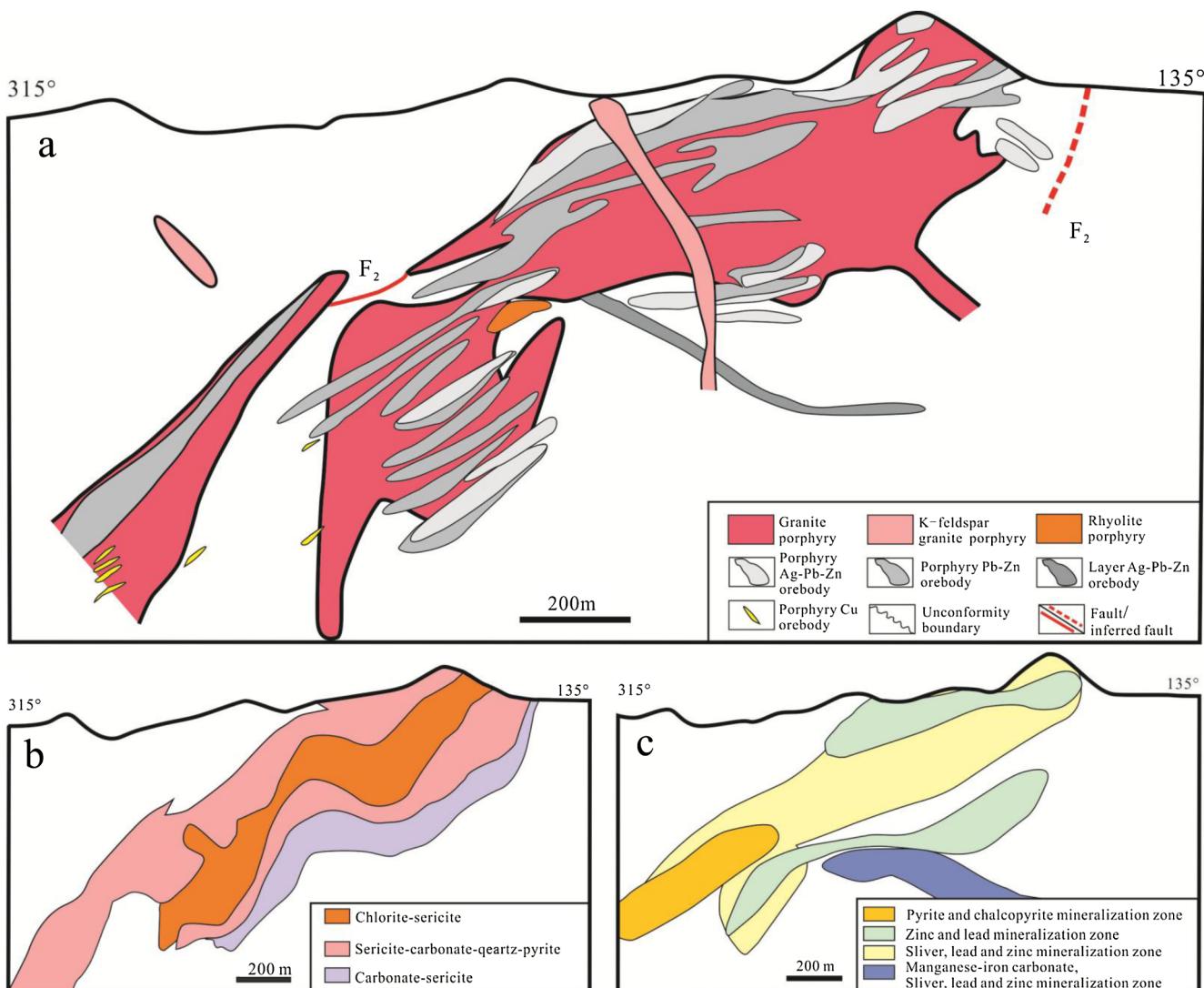
### 3. Deposit geology

The stratigraphic sequence in the Lengshuikeng Ag-(Pb-Zn) deposit contains the Jurassic Daguding and E'huling Formations (Meng et al., 2007). The Daguding Formation occurring in the middle part is comprised of andesite and rhyolitic tuffs and tuffaceous siltstone, and the E'huling Formation outcropping continuously in the northeast consists of tuffs, rhyolite, tuffaceous siltstone, sandstone, and manganese- and iron-rich carbonates. The prominent structural features in the LSKD are NE-striking reverse faults dipping toward NW, including  $F_1$  and  $F_2$  (Fig. 2). The  $F_1$  fault was formed before the eruption and sedimentation of the E'huling and Daguding formations, whereas the  $F_2$  fault may have been initiated during and continued after their eruption and sedimentation (Wang et al., 2014a). The footwall of  $F_2$  fault displays a normal stratigraphic sequence of E'huling ( $J_{3e}$ ) and Daguding ( $J_{3d}$ ), whereas its hanging wall exhibits a sequence of Sinian rocks (Laohutang Formation,  $Z_{2l}$ ) (Fig. 2). The  $F_2$  fault is the most important rock- and

ore-controlling structure in the LSKD. The Jurassic granite porphyry intruded along the  $F_2$  fault, and the occurrence of lead, zinc and silver ore bodies are also controlled by  $F_2$  fault (Qi et al., 2015).

The magmatism in the LSKD mainly developed in the Early Paleozoic, Late Jurassic and Early Cretaceous. The Early Paleozoic igneous rocks comprise of pegmatite and migmatitic granite prior to the metal mineralization. The Jurassic igneous rocks are mainly hypabyssal granite porphyry including the Yinluling and Yinzushan porphyries related to the Ag-Pb-Zn mineralization. The Early Cretaceous rocks include quartz syenite porphyry, rhyolite porphyry and K-feldspar granite porphyry (Fig. 2). Previous studies have reported that rhyolite porphyry and K-feldspar granite porphyry cut the granite porphyry and pyroclastic carbonate ore-hosted rocks as well as the quartz syenite porphyry (Meng et al., 2007). SHRIMP and LA-ICP-MS zircon U-Pb dating has identified the ages for the granite porphyry (155 Ma, 157 Ma, and 162 Ma), K-feldspar granite porphyry (140 Ma), quartz syenite porphyry (139 Ma and 144 Ma) and rhyolite porphyry (140 Ma) (Meng et al., 2012; Qiu et al., 2013; Su et al., 2013; Wang et al., 2013a; Yu et al., 2012).

Two types of mineralization have been identified in the LSKD. One type is vein-veinlet-disseminated Ag-Pb-Zn-Cu-Au mineralization which is mainly developed in the Yinluling porphyry and its periphery. The ore bodies mainly occur in the major body of porphyry granite, with the



**Fig. 3.** (a) Geological features; (b) alteration zoning; and (c) mineralization zoning along No. 100 section in the LSKD.

inner zone in contact between the granite porphyry and country rocks. The other type is massive Ag-Pb-Zn-Fe-Mn mineralization sandwiched in layered volcanic clastic rocks of the Daguding Formation. This type of mineralization is generally under the first type ore body (Fig. 3). In general, the spatial distribution of ore bodies in porphyry is related to alteration and superposition. The Cu-rich ore body is closely associated with chlorite and sericite alteration in the inner zone of porphyry granite, while the Pb-Zn-Ag ore body is hosted in sericitization, carbonatization and silicification zone. The Ag-Pb-Zn ore body with carbonatization and sericitization situated in the outer peripheral (or distal) zone (Fig. 3). Although the occurrence, mineral constituents, and the zoning of alteration assemblages of both mineralization types are distinct from each other, they are considered to have resulted from the same mineralization system closely related to magmatic-hydrothermal fluids of granite porphyry (Qi et al., 2015; Leng and Qi, 2018). The major ore minerals of the LSKD include sphalerite, galena, pyrite and various silver minerals. The dominant silver minerals are acanthite ( $\text{Ag}_2\text{S}$ ) and native silver, which occur in fissures within manganese-iron carbonate or in the intergranular space between manganese-iron carbonate and early sulfides (Lu et al., 2012).

#### 4. Samples and analytical methods

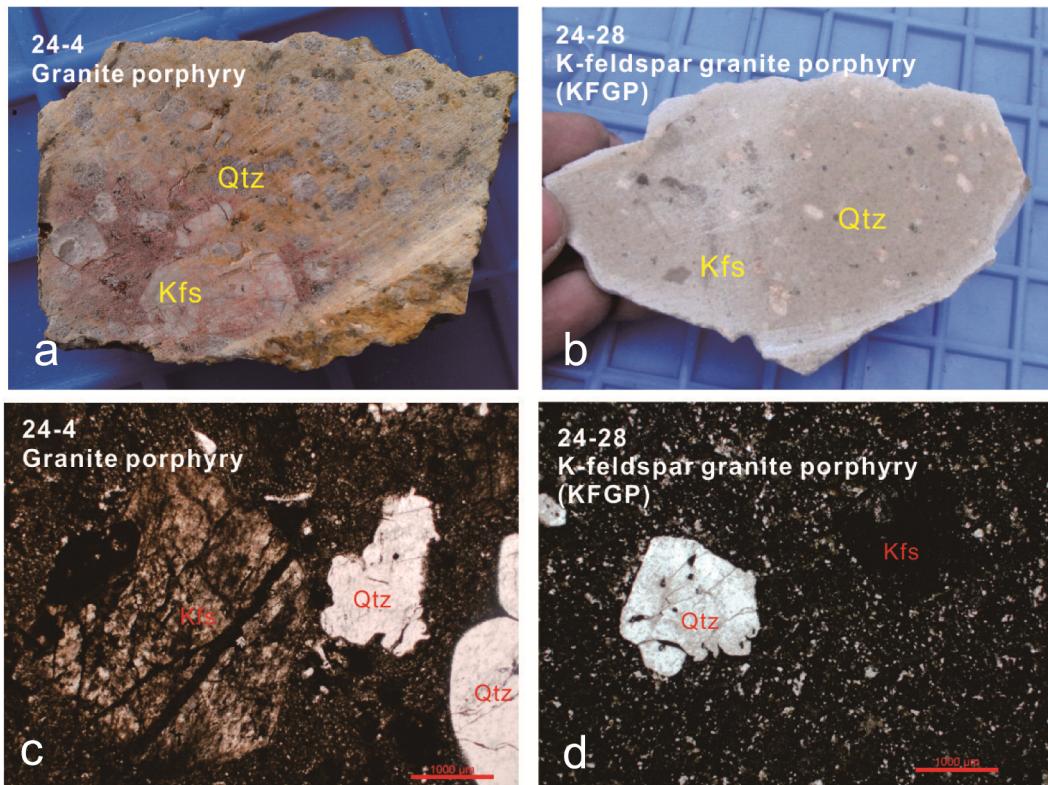
##### 4.1. Samples

###### 4.1.1. Granite porphyry (GP)

The granite porphyry outcrops in two places, with one hosting the main ore-body and the other in the northwest part of the LSKD (Fig. 2), where both plutons exhibit porphyritic texture (Fig. 4). The phenocrysts are mainly quartz and K-feldspar (about 15–35% in volume) with grains of 0.5–10 mm, whereas the groundmass is fine-grained (0.01–0.07 mm). Rock-forming minerals include quartz (37–65%), K-feldspar (21–49%), plagioclase (7–13%), and minor biotite (< 1–2%). Accessory minerals are mainly zircon and apatite. Four GP samples were collected in the northwest part of the mining area, and another sixteen samples of GP were collected in Yinzushan.

###### 4.1.2. K-feldspar granite porphyry (KFGP)

The K-feldspar granite porphyry intrusion outcrops in Yinzushan (Fig. 2) and is pinkish with porphyritic texture (Fig. 4). The phenocrysts (about 5–8%) are euhedral grains of K-feldspar and quartz, whereas the



**Fig. 4.** Photographs and photomicrographs of representative specimens from the granite porphyry (GP) and the K-feldspar granite porphyry (KFGP) in the LSKD. Kfs: K-feldspar; Qtz: quartz.

groundmass shows a fine-grained texture consisting of K-feldspar, quartz and minor biotite. Previous studies yielded a LA-ICP-MS zircon U-Pb ages of 138.6 Ma and 140 Ma, respectively (Su et al., 2014; Wang et al., 2013a). In this study, seven KFGP samples were collected for analysis.

