



# Platinum-group element and Re-Os geochemistry of lamprophyres in the Zhenyuan gold deposit, Yunnan Province, China: Implications for petrogenesis and mantle evolution



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## ABSTRACT

Cenozoic lamprophyres are widespread along the Ailaoshan suture, SW Yunnan, SW China, where there are also many important gold deposits, especially the Zhenyuan deposit. We have carried out a geochemical investigation of the Zhenyuan lamprophyres in terms of major and trace elements, platinum-group elements (PGE), and Os isotopes. The Zhenyuan lamprophyres can be classified into groups with high or low Os concentrations. The  $^{187}\text{Os}/^{188}\text{Os}$  ratios, corrected for *in situ* growth, are highly variable in both types of lamprophyre, ranging from mantle values up to 1.13. The highly radiogenic Os isotopic signatures are interpreted as being due to long-term accumulation of elevated Re/Os in the lithospheric mantle, as a result of subduction-related metasomatism. The highly variable  $^{187}\text{Os}/^{188}\text{Os}$  ratios of the low-Os lamprophyres might also have resulted from metasomatism of a deeply derived carbonate melt, which did not elevate Os concentrations significantly. The Zhenyuan lamprophyres feature low PGE contents and can be classified into two groups: A and B, based on their primitive-mantle-normalized PGE patterns. Group A is characterized by strongly negative Ru anomalies, while Group B is characterized by slightly negative Ru anomalies and low total PGE contents. The PGE characteristics may be explained by a two-stage model of magma evolution. Very high Cu/Pd and low Pt/Y ratios indicate the first stage involved sulfur saturation and sulfide removal, producing variable total-PGE concentrations, especially in Group B. The second stage involved S-undersaturation and the early crystallization of silicate minerals (e.g., olivine) along with laurite and/or Ru-Ir-Os alloy, fractionating PGEs and producing marked negative Eu anomalies.

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## 1. Introduction

The Sanjiang region in southwestern Yunnan Province, SW China, hosts many important mineral deposits of diverse genetic types, including porphyry–skarn Cu–Au–(Mo) and orogenic Au deposits, making this region one of the most widely prospected and metal-productive in China. The Ailaoshan–Red River (ASRR) shear zone is an important feature of the Sanjiang region, and contains one of the most important gold deposits in China (and is thus also called the “Ailaoshan gold belt”). Eocene mantle-derived lamprophyres and potassic volcanic complexes are widespread in the belt (Chung et al., 1998; Guo et al., 2005; Liang and Zhang, 2007; Lu et al., 2015). The Zhenyuan gold deposit, located in the northern section of the Ailaoshan gold belt, is typical of the deposits in this region (Huang et al., 1999, 2002), with widespread Cenozoic lamprophyre dike intrusions occurring across the ore field.

Lamprophyres are generally thought to form from mantle-derived magmas (Foley, 1992; Rock, 1987), and the WNW-trending (ultra)-

potassic lamprophyres in the Sanjiang region therefore can provide significant insight into the composition of the continental lithospheric mantle (CLM) and its metasomatic history beneath the western Yangtze Craton margin. It has previously been suggested that these lamprophyres are calc-alkaline and were derived from low degrees of partial melting of enriched phlogopite harzburgite (Foley, 1992). However, their petrogenesis and the evolution of their lithospheric mantle source are still far from being understood (Chung et al., 1998; Guo et al., 2005; Huang et al., 2010; Li et al., 2002; Wang et al., 2001a; Xu et al., 2001). Two earlier hypotheses considered that lamprophyres in this region originated from partial melting of a metasomatized mantle, and that this metasomatism was induced by oceanic-plate subduction (Guo et al., 2005; Zhou et al., 2002), either due to slab subduction in response to formation of the Panxi–Hannan arc at ca. 1100–900 Ma (Zhou et al., 2002, 2006) or by late Devonian eastward subduction of the paleo-Tethyan oceanic slab (Guo et al., 2005). Contrasting with these subduction-related models, it has been proposed that the enriched lithospheric mantle source was the exotic Tibetan lithosphere, which extruded eastward beneath the Yangtze Craton during Indo-Asia collision at ca. 55 Ma (Xu et al., 2001). A fourth hypothesis suggests that the lithosphere was metasomatized locally by carbonatitic melts from

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the seismic low-velocity zone in the upper mantle, since 250 Ma (Huang et al., 2010).

Platinum-group elements (PGEs; Os, Ir, Ru, Rh, Pt, and Pd) and Re, unlike lithophile elements in mantle peridotites, are chalcophilic and partition strongly into sulfides rather than silicates. Iridium-group PGEs (IPGEs: Os, Ir, and Ru), however, are also compatible with some oxide minerals (e.g., chromite) during the early crystallization of S-undersaturated magmas (Capobianco and Drake, 1990; Capobianco et al., 1994; Keays, 1995). In addition, the behavior of PGEs during magmatic evolution can be influenced by both sulfur and oxygen fugacities ( $fS_2$  and  $fO_2$ , respectively) (Keays and Crocket, 1970; Ringwood, 1955). Research into PGE systematics in mantle-derived magmas is thus important in unraveling the petrogenesis of mafic and ultramafic magmas, and to trace deep mantle and geodynamic processes (Barnes et al., 1985; Greenough and Owen, 1992; Maier et al., 2003a, 2003b; Momme et al., 2006; Puchtel et al., 2009; Vogel and Keays, 1997). The Re–Os isotopic system is a powerful tracer of recycled crust or lithosphere in the mantle because Re behaves as a moderately incompatible element and prefers to enter melt, while Os is highly compatible during melting and remains in the mantle (Shirey and Walker, 1998).