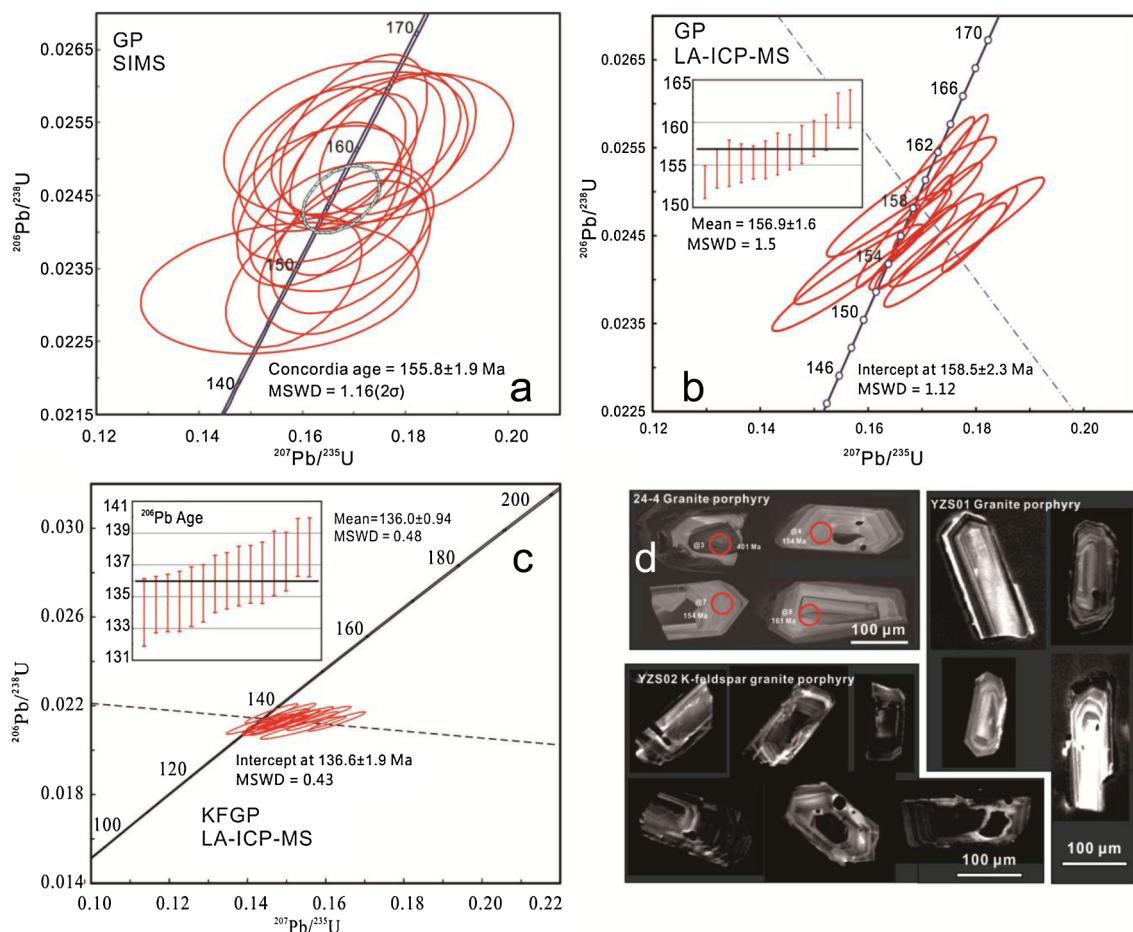
#### 4.2. Analytical methods

Zircons were extracted from samples using conventional heavy liquid and magnetic techniques. Representative zircon grains were handpicked under a binocular microscope and mounted in an epoxy resin mount, and then polished and coated with a gold film, which was documented with transmitted and reflected light micrographs as well as cathodoluminescence (CL) images to reveal their internal structures. The CL images were obtained using LEO1450VP scanning electron microscope at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), Beijing. The zircon U-Pb isotopic analyses and U, Th and Pb concentrations were also determined in IGGCAS, using the Cameca IMS-1280 SIMS. The analytical procedures are the same as those described by Li et al. (2009). The analytical pits were about  $20 \times 30 \mu\text{m}$  in size and ellipsoidal in shape. Pb/U calibration was performed relative to standard zircon 91500 with U and Th concentrations of ca. 81 and 29 ppm, respectively (Wiedenbeck et al., 1995). Analyses of the standard zircon Plésovice were carried out after every 3–4 unknown analyses. U-Th-Pb ratios was calibrated against measured ratios of standard zircon Plésovice with an age of 337 Ma (Sláma et al., 2008). Measured compositions were corrected for common Pb using the measured non-radiogenic  $^{204}\text{Pb}$ . Uncertainties on individual analyses are reported at 1SD level, and the ages for pooled U-Pb analyses are quoted with 2SD. Data reduction was carried out using the Isoplot/Ex v.4.15 program of Ludwig (2008). In order to monitor the external uncertainties of SIMS U-Pb measurements calibrated against Plésovice standard, Qinghu zircon standard was alternately

analyzed as an unknown together with the unknown zircons. A total of 8 measurements were conducted on Qinghu zircon, and the Concordia Age of  $160.3 \pm 1.7$  Ma (2SD) is identical within error with the recommended value of  $159.2 \pm 0.2$  Ma (2SD) (Li et al., 2013a,b).

Zircon U-Pb dating and trace element analyses were simultaneously by LA-ICP-MS at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry Chinese Academy of Sciences (SKLODG, IGGCAS), Guiyang. Laser ablation was performed using a RESolution 193 nm ArF excimer laser. An Agilent 7900 ICP-MS instrument was used to acquire ion-signal intensities. Helium was applied as a carrier gas which was mixed with Argon via a T-connector before entering the ICP-MS. Each analysis incorporated a background acquisition of approximately 30 s (gas blank) followed by 60 s of data acquisition from the sample. Off-line data processing selection and integration of background and analytical signals, time-drift correction and quantitative calibration for trace element analyses and U-Pb dating were performed by ICPMSDataCal (Liu et al., 2010). zircon 91500 was used as the external standard for U-Pb dating and analyzed twice every 6–8 analyses. Uncertainty of preferred values for the external standard 91500 was propagated to the ultimate results of the samples. Concordia diagrams and weighted mean age calculations were made using Isoplot (Ludwig, 2008). Trace element compositions of zircons were calibrated against multiple-reference materials (NIST 610) combined with Si internal standardization. The preferred values of element concentrations for the USGS reference glasses are from the GeoReM database (<http://georem.mpcg-mainz.gwdg.de/>).

Major elements of whole rocks were analyzed using the Axios PW4400 X-ray fluorescence spectrometer on fused lithium tetraborate glass pellets with analytical precision greater than 5% at the SKLODG. Trace elements of whole rocks were analyzed using a PE DRC-e ICP-MS at the SKLODG. Approximately 50 mg of sample powder was dissolved in high-pressure Teflon bombs using an  $\text{HF} + \text{HNO}_3$  mixture. Rh was used as an internal standard to monitor signal drift during analysis. The



**Fig. 5.** (a) Zircon SIMS U-Pb ages of the granite porphyry (GP). (b) LA-ICP-MS U-Pb ages of the granite porphyry (GP). (c) LA-ICP-MS U-Pb ages of the K-feldspar granite porphyry (KFGP). (d) CL images of representative zircons in the LSKD.

analytical uncertainty was generally greater than 5%. The detailed analytical procedures are similar to those given in Qi et al. (2000).

Whole-rock Sr-Nd isotopic measurements were performed on a Triton thermal ionization mass spectrometer at the SKLODG and Tianjin Geological Survey Center, China Geological Survey. Samples for Sr and Nd isotopic analysis were initially dissolved in the mixture of HF, HNO<sub>3</sub>, and HClO<sub>4</sub> in Teflon bombs. Sr, Rb, Sm and Nd were then separated by conventional cation exchange techniques in the HDEHP-coated Kef columns. The mass fractionation corrections for Sr and Nd isotopic ratios are based on <sup>86</sup>Sr/<sup>88</sup>Sr = 0.1194 and <sup>146</sup>Nd/<sup>144</sup>Nd = 0.7219, respectively. The <sup>87</sup>Sr/<sup>86</sup>Sr ratio of the NBS987 Sr standard was determined to be 0.710258 ± 7 (2SD). The <sup>143</sup>Nd/<sup>144</sup>Nd ratios of the JNDI-1 Nd standard solutions were determined to be 0.512104 ± 5 (2SD).

Lead isotope compositions of sulfides were analyzed on an IsoProbe-T thermal ionization mass spectrometer (TIMS) at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology. Lead was separated and purified by a conventional anion-exchange technique (AG1 × 8, 100–200 resin) with diluted HBr used as eluent. The <sup>208</sup>Pb/<sup>206</sup>Pb, <sup>207</sup>Pb/<sup>206</sup>Pb and <sup>204</sup>Pb/<sup>206</sup>Pb ratios of the Standard NBS981 measured in this study were 2.1681 ± 0.0008 (2SD), 0.91464 ± 0.00033 (2SD) and 0.059042 ± 0.000037 (2SD), respectively.

## 5. Results

### 5.1. Zircon U-Pb ages and trace elements

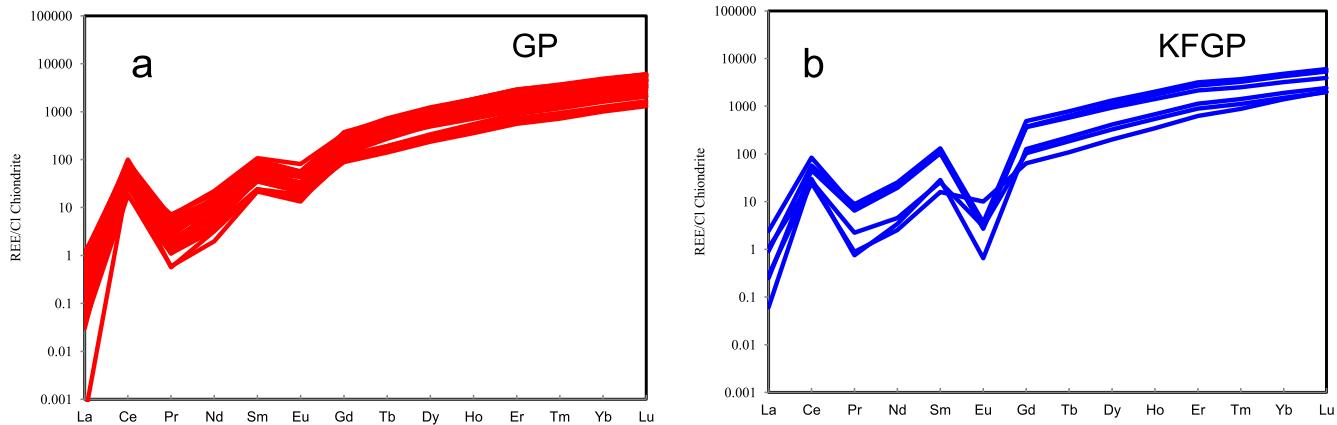
Zircon U-Pb data obtained by SIMS and LA-ICP-MS are listed in

**Appendix Table A1 and A2**, and representative zircon CL images and analytical spots are shown in Fig. 5. Most zircons are light pink to colorless euhedral crystals, with grain sizes of 50–200 μm and length to width ratios from 1.5:1 to 3:1 (Fig. 5). Most zircon grains show typical oscillatory and sector zoning under CL imaging, indicating their magmatic origin.

SIMS analyses of sample 24-4 from GP have shown variable contents of U (68–5012 ppm) and Th (55–1737 ppm) with high Th/U ratios of 0.3–2.1 (Appendix Table A1), indicative of magmatic zircon. Spot 24-4@12 with extreme high contents of U was excluded from the calculation based on the reliability of the age result. Spot 24-4@03 with an old <sup>206</sup>Pb/<sup>238</sup>U age of 401 Ma was also excluded. The remaining 15 spot analyses with lower f<sub>206</sub> and U contents have <sup>206</sup>Pb/<sup>238</sup>U ages ranging from 148.1 to 161.2 Ma (Fig. 5), giving a Concordia age of 155.8 ± 1.9 Ma (2SD). It is interpreted as the magma crystallization age of the granite porphyry.

Sample YZS01 was selected from Yinzushan GP for LA-ICP-MS zircon U-Pb dating (Appendix Table A2). Thirteen analyses on 13 grains have U contents varying from 113 to 1440 ppm, and Th from 126 to 784 ppm. Th/U ratios of these zircons range between 0.5 and 1.4, with an average of 0.8. Thirteen analyses show an intercept age of 158.5 ± 2.3 Ma (Fig. 5), consistent with the weighted mean <sup>206</sup>Pb/<sup>238</sup>U age of 156.9 ± 1.6 Ma.

Sample YZS02 from Yinzushan KFGP was dating by LA-ICP-MS (Appendix Table A2). Fifteen analyses on 15 grains have U contents of 284–898 ppm and Th content of 328–849 ppm, with Th/U ratios between 0.6 and 1.7 (average = 1.0). All data from the 15 analyses yielded an intercept age of 136.6 ± 1.9 Ma (MSWD = 0.43; Fig. 5), consistent with the weighted mean <sup>206</sup>Pb/<sup>238</sup>U age of 136.0 ± 0.9 Ma



**Fig. 6.** Chondrite-normalized REE diagrams for zircons from (a) granite porphyry (GP) and (b) K-feldspar granite porphyry (KFGP) in the LSKD.

(MSWD = 0.48) within uncertainty.

A total of thirty trace element analyses of zircons were conducted for the GP and the KFGP (Appendix Table A3). Trace elements such as Hf, U, Th and REE contents were determined in situ for individual zircon grain. To avoid influence from other mineral inclusions in zircons such as apatite and titanite, during LA-ICP-MS analyses (e.g., Lu et al., 2016), we excluded the spots with Ca > 200 ppm, La > 0.3 ppm or Ti > 20 ppm that, reflect apatite and titanite contamination, respectively (Appendix Table A3). Most of the analyzed zircons show REE patterns that steeply increase from La to Lu, with pronounced positive Ce anomalies (11.03–60.95, mean = 35.48) and negative Eu anomalies (0.77–4.69, mean = 2.23) (Fig. 10 and Appendix Table A3).

The remaining analyses show low LREE and elevated HREE contents, with negative Eu and strongly positive Ce anomalies (Fig. 6). In general, zircon crystals from the GP and KFGP show distinct Eu anomalies ( $\text{Eu}_N/\text{Eu}_{N^*} = \text{Eu}_N/(\text{Sm}_N \times \text{Gd}_N)^{0.5}$ ) and Ti-in-zircon temperatures (Appendix Table A3). Zircon crystals from the GP have relatively low calculated temperatures (average of 764 °C; 661–996 °C) with relatively large and uniform  $\text{Eu}_N/\text{Eu}_{N^*}$  values from 0.24 to 0.46 (mean = 0.34). In contrast, zircon crystals from the KFGP have relatively high calculated temperatures (average of 790 °C; 664–943 °C) with relatively low  $\text{Eu}_N/\text{Eu}_{N^*}$  values from 0.01 to 0.32 (mean = 0.07).

## 5.2. Whole rock geochemistry

Major element oxide and trace element concentrations of all samples were reported in Table 1. On the Zr/Ti versus Nb/Y diagram (Fig. 7a), the GP data straddle on the boundary between rhyolite, pantellerite, trachyandesite, and trachyte, whereas the KFGP were mainly plot within the field of pantellerite.

The KFGP shows a small range of SiO<sub>2</sub> (75.26–76.92%), K<sub>2</sub>O (5.84–6.32%), Na<sub>2</sub>O (1.14–2.31%), Al<sub>2</sub>O<sub>3</sub> (12.39–13.61%) and Fe<sub>2</sub>O<sub>3</sub> (0.44–1.99%). The GP shows a relatively wide range of SiO<sub>2</sub> (73.24–82.63%) with K<sub>2</sub>O (4.78–5.20%), Na<sub>2</sub>O (0.14–3.08%), Al<sub>2</sub>O<sub>3</sub> (9.01–14.06%) and Fe<sub>2</sub>O<sub>3</sub> (0.69–1.47%). The A/CNK ratios of all samples range from 1.2 to 3.0 with a mean of 1.5, and fall within the peraluminous field in the A/NK vs. A/CNK diagram (Fig. 7b).

All samples are enriched in light rare earth elements (LREE) (Fig. 8), with (La/Yb)<sub>N</sub> of 7.0–19.1 for the GP, and 1.8–34.3 for KFGP (Table 1). The GP exhibits relatively consistent REE features and moderate negative Eu anomalies with  $\text{Eu}_N/\text{Eu}_{N^*}$  of 0.07–0.67, and the KFGP shows scattered REE features and strong negative Eu anomalies with  $\text{Eu}_N$

$\text{Eu}_{N^*}$  of 0.02–0.05. The REE pattern of KFGP revealed in this study is consistent with the former studied one (Fig. 8).

All rocks in the LSKD are enriched in large ion lithophile elements (LILE, i.e., Rb, Th, U, K and Pb) and depleted in high field strength elements (HFSE, e.g., Nb, Ta and Ti) as well as Ba, Sr, and P (Fig. 9). The GP in this study exhibits the same trace element pattern as that of the ore-bearing granites, exception for relatively weak depletion in Ba, Sr and P, and enrichment in Pb in ore-bearing GP. The studied KFGP shows similar trace elements patterns to that of the former studied one.

## 5.3. Sr-Nd-Pb isotopes

For the samples with low Sr contents and extremely high and variable  $^{87}\text{Rb}/^{86}\text{Sr}$  ratios, their calculated initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are not meaningful to constrain their petrogenesis (e.g. Su et al., 2014; Wu et al., 2002). Hence, we only presented Nd isotopic data of granites in the LSKD in Table 2 and calculated the  $\varepsilon_{\text{Nd}}(t)$  values against the respective zircon U-Pb ages in this study. The GP has  $\varepsilon_{\text{Nd}}(t)$  values ranging from -10.0 to -9.7 with  $T_{\text{DM2}}$  values of 1688–1915 Ma, whereas the KFGP has higher  $\varepsilon_{\text{Nd}}(t)$  values ranging from -7.5 to -7.6 with younger  $T_{\text{DM2}}$  values of 1538–1548 Ma.

The Lengshuikeng porphyries show similar high radiogenic Pb isotopic compositions with present-day whole-rock Pb isotopic ratios of  $^{206}\text{Pb}/^{204}\text{Pb} = 17.853\text{--}18.365$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.571\text{--}15.606$  and  $^{208}\text{Pb}/^{204}\text{Pb} = 38.358\text{--}39.124$  (Table 3). Initial Pb isotopic ratios of samples were calculated using the whole-rock Pb isotopic ratios and U, Th and Pb contents against individual zircon U-Pb ages. The calculated initial Pb isotopic ratios are  $(^{206}\text{Pb}/^{204}\text{Pb})_i = 17.647\text{--}17.952$ ,  $(^{207}\text{Pb}/^{204}\text{Pb})_i = 15.555\text{--}15.604$  and  $(^{208}\text{Pb}/^{204}\text{Pb})_i = 37.851\text{--}38.541$ . In Fig. 10, all samples lie well above the northern hemisphere reference line (NHRL) of Hart (1984), and define a positively-correlated linear array roughly parallel to the NHRL.

## 6. Discussion

### 6.1. Ages of GP and KFGP

Our dating reveal two episodes of magmatism occurred in the LSKD, with the earlier episode around 156 Ma and the later episode from 134 Ma to 139 Ma. The granite porphyry and crystal tuff from the first member of the E'huling Formation were dated at ca. 155.6–162 Ma by LA-ICP-MS and SHRIMP zircon U-Pb dating (Zuo et al. 2010; Meng et al. 2012; Qiu et al. 2013; Su et al. 2013, 2014). Increasing studies

**Table 1**  
The analytical results of major (wt.%) and trace elements (ppm) of GP and KFGP in LSKD.

Sample	188-1-01	188-1-02	188-1-03	188-1-04	188-1-05	188-1-06	188-1-07	188-1-08	188-1-09	188-1-10	188-1-11	188-1-12	188-1-13	
Rock type	Granite porphyry (GP)													
SiO <sub>2</sub>	74.85	77.7	78.09	78.76	79.78	77.74	77.13	75.82	75.39	75.49	76.65	76.38	78.39	
TiO <sub>2</sub>	0.07	0.07	0.07	0.07	0.08	0.09	0.1	0.11	0.13	0.13	0.16	0.07	0.08	
Al <sub>2</sub> O <sub>3</sub>	12.54	12.67	11.77	12.1	11.02	12.63	12.69	13.37	13.6	12.73	12.38	12.33	11.83	
Fe <sub>2</sub> O <sub>3</sub>	1.86	1.05	1.48	1.19	0.87	1.08	1.02	1.1	1.2	1.87	1.54	2.98	1.43	
MnO	0.8	0.06	0.15	0.13	0.03	0.04	0.04	0.03	0.02	0.02	0.03	0.06	0.04	
MgO	0.19	0.28	0.33	0.26	0.25	0.33	0.31	0.28	0.27	0.37	0.27	0.21	0.28	
CaO	0.14	0.07	0.58	0.13	0.02	0.08	0.02	0.01	0.02	0.04	0.01	0.01	0	
Na <sub>2</sub> O	1.90	0.15	0.11	0.09	0.12	0.11	0.12	0.11	0.14	0.19	0.15	0.06	0.08	
K <sub>2</sub> O	5.03	5.49	4.85	4.88	5.19	5.2	6.19	6.27	6.72	6.62	6.21	3.62	4.62	
P <sub>2</sub> O <sub>5</sub>	0.02	0.02	0.03	0.11	0.02	0.02	0.02	0.01	0.01	0.03	0.02	0.02	0.01	
BaO	0.05	0.05	0.05	0.05	0.05	0.06	0.06	0.07	0.08	0.08	0.07	0.01	0.03	
LiO	2.29	2.13	2.3	2.25	1.58	1.73	1.81	2.04	2.16	2.42	2.16	3.28	2.23	
Total	99.7	99.7	99.8	100.0	99.0	100.2	99.5	99.2	99.7	99.8	99.0	99.0	99.0	
CaO/Al <sub>2</sub> O <sub>3</sub>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
K <sub>2</sub> O/Na <sub>2</sub> O	2.6	36.6	44.1	54.2	43.3	4.0	51.6	57.0	48.0	34.8	41.4	60.3	57.8	
A/NK	1.5	2.0	2.2	2.2	1.9	1.6	1.8	1.9	1.8	1.7	1.8	3.1	2.3	
A/CNK	1.4	2.0	1.8	2.1	1.9	1.6	1.8	1.9	1.8	1.7	1.8	3.1	2.3	
Ba	41.2	434	367	423	543	493	557	598	722	687	586	84.7	231	
Rb	186	208	204	195.5	187	183	240	265	259	270	268	178	207	
Sr	82.5	57.1	58.6	70.5	59.4	83.6	80.6	76.2	80.2	83.8	75.4	46.4	54.5	
Y	14.7	14.1	13.5	13.7	12.1	13.2	18.2	19.3	20.2	18.8	14.2	20.5	20.2	
Zr	81.2	67	71	75.7	72.8	79.6	90.5	91	88.7	82.6	96.4	73.5	87.3	
Nb	18.2	16.5	15.8	15.5	13.8	15.6	17.3	22.1	21.5	21.4	20.8	20.4	20.9	
Th	18.2	15.5	17.6	16.5	15.4	15.8	16.9	16.4	10.7	20	12.1	17.8	18.6	
Pb	37	19.5	26.7	192.5	58.9	36.4	177	66.3	78.1	139	30.2	1430	241	
Ga	16.2	15.2	15.3	14.15	12.2	14.6	15.5	16.8	16.6	18	17.6	15.4	15.4	
Zn	13.5	14.3	14.8	505.1	82.1	16.7	146.2	236.6	317.2	93.9	83.3	99.25	93.9	
Cu	9.4	13.0	5.4	16.8	12.8	3.6	16.4	4.5	3.4	18.1	4.6	9.6	3.5	
Ni	1.59	1.54	0.93	2.19	1.80	1.80	1.21	0.79	0.32	0.60	0.34	0.01	0.01	
V	6.03	4.98	6.71	6.24	6.95	7.07	6.8	6.61	6.51	11.9	14.8	3.19	3.29	
Cr	20.8	13.9	14.1	13.8	16.7	19.5	14.1	7.21	8.54	10.5	9.65	8.45	14.5	
Hf	2.99	2.28	2.64	2.655	2.26	2.62	2.88	3.04	3.27	3.07	3.38	2.74	3.06	
Cs	4.14	5.01	3.28	4.71	3.63	3.36	3.18	8.77	7.22	7.34	6.32	3.47	3.30	
Sc	3.80	2.70	2.59	2.30	1.94	2.87	2.90	3.48	3.14	3.90	4.17	2.43	2.98	
Ta	1.53	1.41	1.46	1.26	1.13	1.22	1.30	1.69	1.84	1.67	1.68	1.75	1.72	
Co	0.81	0.58	0.80	0.79	0.88	1.02	0.52	0.67	1.11	1.37	1.11	0.31	0.61	
Ag	0.35	1.01	0.81	1.01	0.53	2.03	2.33	2.33	2.33	1.23	0.54	1.95	1.72	
U	5.33	4.42	4.26	5.64	4.27	4.69	4.58	4.99	4.60	5.62	4.36	5.61	6.07	
La	27.30	27.00	26.60	26.70	24.80	26.40	28.10	31.50	30.50	32.00	36.00	26.10	22.90	
Ce	54.80	53.90	53.50	53.40	49.70	53.00	56.30	63.60	61.80	64.50	70.70	55.60	48.80	
Pr	5.89	5.78	5.73	5.62	5.33	5.60	5.95	6.95	6.64	6.79	7.57	6.10	5.31	
Nd	20.60	19.80	19.90	19.60	18.40	19.30	20.00	23.70	23.40	23.60	25.60	21.80	23.23	
Sm	4.01	3.46	3.91	3.58	3.44	3.57	3.81	4.47	4.44	4.73	4.47	4.74	4.15	
Eu	0.56	0.59	0.63	0.69	0.56	0.48	0.57	0.52	0.55	0.54	0.56	0.70	0.45	
Gd	3.07	2.34	2.74	2.81	2.45	2.79	3.08	3.60	3.53	3.55	3.06	3.47	3.23	
Tb	0.52	0.48	0.53	0.50	0.40	0.44	0.57	0.60	0.59	0.61	0.49	0.64	0.58	
Dy	2.73	2.43	2.65	2.355	2.12	2.38	3.01	3.12	3.14	3.2	3.32	3.29	3.23	
Ho	0.54	0.49	0.47	0.48	0.39	0.44	0.59	0.64	0.58	0.64	0.45	0.64	0.64	
Er	1.45	1.38	1.39	1.315	1.17	1.21	1.52	1.7	1.83	1.78	1.37	1.82	1.67	
Tm	0.21	0.20	0.21	0.21	0.16	0.17	0.22	0.26	0.28	0.27	0.22	0.27	0.27	
Yb	1.38	1.15	1.21	1.225	1.19	1.32	1.52	1.62	1.73	1.76	1.35	1.72	1.63	
Lu	0.20	0.19	0.19	0.17	0.17	0.18	0.22	0.24	0.24	0.22	0.22	0.22	0.22	

Table 1 (continued)

Sample	188-1-01	188-1-02	188-1-03	188-1-04	188-1-05	188-1-06	188-1-07	188-1-08	188-1-09	188-1-10	188-1-11	188-1-12	188-1-13
Rock type	Granite porphyry (GP)												
Sample	188-1-14	188-1-15	188-1-16	188-1-17	188-1-18	188-1-19	188-1-20	188-1-21	188-1-22	188-1-23	188-1-24	188-1-25	188-1-26
Rock type	Granite porphyry (GP)												
SiO <sub>2</sub>	73.33	75.22	73.62	73.24	73.9	79.9	82.6	75.67	75.99	76.92	75.26	76.47	76.47
TiO <sub>2</sub>	0.07	0.64	0.06	0.21	0.12	0.09	0.1	0.09	0.09	0.09	0.09	0.08	0.08
Al <sub>2</sub> O <sub>3</sub>	12.34	12.43	11.26	14.06	13.9	11.5	9.01	12.84	13.61	12.39	12.4	12.4	12.7
Fe <sub>2</sub> O <sub>3</sub>	2.46	1.55	2.43	1.36	1.47	0.69	1.26	1.19	0.85	1.39	1.99	0.99	0.99
MnO	1.74	1.12	2.15	0.05	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MgO	0.26	0.27	0.33	0.33	0.41	0.29	0.21	0.06	0.06	0.06	0.04	0.05	0.05
CaO	0.07	0.05	0.16	0.13	0.14	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na <sub>2</sub> O	0.15	0.16	0.13	3.08	3.00	0.60	0.14	2.31	1.14	1.87	1.89	2.09	2.09
K <sub>2</sub> O	6.6	6.75	5.78	5.2	5.1	4.84	4.78	5.84	6.32	5.95	6.05	6.1	6.1
P <sub>2</sub> O <sub>5</sub>	0.01	0.02	0.05	0.05	0.07	0.03	0.03	0.01	0.01	0.01	0.01	0.01	0.01
BaO	0.05	0.05	0.04	0.05	0.06	0.1	0.08	0.02	0.02	0.04	0.02	0.03	0.03
LOI	3.23	2.45	3.5	1.58	1.7	2	1.65	1.2	1.95	1.24	1.42	1.06	1.06
Total	100.3	100.1	99.5	99.4	100.0	100.1	99.9	99.2	100.0	99.9	99.6	99.6	99.6
CaO/Al <sub>2</sub> O <sub>3</sub>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K <sub>2</sub> O/Na <sub>2</sub> O	44.0	42.2	44.5	1.7	1.7	8.1	34.1	2.5	5.5	3.2	3.2	2.9	2.9
A/NK	1.7	1.6	1.7	1.3	1.3	1.8	1.7	1.3	1.6	1.3	1.3	1.3	1.3
A/CNK	1.6	1.6	1.7	1.3	1.3	1.8	1.7	1.3	1.6	1.3	1.3	1.3	1.3
Ba	467.5	440	422	582	699	969	841	145	96.1	267	105	154	154
Rb	273	274	244	186	177	180	173	302	290	249	199	199	199
Sr	70	75	74.4	102	99.2	15.6	18.2	65.9	54.7	60	52.1	52.3	52.3
Y	21.2	21.9	21.6	24.4	26.5	16.6	32.3	43.6	32.3	35.1	42.3	36.6	36.6
Zr	89.35	72.9	72.8	131	106	75.5	91.2	249	245	216	226	217	217
Nb	22.3	21.4	19.9	29.0	28.4	25.1	22.1	36.8	32.8	31.0	33.9	32.0	32.0
Th	21.7	19.3	19.7	25.9	25.4	22.3	20.1	41.9	30	24.1	31.8	29.6	29.6
Pb	38.9	29	21.2	26.9	18.4	14.4	56.3	43.6	21.3	77.8	42.2	19.5	19.5
Ga	17.15	16.8	17	17.7	18.1	14	11.3	17.6	15.2	14.8	16.7	14.6	14.6
Zn	445.7	534.3	816.1	100.5	91.6	9.2	24.8	123.2	177.2	118.7	145.3	77.8	77.8
Cu	11.7	9.8	5.5	1.9	2.5	2.4	5.0	9.0	5.6	6.5	10.0	2.9	2.9
Ni	2.04	0.82	0.88	1.01	0.99	4.31	4.44	4.44	4.44	0.86	0.74		
V	2.715	2.59	2.95	19.1	19.6	10	6.26	2.39	1.38	1.27			
Cr	12.25	9.01	9.95	1.14	2.22	1.72	4.38	14	4.25	8.5	4.88	5.12	5.12
Hf	3.545	2.87	2.72	3.84	3.47	2.58	3.75	8.29	7.66	6.99	7.82	7.21	7.21
Cs	7.25	5.45	4.10	4.29	4.45	3.13	2.79	4.07	3.49	3.35	3.37	3.54	3.54
Sc	3.87	3.40	2.73	4.78	5.47	2.64	1.84	5.95	3.83	4.51	4.71	2.75	2.75
Ta	1.95	1.95	1.73	2.30	2.28	2.42	1.60	2.15	2.00	1.81	2.08	1.93	1.93
Co	0.71	0.54	0.64	92.00	94.40	78.70	80.10	0.28	0.15	0.18	0.13	0.12	0.12
Ag	6.08	3.03	3.92	0.54	1.08	0.53	0.33	0.42	0.36	0.53	0.30	0.25	0.25
U	7.59	7.30	9.46	3.77	5.37	5.66	3.80	6.26	5.55	4.99	5.77	5.62	5.62
La	19.40	22.50	21.20	37.30	42.60	28.20	12.00	28.30	32.80	9.68	13.60	57.80	57.80
Ce	41.95	47.90	44.20	80.10	55.60	52.80	51.40	73.20	22.10	50.10	50.10	70.00	70.00
Pr	4.60	5.29	4.88	8.22	9.16	6.25	3.57	5.96	8.03	2.24	3.16	11.40	11.40
Nd	16.70	19.00	17.70	27.80	31.20	21.50	14.60	20.70	27.40	8.17	11.10	38.30	38.30
Sm	4.06	4.42	3.93	5.15	5.97	4.68	4.46	4.24	5.94	1.88	2.72	6.84	6.84

Table 1 (continued)

Sample	188-1-14	188-1-15	188-1-16	124-3	124-4	124-5	124-6	188-2-01	188-2-02	188-2-03	188-2-04	188-2-05
Rock type	K-feldspar granite porphyry (KFGP)											
<b>Eu</b>												
Gd	0.36	0.49	0.59	0.52	0.67	0.32	0.10	0.05	0.05	0.01	0.04	0.05
Tb	3.57	3.40	3.87	4.19	4.72	3.63	4.54	4.41	4.72	2.49	3.46	5.69
Dy	0.64	0.65	0.63	0.75	0.83	0.61	0.89	1.01	0.96	0.73	1.01	1.12
Ho	3.7	3.8	3.49	4.21	4.61	2.94	5.4	6.99	5.69	5.7	6.78	6.35
Er	0.73	0.70	0.68	0.85	0.93	0.62	1.19	1.62	1.18	1.32	1.52	1.37
Tm	2.06	2.08	1.91	2.49	2.55	1.8	3.35	4.73	3.31	3.87	4.52	3.9
Yb	0.29	0.30	0.30	0.35	0.40	0.29	0.50	0.73	0.51	0.58	0.68	0.52
Lu	1.99	1.92	1.95	2.19	2.37	1.72	3.17	4.35	3.11	3.77	4.36	3.51
ZREE	100	113	106	174	162	126	83	135	167	63	104	207
$\text{Eu}_{\text{N}}/\text{Eu}_{\text{N}^*}$	0.29	0.39	0.46	0.34	0.38	0.24	0.07	0.04	0.03	0.02	0.04	0.03
$\text{Sr}/\text{Y}$	3.3	3.4	3.4	4.2	3.7	0.9	0.6	1.5	1.7	1.7	1.2	1.4
$\text{Rb}/\text{Sr}$	3.9	3.7	3.3	1.8	1.8	11.5	9.5	4.6	5.3	4.2	5.2	3.8
$(\text{La/Yb})_{\text{N}}$	8.4	7.8	12.2	12.9	11.8	2.7	36.9	4.7	7.6	1.8	2.2	11.8

LOI = loss on ignition.  $(\text{La/Yb})_{\text{N}}$  normalised data after Sun and McDonald (1989).

have shown extensive magmatic and mineralization activities in the Late Jurassic also occurred in the NWA. Zircons of granites from the Yongping Cu deposit, Zhoujia Pb-Zn deposit, and Xiongjiashan Mo deposit yielded U-Pb ages within 155–164.6 Ma using LA-ICP-MS (Ding et al., 2005; Qin, 2011; Qiu et al., 2015). The molybdenites Re-Os ages range from 155.7 to 162.8 Ma for the Yongping Cu deposit and the Xiongjiashan Mo deposit (Li et al., 2007; Meng et al., 2007).

The late Jurassic magmatism occurred not only in the NWA, but also in a wide range of Nanling as an important W-Sn metallogenic province in China. Mao et al. (2007) proposed that the large-scale W-Sn mineralization and associated magmatism in Nanling occurred during the Middle to Late Jurassic (i.e., 165–150 Ma). The metallogenic ages (e.g. Molybdenite Re-Os and cassiterite U-Pb, Yao et al., 2005, 2007; Yuan et al., 2008, 2011, 2018), zircons U-Pb ages and muscovite Ar-Ar ages of ore-related granites (Ma et al., 2006; Guo et al., 2011; Yuan et al., 2018, 2019; Zhang et al., 2011) are highly consistent. Therefore, the early magmatism (155.8 Ma) in the LSKD are consistent with the North Wuyi and Nanling geological events between 165 and 150 Ma (Mao et al., 2007), implying widespread mineralization and magmatism across South China during this period.

The late episode magmatism (134–139 Ma) is similar to the volcanic-intrusive rock ages of ~144–137 Ma (except for granite porphyry) in Tianhuashan Basin (Su et al., 2013). A wide range of mineralization and magmatism in Early Cretaceous also occurred in the NWA. The host rhyodacite and rhyodacitic porphyry rocks from the Xiangshan uranium deposit in the western NWA, yielded LA-ICP-MS zircon  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $135.1 \pm 1.7$  and  $134.8 \pm 1.1$  Ma, respectively (Yang et al., 2012). The Shengmikeng vein-type Pb-Zn ore deposit situated in the Huanggangshan Basin 30 km to the east of the LSKD (see Fig. 1), gave a SHRIMP zircon U-Pb age of  $138.3 \pm 1.4$  Ma for the host potassic trachyte porphyry (Luo et al., 2009). Zhang et al. (2009) obtained a molybdenite Re-Os age ( $135.5 \pm 5.7$  Ma) in the recently discovered Jinzhuping polymetallic deposit which is genetically associated with the concealed granite pluton in the Lizikeng basin, 80 km to the northeast of the LSKD (Fig. 1). The early magmatism and mineralization mainly distributed in Nanling, while the late magmatism (139–134 Ma) in the NWA show more similar distribution to magmatism in the lower Yangtze (Zhou et al., 2012), North Jiangxi Province (Feng et al., 2012; Huang and Jiang, 2014), Northwest Zhejiang Province and South Anhui Province (Wu et al., 2012; Xie et al., 2012), and the coastal area (JH, Li et al., 2014). These show a wide range of magmatism and mineralization in South China. Meanwhile, evidence from mafic rocks in the GHTB and A-type granites in its adjacent regions indicates the extension peak may have occurred from 130 to 120 Ma (ZL, Li et al., 2013b; Qi et al., 2012, 2016).

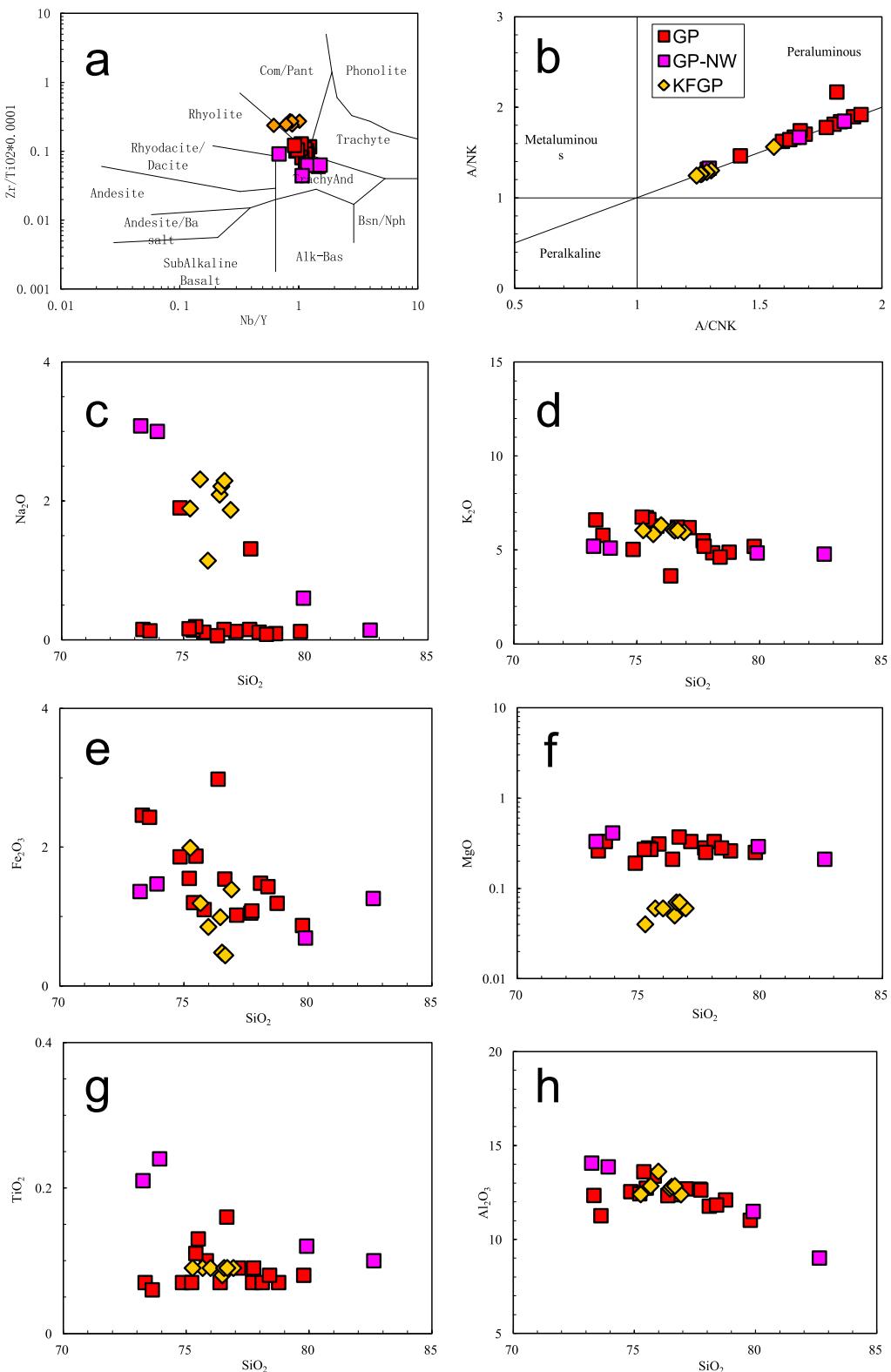
## 6.2. Petrogenesis

### 6.2.1. Alteration effects

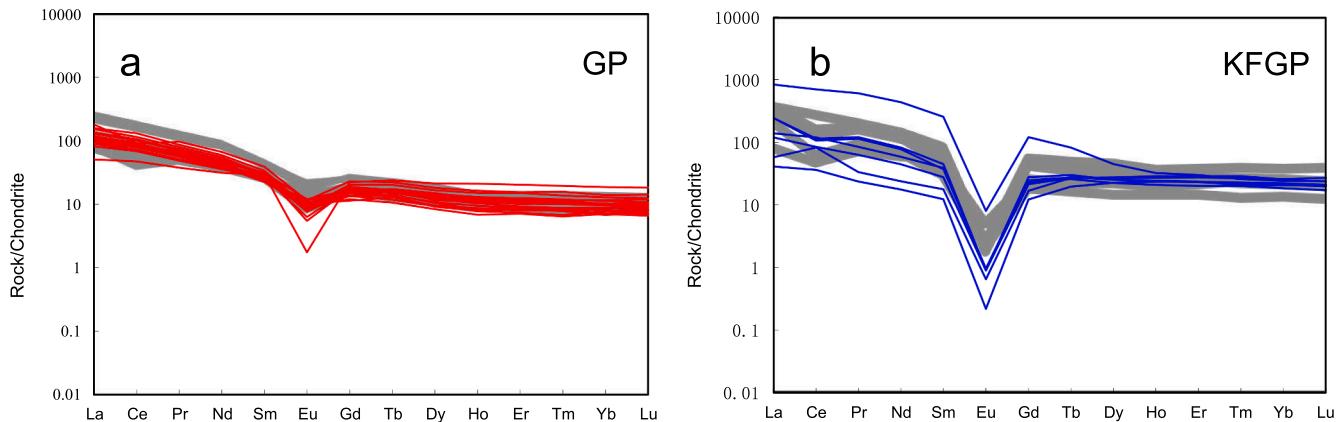
Petrographic observations show various degrees of alteration in the studied samples represented by differences in total major elements contents and LOI values (1.06–3.50%). During alteration, Ca, Na, K, and LILE (e.g., Rb, Sr, and Ba) are generally mobile (e.g., Zhou 1999). In Harker diagrams ( $\text{SiO}_2$  versus selected major elements; Fig. 7), the alkali elements ( $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ ) are significantly scattered. This is most likely due to hydrothermal alteration as indicated by a rough correlation between the alkali contents ( $\text{K}_2\text{O} + \text{Na}_2\text{O}$ ) and LOI.

### 6.2.2. Genetic type

The S-type granites are characterized by peraluminous ( $\text{ACNK} > 1.1$ ), high Rb low Sr contents, and presence of aluminous primary minerals, such as muscovite, cordierite, tourmaline, andalusite, and garnet (Chappell and White, 2001). The two studied granites in the LSKD are both strongly peraluminous, with high alkali oxides contents ( $\text{K}_2\text{O} + \text{Na}_2\text{O} = 3.7\text{--}6.9\%$  for GP; 7.5–8.3%, for the KFGP) and rich in K ( $\text{K}_2\text{O}/\text{Na}_2\text{O} = 2.65\text{--}60.33$ , mean = 41.65, for the GP; 2.53–5.54,



**Fig. 7.** (a) Zr/Ti vs. Nb/Y (Winchester and Floyd, 1977); (b) A/NK vs. A/CNK; (c) Na<sub>2</sub>O vs. SiO<sub>2</sub>; (d) K<sub>2</sub>O vs. SiO<sub>2</sub>; (e) Fe<sub>2</sub>O<sub>3</sub> vs. SiO<sub>2</sub>; (f) MgO vs. SiO<sub>2</sub>; (g) TiO<sub>2</sub> vs. SiO<sub>2</sub>; and (h) Al<sub>2</sub>O<sub>3</sub> vs. SiO<sub>2</sub> Harker diagram for the granite porphyry (GP), and the K-feldspar granite porphyry (KFGP) in the LSKD.



**Fig. 8.** Chondrite-normalized REE diagrams for (a) granite porphyry (GP) and (b) K-feldspar granite porphyry (KFGP) in LSKD. REE abundances for chondrite are after Sun and McDonough (1989). Grey areas are data of granite porphyry and K-feldspar granite porphyry from Su et al. (2014), and CM, Wang et al. (2013).

mean = 3.25 for the KFGP). They also have high  $\text{Al}_2\text{O}_3$  contents (11.02–13.60%, mean = 12.36% for the GP; 12.39–13.61%, Mean = 12.80% for the KFGP) and contain primary muscovite. The typical I-type granites indicators of hornblende (Chappell and White, 2001) and relatively low Rb/Sr ratios (< 0.9) (e.g. Wang et al., 1993) are not consistent with the studied samples which have no hornblende present with relative high Rb/Sr ratios of 2.2–3.9 for the GP and 3.8–16.1, for the KFGP. Therefore, we suggest the studied granites in the LSKD are likely S-type granites.

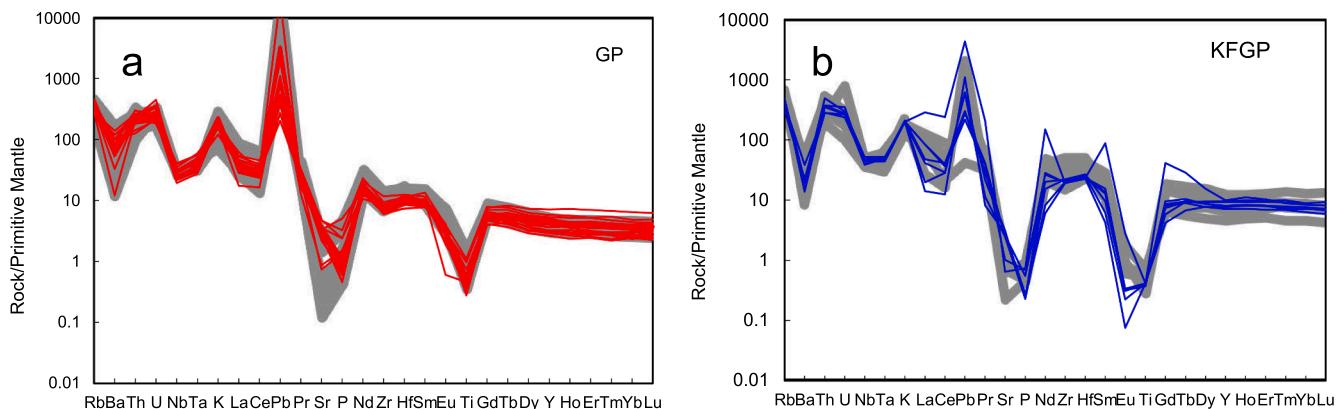
#### 6.2.3. Petrogenesis

Despite some elements are mobile during alteration, the alteration processes do not significantly affect HFSE and REE even during the most intensive hydrothermal alteration (Pearce et al., 1992). Both the relatively fresh samples and the highly altered granite samples in the LSKD show subparallel REE patterns (except for Eu) and HFSE concentrations, indicating these rocks still preserve their original REE and HFSE signatures. In addition, the relatively constant  $\varepsilon_{\text{Nd}}(\text{t})$  values in studied samples indicate negligible effects of alteration on Nd-isotope composition.  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ , and  $\text{Al}_2\text{O}_3$  show roughly correlated trends with  $\text{SiO}_2$  (Fig. 7), suggesting they may not be in a broadly co-genetic suite. Similar evidence is from the different trace element compositions, REE and Eu anomalies ( $\text{Eu}_{\text{N}}/\text{Eu}_{\text{N}}^{*}$ ) of two granites. However, the identical  $\varepsilon_{\text{Nd}}(\text{t})$  and previous zircon Hf isotopes suggest

that these rocks possibly originated from similar source materials.

As for the GP, the obvious negative  $\varepsilon_{\text{Nd}}(\text{t})$  values of -10.0 to -9.7 suggest that they were most probably derived from ancient crustal rocks. The zircon  $\varepsilon_{\text{Hf}}(\text{t})$  values of felsic rocks from the Tianhuashan basin with the highest values concentrated between -6 and -10 (Su et al., 2014) also support their crustal rock sources. In addition, previous studies have shown the Cathaysia Block has a Paleo- to Mesoproterozoic basement, which consists mainly of schists, granulites, and amphibolites (e.g., Fletcher et al., 2004; Jiang et al., 2006; Ling et al., 1998; Su and Zhang, 2012). As for the KFGP, the relative higher  $\varepsilon_{\text{Nd}}(\text{t})$  values of -7.6 to -7.5 compared to the GP, suggests that minor mantle contribution involved in its petrogenesis, despite that they share similar magma source to the GP. Based on their relatively low whole-rock  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$  contents, the low-grade meta-sedimentary rock rich of muscovite and biotite may be the most likely candidate source rock. This is also supported by the Pb isotopic compositions (Table 3, Fig. 10). In summary, these features suggest that the GP and KFGP may have different melting conditions such as temperatures, source materials and contents of aqueous fluids, etc.

Pervasive free aqueous fluids do not exist in the continental crust at depths greater than the uppermost few kilometers (Yardley and Valley, 1997), except where low-grade rocks are rapidly underthrusted beneath higher-grade rocks (Patino Douce, 1999). Dehydration melting of hydrous minerals, such as muscovite, biotite, and amphibolite, in the



**Fig. 9.** Primitive mantle-normalized trace element diagram for (a) the granite porphyry (GP) and (b) the K-feldspar granite porphyry (KFGP) in the LSKD. The primitive mantle values are after Sun and McDonough (1989). Grey areas are data of granite porphyry and K-feldspar granite porphyry from Su et al. (2014) and Wang et al. (2013).

**Table 2**

Whole-rock Nd isotope compositions for granites in LSKD.

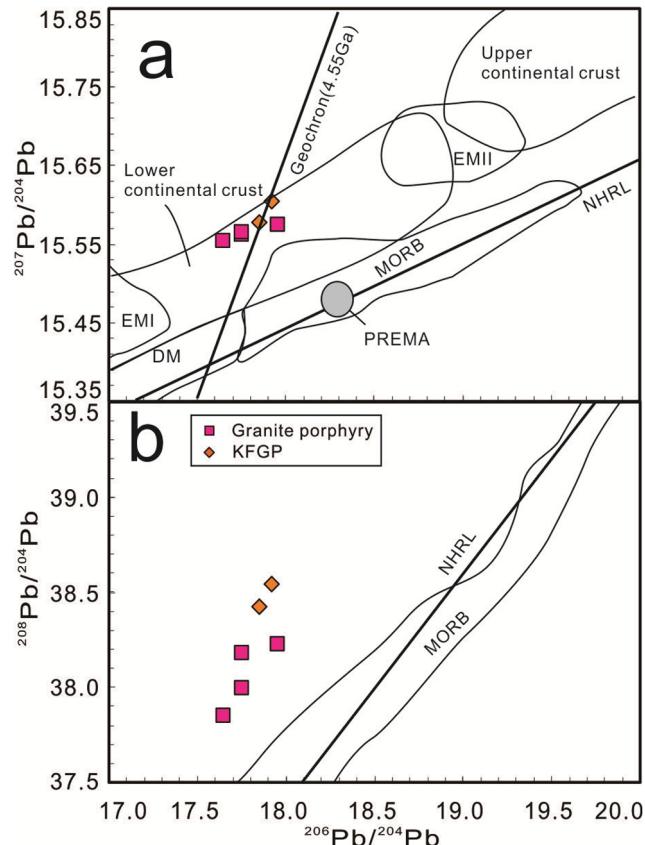
Sample	Rock Type	Age	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2\sigma$	$^{143}\text{Nd}/^{144}\text{Nd}_i$	$\varepsilon_{\text{Nd}}(t)$	$T_{\text{DM}}(\text{Ma})$	$T_{\text{DM}2}(\text{Ma})$
24-3	GP	156	0.1080	0.512048	0.000002	0.511938	-9.7	1586	1735
24-4	GP	156	0.1175	0.512058	0.000003	0.511938	-9.7	1726	1734
24-5	GP	156	0.1311	0.512060	0.000002	0.511926	-10.0	2005	1752
24-6	GP	156	0.1914	0.512126	0.000004	0.511931	-9.9	6850	1714
24-28	KFGP	137	0.1148	0.512173	0.000002	0.512071	-7.6	1502	1548
24-29	KFGP	137	0.1070	0.512173	0.000008	0.512078	-7.5	1392	1538

Note: all the initial isotopic ratios were corrected to the corresponding zircon ages. Sm and Nd abundances for the samples were determined by ICP-MS.  $\varepsilon_{\text{Nd}}(t)$  values are calculated using present-day  $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}} = 0.1967$  and  $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} = 0.512638$ .  $T_{\text{DM}}$  values are calculated using present-day  $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{DM}} = 0.2137$  and  $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{DM}} = 0.51315$ . The details for single- $(T_{\text{DM}1})$  or two-stage ( $T_{\text{DM}2}$ ) Nd model age calculations are given by Wu et al. (2002). Two-stage Nd model age ( $T_{\text{DM}2}$ ) is calculated using the same formulation as Keto and Jacobsen (1987).

continental crust is an important mechanism of magma formation (Patiño Douce, 1999). The Cs and U are exclusively concentrated in magmas formed from direct melting of meta-sedimentary rock sources, and are not elevated in magmas that have experienced an earlier episode of melting (Dostal and Capedri, 1978; Förster et al., 1999). For the GP and KFGP, the weak correlation between U, Cs and SiO<sub>2</sub> (Fig. 11) indicates the high U and Cs concentrations may not have resulted from the evolution of the magma but inherited from the magma source (Hall et al., 1993). The GP has a relative higher Cs concentration than the KFGP, and relative low Ti-in-Zircon temperatures, suggesting GP may be from direct melting of these fertile meta-sedimentary rock sources and experienced an earlier episode of melting (Dostal and Capedri, 1978; Förster et al., 1999). The accordant U value may be from the main rock-forming minerals such as biotite and muscovite, rather than from amphiboles that are rich in U than Cs (Dostal and Capedri, 1978). The KFGP has a younger  $T_{\text{DM}2}$  values with a relative high  $\varepsilon_{\text{Nd}}(t)$  (-7.6 to -7.5) compared to the GP ( $\varepsilon_{\text{Nd}}(t)$ , -10.0 to -9.7), indicating minor contribution from mantle-derived magmas occurred in younger granite.

Based on the above discussion, we suggest both studied rocks from the LSKD were mainly formed from the dehydration melting of fertile Proterozoic meta-sedimentary rocks. The early GP experienced relatively low temperature melting with more contribution of aqueous fluids from dehydration, whereas the later KFGP with higher melting temperature may obtain more materials and heat from the mantle. Mafic rocks in GHTB and A-type granites in the adjacent regions of NWA indicate that the extension peak occurred from 130 to 120 Ma (Li et al., 2013b; Qi et al., 2016). The mantle contribution could have probably played an important role in an extensional geodynamic setting in the later period (Qi et al., 2012, 2016).

The rare presence of zircons with old ages in the studied samples, except for one age of 401 Ma in the GP, and a few other spots in the KFGP, and lack of wall-rock-derived enclaves indicate very limited effects of wall-rock contamination. Hence, we propose rare crustal contamination occurred in the genesis of studied rocks in the LSKD. We favor the interpretation that felsic volcanic-intrusions could undergo fractional crystallization in the upper crustal level (Li et al., 2013b). Fractionation of plagioclase can result in negative Sr and Eu anomalies, whereas fractionation of K-feldspar leads to negative Ba and Eu anomalies. In addition, the high Rb/Sr ratios of granites also indicate

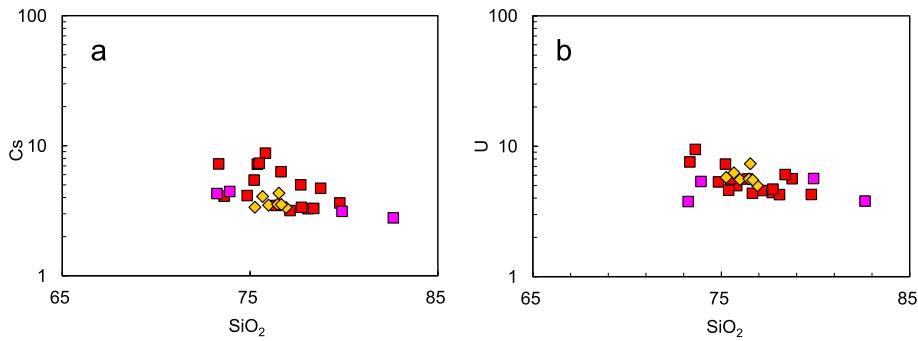


**Fig. 10.** Pb isotopic ratios for the granite porphyry (GP), and the K-feldspar granite porphyry (KFGP) in the LSKD. (a)  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$ ; (b)  $^{208}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$ . Fields for depleted mantle (DM), prevalent mantle (PREMA), enrichment mantle I and II (EMI and EMII), and upper and lower continental crust are after Zindler and Hart (1986); Pacific mid-ocean ridge basalt (MORB) are after Zou et al. (2000); and the NHRL (Northern Hemisphere Reference Line) is after Hart (1984).

**Table 3**

Whole-rock Pb isotopic data of granites from LSKD.

Sample	Rock Type	Age	$^{206}\text{Pb}/^{204}\text{Pb}$	$2\sigma$	$^{207}\text{Pb}/^{204}\text{Pb}$	$2\sigma$	$^{208}\text{Pb}/^{204}\text{Pb}$	$2\sigma$	$(^{206}\text{Pb}/^{204}\text{Pb})_i$	$(^{207}\text{Pb}/^{204}\text{Pb})_i$	$(^{208}\text{Pb}/^{204}\text{Pb})_i$
24-3	GP	159	18.170	0.002	15.586	0.002	38.718	0.004	17.952	15.575	38.229
24-4	GP	159	18.099	0.001	15.577	0.001	38.550	0.003	17.647	15.555	37.851
24-5	GP	159	18.365	0.001	15.592	0.001	38.784	0.003	17.751	15.562	37.994
24-6	GP	159	17.853	0.002	15.571	0.001	38.358	0.003	17.749	15.566	38.178
24-28	KFGP	136.5	17.954	0.001	15.606	0.001	38.587	0.003	17.922	15.604	38.541
24-29	KFGP	136.5	18.342	0.003	15.602	0.002	39.124	0.006	17.852	15.578	38.425



**Fig. 11.** (a) Cs vs.  $\text{SiO}_2$ ; and (b) U vs.  $\text{SiO}_2$  diagrams.

high degrees of fractionation of plagioclase (Bouseilly and El Sokkary, 1975). Moreover, the studied granites show enrichment of LILE (e.g., Rb, Th, and K) and depletion of Ba, Nb, Sr, Eu and Ti (Fig. 9), implying fractional crystallization of feldspar and ilmenite/magnetite.

In summary, both granites were dominantly derived from the dehydration melting of fertile Proterozoic meta-sedimentary rocks, with more contribution of dehydration fluids to the GP and relatively more mantle contribution to the KFGP. Both granites underwent fractional crystallization of plagioclase, K-feldspar and ilmenite/magnetite followed by minor assimilation of the upper crust.

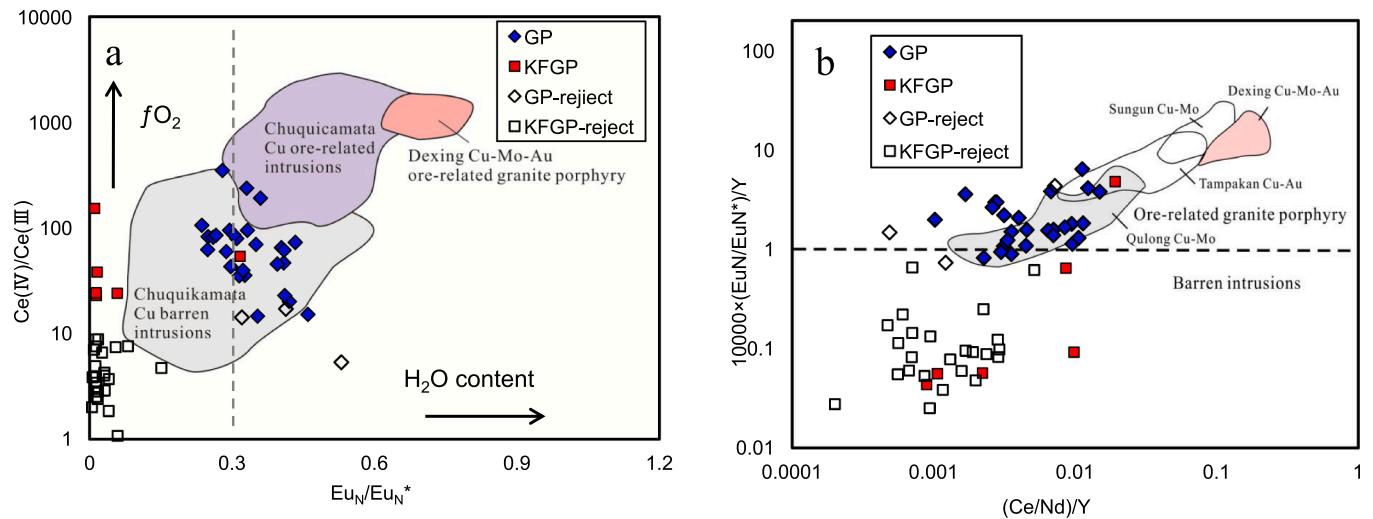
### 6.3. Relatively oxidized hydrous magma

Previous studies have shown magmatic oxidation state ( $f\text{O}_2$ ), water, sulfur and chlorine contents in associated magma could play important roles in the formation of porphyry Cu deposits (e.g., Burnham, 1979; Candela, 1992; Richards, 2003; Loucks, 2014). The magma with a high oxygen fugacity ( $f\text{O}_2$ ) may have been more conducive to the mineralization of chalcophile elements (Cu, Au, Mo, Ag etc. e.g. Richards, 2003). Because the behavior of chalcophile elements is controlled by sulfide, and the speciation and behavior of sulfur are controlled by oxygen fugacity. Hence, it is speculated that a relatively high oxygen fugacity may also be a necessary condition for the formation of a porphyry silver deposit. In addition, high water content can facilitate the melting of magma source and much more formation of hydrothermal

fluids, contributing to the metallogenesis at a late stage (Richards, 2011; Wang et al., 2014b,c). However, it is difficult to estimate the original magmatic water contents from variable altered granites. The geochemistry characteristics of associated and barren granites can help us to roughly assess the water content of magma source.

The ore-forming magmas often show distinctive whole-rock chemical signatures, such as high Sr/Y and Eu/Eu<sup>\*</sup> ratios, which can be used as ore fertility indicators of high magmatic water and sulfur contents (Richards and Kerrich, 2007; Chiaradia et al., 2012; Loucks, 2014), and high oxidation states of magma (Streck and Dilles, 1998; Chambeffet et al., 2008; Richards, 2011; Wang et al., 2014b,c; Lu et al., 2015). In this study, the GP and KFGP in the LSKD show relatively low Sr/Y ratios and high Y contents, different from the high Sr/Y ratios and low Y features of associated granites in the porphyry Cu ± Mo ± Au deposits. These features indicate amphibole may not be a major mineral in their magma source, and the water content of magma associated with porphyry Ag deposits is lower than that of magma related to porphyry Cu deposits, and should be in a relatively moderate level. Furthermore, early plagioclase crystallization can be suppressed due to the presence of water in hydrous magmas (Moore and Carmichael, 1998), resulting in no pronounced depletion of Eu in melts (Eu<sup>2+</sup> substitutes for Ca<sup>2+</sup> in plagioclase). Therefore, the whole-rock moderate negative Eu anomalies for GP could further suggest more water content in the GP magma than that in the KFGP as indicated by its strong negative Eu anomalies.

However, whole-rock Sr/Y and Eu/Eu<sup>\*</sup> ratios are easily affected by



**Fig. 12.** (a) Zircon Ce(IV)/Ce(III) vs.  $\text{Eu}_N / \text{Eu}_N^*$ ; and (b)  $10000 \times (\text{Eu}_N / \text{Eu}_N^*) / \text{Y}$  vs.  $(\text{Ce}/\text{Nd})/\text{Y}$  diagrams. Dexing data in (a) are after Zhang et al., (2013) and Chuquicamata data are after Ballard et al., (2002). All data in (b) are after Lu et al., (2016).

weathering or hydrothermal alteration. As a ubiquitous mineral in intermediate to felsic igneous rocks, zircon could survive intense hydrothermal alteration and weathering and record the compositional evolution and varying conditions of the parent melts (Ballard et al., 2002; Claiborne et al., 2010; Kemp et al., 2011; Dilles et al., 2015). Many studies have shown that trace element compositions in zircon are sensitive to magmatic water content (Wang et al., 2014b; Lu et al., 2016; Zhu et al., 2018) and oxygen fugacity (Ballard et al., 2002; Liang et al., 2006; Wang et al., 2014c; Dilles et al., 2015; Lu et al., 2016; Xu et al., 2016; Loader et al., 2017; Zhu et al., 2018).

Zircon Ce<sup>4+</sup>/Ce<sup>3+</sup> ratio could be regarded as an indicator of magmatic oxidation state (Ballard et al., 2002). However, because La and Pr abundances are low and close to the analytical detection limit, Dilles et al. (2015) and Lu et al. (2016) argued it was difficult to accurately estimate oxygen fugacity values when using La and Pr as a baseline to calculate the Ce anomaly. Considering that, we calculated and compared the zircon Ce<sup>4+</sup>/Ce<sup>3+</sup> ratios of the GP and KFGP to assess the relative oxygen fugacity of magma using the method of Ballard et al. (2002), after excluding the data with contents of Ca > 200 ppm, La > 0.3 ppm or Ti > 20 ppm. For comparison, we also calculated the element ratios (e.g. Ce(IV)/Ce(III) and (Ce/Nd)/Y) of spots that had been rejected due to high contents of Ca, La and Ti. The GP generally has much higher zircon Ce(IV)/Ce(III) ratios than the post-mineralization KFGP, suggesting the GP has a relatively high fO<sub>2</sub> than the barren KFGP (Fig. 12). The lower Ce(IV)/Ce(III) ratios in the rejected spots compared to selected spots in the KFGP, suggest great influence from high-La minerals. However, limited data of the KFGP hinder further discussion on the oxygen fugacity of magma. Lu et al. (2016) found that Ce(IV)/Ce(III) and Ce/Nd have an exponential relationship and they suggested the Ce/Nd ratio in zircon can be an alternative method to estimate the amplitude of the Ce anomaly. In Fig. 12, the roughly consistent ranges of (Ce/Nd)/Y between selected and rejected data indicate that using zircon (Ce/Nd)/Y can effectively reduce the interference of high La content. The GP generally has much higher zircon (Ce/Nd)/Y (average = 0.006) values than the KFGP (average = 0.003), indicating more oxidized conditions in GP magma. We speculate that the high oxygen fugacity in the GP may be inherited from the crust, and this is consistent with much more negative ε<sub>Nd(t)</sub> values ( $-10.0 \sim -9.7$ ) in the GP than the ε<sub>Nd(t)</sub> values ( $-7.6 \sim -7.5$ ) in the KFGP.

Eu<sup>3+</sup> as the predominant valence state in oxidized magmas, can be easily partitioned into zircon along with other REE (Ballard et al., 2002; Hoskin and Schaltegger, 2003; Trail et al., 2011, 2012; Dilles et al., 2015). Considering the suppression of plagioclase crystallization in water-rich magmas and its strong incorporation of Eu, relatively elevated negative Eu anomalies in zircons could indicate relatively high magmatic water contents and/or oxidation states (Ballard et al., 2002; Dilles et al., 2015; Lu et al., 2016). Lu et al. (2016) proposed fertile magmatic suites have collectively higher zircon Eu/Eu\* (> 0.3) and  $10,000 \times (\text{Eu}/\text{Eu}^*)/\text{Y}$  (> 1) than infertile suites in porphyry Cu system.

In the zircon Eu<sub>N</sub>/Eu<sub>N</sub>\* vs. Ce(IV)/Ce(III) diagram (Fig. 12), the GP data plot in the field between the associated granites and barren granites in the porphyry Cu deposit, indicating a relatively moderate oxygen fugacity for the porphyry Ag deposit. In addition, the zircon  $10,000 \times (\text{Eu}_N/\text{Eu}_N^*)/\text{Y}$  values range from 0.82 to 6.40 with a mean of 2.14 for the GP and from 0.04 to 4.79 with a mean of 0.95 for the KFGP. The higher  $10,000 \times (\text{Eu}_N/\text{Eu}_N^*)/\text{Y}$  values of the GP are attributed to the suppression of plagioclase crystallization under more water system

(Lu et al., 2016), consistent with the high water melting conditions in the GP. On the other hand, using the Ti-in-zircon thermometer, the causative GP has much lower temperatures (average of 764 °C; range = 661–996 °C) than the barren KFGP (average of 790 °C; range = 664–943 °C). As mentioned above, both granites result from partial melting of ancient crusts, and the addition of water in the formation of granites can effectively lower the melting temperature. The lower melting temperature of the GP indicates more water content in its magma source compared to the KFGP.

In conclusion, our comparison of magmatic oxidized hydrous conditions shows that magma associated with porphyry silver deposit probably has a relatively moderate oxidation state and water content.

## 7. Conclusions

Whole rock major and trace elements, Nd-Pb isotopes, and Zircon U-Pb ages and trace element analyses of the Mesozoic associated GP and barren KFGP in the LSKD, NWA have allowed us to reach the following conclusions:

- (1) The GP related to Ag mineralization was emplaced in 156 Ma, and the barren KFGP was emplaced in 137 Ma. Both granites are peraluminous and akin to typical S-type granites;
- (2) The GP and KFGP were predominantly derived from dehydration melting of Proterozoic *meta*-sedimentary rocks, with more dehydration fluids contribution to the GP and relatively more mantle contribution to the KFGP. Both granites underwent fractional crystallization of plagioclase, K-feldspar and ilmenite/magnetite followed by minor assimilation of upper-crust;
- (3) The comparison of magmatic oxidizing hydrous conditions shows that relatively moderate oxidation state and water content in associated magma are probably important factors in porphyry silver mineralization.

## CRediT authorship contribution statement

**Youqiang Qi:** Conceptualization, Funding acquisition, Methodology, Project administration, Investigation, Visualization, Writing - original draft, Writing - review & editing. **Ruizhong Hu:** Conceptualization. **Jianfeng Gao:** Conceptualization, Funding acquisition, Methodology, Project administration, Writing - original draft, Writing - review & editing. **Chengbiao Leng:** Investigation. **Haotian Gong:** Visualization. **Wei Gao:** Investigation.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A

See Appendix Tables A1–A3.

**Appendix Table A1**

SIMS zircon U–Pb isotopic analysis of mineralized granite porphyry from LSKD, South China.

Dating spot No.	U ppm	Th ppm	Th/U	f <sub>206</sub> %	<sup>207</sup> Pb/ <sup>206</sup> Pb	± 1σ %	<sup>207</sup> Pb <sup>235</sup> U	± 1σ %	<sup>206</sup> Pb <sup>238</sup> U	± 1σ %	t <sub>207/235</sub> Ma	± 1σ	t <sub>206/238</sub> Ma	± 1σ
<i>Graniteporphyry 24-4</i>														
24-4@01	236	218	0.9	0.00	0.04857	3.51	0.1633	3.98	0.0244	1.87	154	6	155	3
24-4@02	203	346	1.7	0.14	0.05034	2.51	0.1584	3.38	0.0233	1.57	149	5	149	2
24-4@03	204	55	0.3	0.09	0.05546	1.50	0.4851	2.29	0.0642	1.55	402	8	401	6
24-4@04	79	102	1.3	0.17	0.04849	4.03	0.1639	4.32	0.0245	1.56	154	6	156	2
24-4@05	125	142	1.1	0.00	0.05138	3.22	0.1691	3.64	0.0239	1.69	159	5	152	3
24-4@06	80	124	1.6	0.34	0.04951	4.62	0.1714	4.94	0.0251	1.75	161	7	160	3
24-4@07	94	106	1.1	0.28	0.04759	3.68	0.1640	4.02	0.0250	1.62	154	6	159	3
24-4@08	122	215	1.8	0.00	0.05015	3.25	0.1712	3.94	0.0248	2.23	160	6	158	3
24-4@09	86	76	0.9	0.00	0.05056	4.09	0.1678	4.35	0.0241	1.50	158	6	153	2
24-4@10	125	106	0.8	0.00	0.05139	3.10	0.1786	3.47	0.0252	1.55	167	5	160	2
24-4@11	68	72	1.1	0.00	0.04813	5.33	0.1678	5.59	0.0253	1.69	158	8	161	3
24-4@13	87	170	1.9	0.59	0.05323	3.74	0.1557	7.07	0.0232	1.57	147	10	148	2
24-4@14	147	183	1.2	0.18	0.04869	2.94	0.1700	3.43	0.0253	1.78	159	5	161	3
24-4@15	76	160	2.1	0.00	0.05119	5.14	0.1775	5.40	0.0252	1.65	166	8	160	3
24-4@16	138	212	1.5	0.00	0.05159	3.60	0.1683	4.03	0.0237	1.81	158	6	151	3
24-4@17	335	415	1.2	0.14	0.05050	2.14	0.1701	2.96	0.0250	1.51	159	4	159	2

**Appendix Table A2**

LA–ICP–MS U–Pb isotopic data for zircons for GP and KFGP from LSKD, South China.

Spot	Th	U	Th/U	Isotopic ratios				Age (Ma)							
				<sup>207</sup> Pb/ <sup>206</sup> Pb	1σ	<sup>207</sup> Pb/ <sup>235</sup> U	1σ	<sup>206</sup> Pb/ <sup>238</sup> U	1σ	<sup>207</sup> Pb/ <sup>235</sup> U	1σ	<sup>206</sup> Pb/ <sup>238</sup> U	1σ		
<i>Granite porphyry</i>															
YZS01-02	161	113	1.42	0.0472	0.0028	0.1563	0.0093	0.0240	0.0004	147	3	153	2	171	3
YZS01-06	753	1171	0.64	0.0534	0.0014	0.1807	0.0046	0.0246	0.0003	169	4	157	2	135	3
YZS01-09	762	1440	0.53	0.0504	0.0011	0.1764	0.0038	0.0254	0.0003	165	6	162	2	145	4
YZS01-12	784	1172	0.67	0.0499	0.0011	0.1701	0.0037	0.0247	0.0003	160	6	157	2	137	5
YZS01-13	542	754	0.72	0.0495	0.0013	0.1730	0.0044	0.0254	0.0003	162	5	161	2	141	5
YZS01-15	279	193	1.45	0.0527	0.0029	0.1783	0.0095	0.0245	0.0004	167	7	156	2	161	5
YZS01-16	295	313	0.94	0.0507	0.0021	0.1708	0.0070	0.0244	0.0004	160	5	156	2	156	4
YZS01-18	532	713	0.75	0.0503	0.0015	0.1689	0.0050	0.0244	0.0003	159	8	155	3	150	5
YZS01-19	639	1112	0.57	0.0521	0.0023	0.1744	0.0075	0.0243	0.0004	163	7	155	2	123	4
YZS01-21	140	256	0.54	0.0479	0.0029	0.1609	0.0096	0.0244	0.0004	152	6	155	2	118	6
YZS01-23	126	174	0.72	0.0489	0.0031	0.1681	0.0104	0.0249	0.0005	158	5	159	2	143	7
YZS01-28	344	493	0.70	0.0505	0.0016	0.1729	0.0054	0.0248	0.0003	162	5	158	2	153	4
YZS01-29	560	834	0.67	0.0487	0.0011	0.1637	0.0039	0.0244	0.0003	154	3	155	2	134	3
<i>K-feldspar granite porphyry</i>															
Yzs02-01	480	503	0.95	0.0489	0.0015	0.1462	0.0045	0.0217	0.0003	139	4	138	2	119	3
Yzs02-02	356	498	0.71	0.0521	0.0017	0.1545	0.0050	0.0215	0.0003	146	4	137	2	119	4
Yzs02-04	548	625	0.88	0.0533	0.0015	0.1567	0.0043	0.0213	0.0003	148	4	136	2	120	3
Yzs02-05	663	658	1.01	0.0501	0.0018	0.1478	0.0053	0.0214	0.0003	140	5	137	2	118	4
Yzs02-06	362	327	1.10	0.0530	0.0021	0.1570	0.0063	0.0215	0.0003	148	6	137	2	116	4
Yzs02-09	627	540	1.16	0.0497	0.0015	0.1454	0.0044	0.0212	0.0003	138	4	135	2	107	3
Yzs02-10	705	898	0.79	0.0505	0.0019	0.1470	0.0055	0.0211	0.0003	139	5	135	2	118	5
Yzs02-12	328	538	0.61	0.0487	0.0017	0.1422	0.0050	0.0212	0.0003	135	4	135	2	123	4
Yzs02-14	518	405	1.28	0.0510	0.0018	0.1505	0.0052	0.0214	0.0003	142	5	136	2	119	4
Yzs02-15	838	671	1.25	0.0501	0.0015	0.1457	0.0043	0.0211	0.0003	138	4	135	2	116	4
Yzs02-16	849	507	1.68	0.0554	0.0017	0.1628	0.0049	0.0213	0.0003	153	4	136	2	113	3
Yzs02-19	401	489	0.82	0.0503	0.0016	0.1504	0.0047	0.0217	0.0003	142	4	138	2	117	4
Yzs02-20	331	284	1.16	0.0532	0.0025	0.1542	0.0072	0.0210	0.0003	146	6	134	2	117	5
Yzs02-25	332	492	0.67	0.0507	0.0016	0.1476	0.0046	0.0211	0.0003	140	4	135	2	103	3
Yzs02-26	597	531	1.12	0.0514	0.0016	0.1516	0.0046	0.0214	0.0003	143	4	136	2	116	4

**Appendix Table A3**  
LA-ICP-MS zircon trace elements for GP and KFGP from LSKD, South China.<sup>1</sup>

Analyzed Spot	Ca	Ti	Y	Hf	Th	U	La	Ce	Pr	Nd	Sm	Eu	Gd
<i>Granite porphyry</i>													
YZS01-01	Below LOD	10.58	1193	9118	299	269	0.21	28.7	0.67	8.87	12.07	2.72	45.73
YZS01-02	Below LOD	12.00	1285	9632	161	113	0.06	15.5	0.48	7.23	10.55	3.26	44.51
YZS01-03	Below LOD	4.64	722	10,758	123	191	0.07	17.0	0.11	1.92	3.70	0.84	19.94
YZS01-04	Below LOD	4.71	631	9613	75	94	0.01	11.0	0.11	1.56	3.67	1.08	18.20
YZS01-05	153	3043	11,877	842	1389	0.20	43.4	0.45	4.56	13.08	3.27	71.49	
YZS01-06	Below LOD	2.42	3051	12,721	753	1171	0.02	35.0	0.25	5.08	13.69	2.65	76.83
YZS01-07	Below LOD	2.24	2648	11,438	736	1229	0.02	33.5	0.20	3.58	9.29	1.81	58.90
YZS01-08	Below LOD	3.97	1966	13,224	444	826	0.08	40.0	0.15	2.90	7.24	1.81	44.01
YZS01-09	Below LOD	3.69	2295	12,512	762	1440	0.16	44.9	0.15	2.05	5.85	1.34	42.32
YZS01-10	Below LOD	7.97	2264	12,644	910	1077	0.13	61.0	0.31	4.19	9.57	2.58	52.95
YZS01-11	Below LOD	15.21	2764	11,287	590	681	0.10	56.6	0.32	4.51	9.57	3.26	55.27
YZS01-12	Below LOD	3.95	2153	12,609	784	1172	0.01	52.1	0.10	2.29	6.43	1.51	42.30
YZS01-13	Below LOD	4.66	2214	10,948	542	754	0.02	38.2	0.28	4.88	9.85	2.52	54.50
YZS01-14	92	12.45	2557	13,882	1112	1320	0.22	54.9	0.59	6.46	14.92	3.31	69.08
YZS01-15	Below LOD	6.74	2124	9916	279	193	0.05	22.4	0.65	10.35	16.42	4.69	70.65
YZS01-18	Below LOD	5.67	1839	10,128	532	713	0.01	53.5	0.15	3.09	6.74	1.74	38.35
YZS01-19	Below LOD	6.98	3145	12,994	639	1112	0.03	52.5	0.38	5.59	13.04	2.92	70.23
YZS01-20	Below LOD	5.70	2198	12,871	889	1352	0.08	47.7	0.20	3.10	7.95	1.95	48.38
YZS01-21	Below LOD	3.51	949	12,452	140	256	0.00	21.0	0.05	1.49	3.47	1.03	22.05
YZS01-22	Below LOD	7.71	1374	11,376	190	167	0.02	19.2	0.29	5.02	8.79	2.50	39.73
YZS01-23	Below LOD	6.39	845	10,739	126	174	0.04	16.8	0.14	2.95	5.41	1.23	25.01
YZS01-24	Below LOD	2.41	1498	13,089	374	744	0.04	11.6	0.06	0.92	3.32	0.77	27.05
YZS01-25	Below LOD	4.64	2452	12,204	645	1193	0.04	32.0	0.17	2.91	7.60	1.68	48.86
YZS01-26	Below LOD	4.84	1798	10,888	382	431	0.06	35.8	0.40	6.34	10.90	3.06	51.36
YZS01-28	Below LOD	4.86	1978	10,415	344	493	0.05	39.8	0.30	5.05	10.22	3.16	54.39
YZS01-29	Below LOD	2.79	1579	11,550	560	834	0.26	48.0	0.18	2.68	5.36	1.25	32.85
YZS01-30	Below LOD	7.32	1556	10,937	285	293	0.27	25.8	0.12	6.38	10.21	2.87	44.62
<i>K-feldspar granite porphyry</i>													
YZS02-05	Below LOD	4.69	2898	10,613	663	658	0.06	28.0	0.62	9.10	15.84	0.19	76.80
YZS02-07	Below LOD	2.97	1174	10,972	290	419	0.01	18.3	0.07	1.59	4.33	0.04	26.07
YZS02-15	Below LOD	5.73	3342	9217	838	671	0.22	35.0	0.84	11.74	20.00	0.21	100.24
YZS02-16	Below LOD	8.01	2407	7742	849	507	0.57	51.0	0.73	9.60	16.23	0.16	74.90
YZS02-27	Below LOD	6.99	908	9333	212	257	0.26	16.6	0.21	2.13	3.92	0.18	21.27
YZS02-29	Below LOD	4.77	662	9488	276	547	0.07	15.1	0.08	1.19	2.43	0.59	13.09
Analyzed Spot	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE	Ce(IV)/Ce(III)	Eu <sub>N</sub> /Eu <sub>N*</sub>	10000 × (Eu <sub>N</sub> /Eu <sub>N*</sub> ) <sup>Y</sup>	(Ce/Nd)/Y	T (°C) <sup>2</sup>
<i>Granite porphyry</i>													
YZS01-01	11.58	124.7	40.3	172.8	32.4	281.4	53.4	815	14.60	0.35	2.966	0.003	802
YZS01-02	12.09	131.8	43.5	191.8	35.1	308.2	59.5	864	15.16	0.46	3.580	0.002	815
YZS01-03	5.80	68.7	23.7	109.0	21.3	193.1	37.9	503	43.04	0.30	4.120	0.012	722
YZS01-04	5.24	59.9	20.1	92.1	18.3	170.7	33.2	435	65.09	0.40	6.398	0.011	724
YZS01-05	27.08	310.6	102.3	470.0	89.9	804.0	152.1	2092	35.58	0.33	1.074	0.003	820
YZS01-06	25.24	298.3	104.1	482.2	91.5	801.5	151.3	2088	82.79	0.25	0.819	0.002	667
YZS01-07	19.68	241.8	87.2	414.8	80.4	715.5	135.4	1802	105.95	0.24	0.893	0.004	661
YZS01-08	15.10	186.5	66.1	309.1	61.1	549.5	101.7	1385	79.37	0.31	1.577	0.007	708
YZS01-09	15.61	202.7	76.3	368.3	73.4	663.5	127.3	1624	81.66	0.26	1.134	0.010	702
YZS01-10	17.76	210.9	75.1	349.4	67.6	601.7	114.2	1567	69.81	0.35	1.548	0.006	773
YZS01-11	18.86	238.2	86.5	415.8	83.6	763.2	142.8	1879	72.95	0.43	1.568	0.005	841
YZS01-12	15.04	190.7	71.6	340.0	66.9	603.0	116.0	1508	350.02	0.28	1.300	0.011	708
YZS01-13	17.09	206.9	73.9	345.5	65.7	589.7	113.1	1522	94.90	0.33	1.502	0.004	723
YZS01-14	23.72	262.7	85.9	392.4	75.2	660.5	123.0	1773	35.17	0.32	1.233	0.003	819
YZS01-15	19.46	207.7	69.2	303.2	55.8	484.5	90.8	1356	20.08	0.42	1.982	0.001	757

Appendix Table A3 (continued)

Analyzed Spot	Tb	Dy	Ho	Er	Tm	Yb	Lu	$\Sigma$ REE	Ce(IV)/Ce(II)	$\text{Eu}_{\text{N}}/\text{Eu}_{\text{N}^*}$	$10000 \times (\text{Eu}_{\text{N}}/\text{Eu}_{\text{N}^*})/Y$	(Ce/Nd)/Y	T (°C) <sup>2</sup>	
YZS01-18	12.54	157.8	59.3	289.1	57.7	532.4	105.0	1317	237.68	0.33	1.799	0.009	740	
YZS01-19	23.77	291.3	102.2	477.2	93.5	831.6	153.1	2117	95.09	0.29	0.938	0.003	760	
YZS01-20	17.20	208.4	72.7	343.7	67.7	604.7	113.1	1537	85.99	0.30	1.383	0.007	741	
YZS01-21	7.13	85.5	31.4	148.1	29.8	273.5	52.3	677	191.63	0.36	3.792	0.015	698	
YZS01-22	11.35	131.0	45.9	209.0	40.7	370.6	71.1	955	46.62	0.41	2.977	0.003	770	
YZS01-23	7.16	80.6	26.9	122.0	23.8	214.6	41.9	568	39.59	0.32	3.825	0.007	792	
YZS01-24	10.19	131.2	49.0	238.5	47.3	426.5	83.2	1030	62.33	0.25	1.661	0.008	701	
YZS01-25	17.29	216.6	80.4	390.1	76.9	707.0	137.1	1719	85.13	0.27	1.087	0.004	760	
YZS01-26	15.10	171.4	59.1	271.0	52.6	472.3	89.9	1239	45.51	0.40	2.200	0.003	764	
YZS01-28	16.43	189.4	64.9	295.8	56.3	500.9	93.6	1330	61.53	0.41	2.071	0.004	765	
YZS01-29	11.56	144.7	51.6	243.0	48.2	438.5	82.0	1110	59.74	0.29	1.824	0.011	713	
YZS01-30	12.96	145.0	49.3	227.6	43.9	399.2	79.2	1047	22.89	0.41	2.641	0.003	806	
<i>K-feldspar granite porphyry</i>														
YZS02-05	23.76	276.5	97.8	452.1	83.1	721.4	136.2	1921	38.22	0.02	0.056	0.001	761	
YZS02-07	8.45	105.5	38.7	187.5	36.1	325.5	61.6	814	153.17	0.01	0.092	0.010	719	
YZS02-15	29.28	335.5	114.0	525.3	94.4	818.9	152.1	2238	22.94	0.01	0.044	0.001	781	
YZS02-16	21.64	237.1	80.5	354.8	63.9	545.8	99.9	1557	24.34	0.01	0.057	0.002	816	
YZS02-27	6.90	83.0	30.6	148.0	28.4	255.5	50.2	647	24.04	0.06	0.645	0.009	802	
YZS02-29	4.07	51.0	19.7	103.1	22.6	236.9	51.5	521	53.81	0.32	4.791	0.019	763	
Reject data				Ce(IV)/Ce(III)					$10000 \times (\text{Eu}_{\text{N}}/\text{Eu}_{\text{N}^*})/Y$				(Ce/Nd)/Y	
<i>Granite porphyry</i>														
YZS01-16	5.35				0.53					1.476			0.000	
YZS01-17	14.22				0.32					0.732			0.001	
YZS01-27	17.14				0.41					4.338			0.007	
<i>K-feldspar granite porphyry</i>														
YZS02-01	3.43				0.02					0.078			0.001	
YZS02-02	7.04				0.01					0.048			0.002	
YZS02-03	4.90				0.01					0.088			0.002	
YZS02-04	2.83				0.02					0.060			0.001	
YZS02-06	1.07				0.06					0.221			0.001	
YZS02-08	1.85				0.04					0.144			0.001	
YZS02-09	2.52				0.01					0.053			0.001	
YZS02-10	4.00				0.03					0.082			0.001	
YZS02-11	4.27				0.03					0.133			0.001	
YZS02-12	8.80				0.01					0.082			0.003	
YZS02-13	3.95				0.01					0.060			0.002	
YZS02-14	2.39				0.02					0.055			0.001	
YZS02-17	3.12				0.01					0.095			0.002	
YZS02-18	3.86				0.01					0.025			0.001	
YZS02-19	7.55				0.01					0.098			0.003	
YZS02-20	4.71				0.15					0.657			0.001	
YZS02-21	8.83				0.02					0.123			0.003	
YZS02-22	3.71				0.04					0.114			0.001	
YZS02-23	7.43				0.06					0.618			0.005	
YZS02-24	6.61				0.03					0.028			0.000	
YZS02-25	2.01				0.01					0.039			0.001	
YZS02-26	3.89				0.01					0.092			0.002	
YZS02-28	2.89				0.03					0.249			0.002	
YZS02-30	7.59				0.08					0.172			0.000	

<sup>1</sup> The analyses with Ca > 200 ppm or La > 0.3 ppm may reflect apatite contamination, and those data with Ti > 20 ppm may reflect titanite contamination, all of which have been omitted.<sup>2</sup> Temperatures were calculated using the Ti-in-zircon thermometer (Ferry and Watson, 2007): log (ppm Ti-in-zircon) = (5.711 ± 0.072) - (4800 ± 86)/T (K) - log as<sub>102</sub> + log ar<sub>102</sub>, wherein as<sub>102</sub> = 0.6 due to the presence of the titanite.

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