Consequently, continental and oceanic crust both possess high Re/Os ratios and develop a range of radiogenic Os isotopic signatures over time, allowing the tracing of recycled materials mixed back into the mantle.

In this study, major- and trace-element and PGE geochemical analyses, and Re–Os isotopic studies, were conducted on the Zhenyuan lamprophyres. The resulting data are used to reconstruct the evolution of lamprophyres during magmatic differentiation, and to identify the mechanism of mantle enrichment.

## 2. Geological setting and petrology

The Zhenyuan gold deposit is situated in the northern ASRR shear zone, located at the boundary between the Yangtze Craton and the Indochina block (Fig. 1b). The deposit is dominated by the Laowangzhai and Donggualin ore bodies and several other smaller ore segments, such as the Daqiaoqing, Kudumu, and Langnitang segments (Fig. 1c). Lamprophyre dikes occur mainly along NW-trending faults and subsidiary structures, intruding the local stratigraphy and other magmatic rocks, and are spatially related to both the Laowangzhai and Donggualin ore bodies (Fig. 2). Phlogopite  $^{40}\text{Ar}/^{39}\text{Ar}$  ages, Rb–Sr ages, and apatite

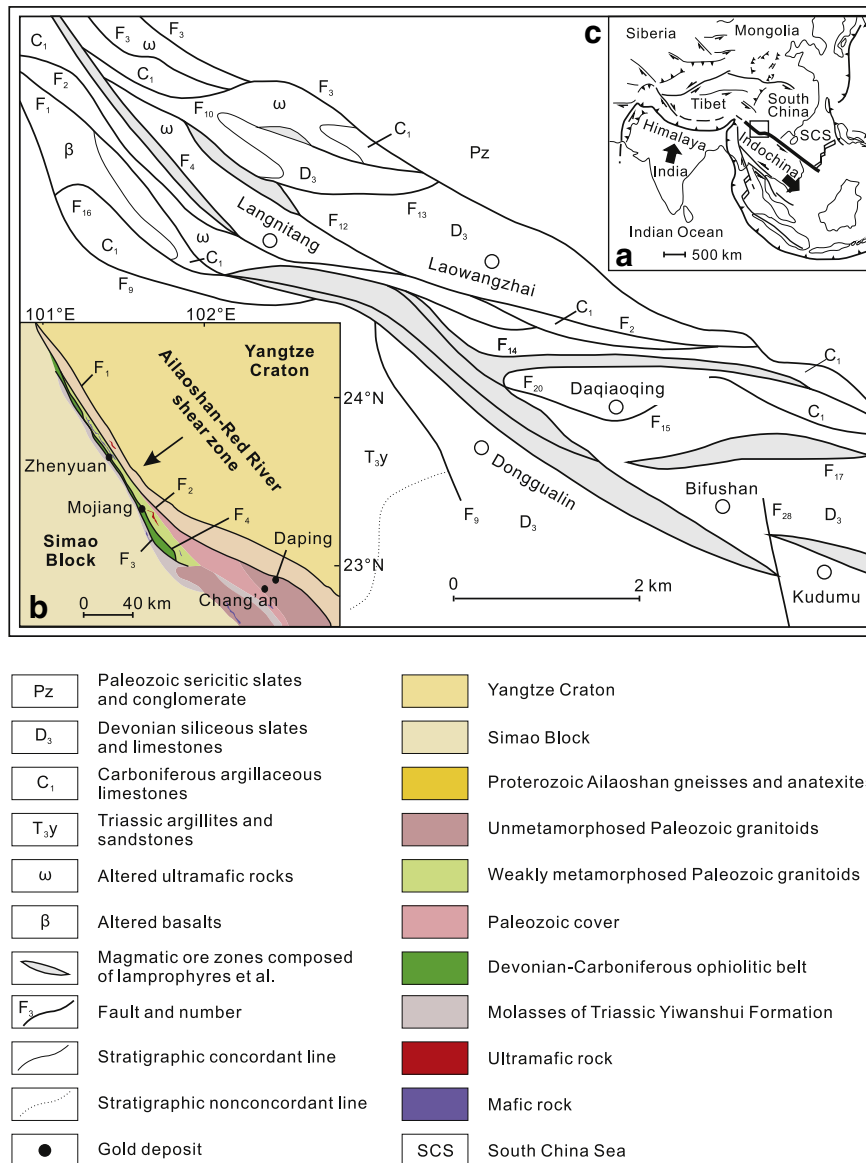


Fig. 1. (a) Simplified tectonic map of Asia showing the Sanjiang region in SW China. (b) Simplified geologic map of the Ailaoshan fold belt. The major faults F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>, and F<sub>4</sub> represent the Honghe, Ailaoshan, Jiujia-Anding, and Amojiang fault, respectively. (c) Geologic map of the Zhenyuan gold deposit, showing the distribution of lamprophyres.

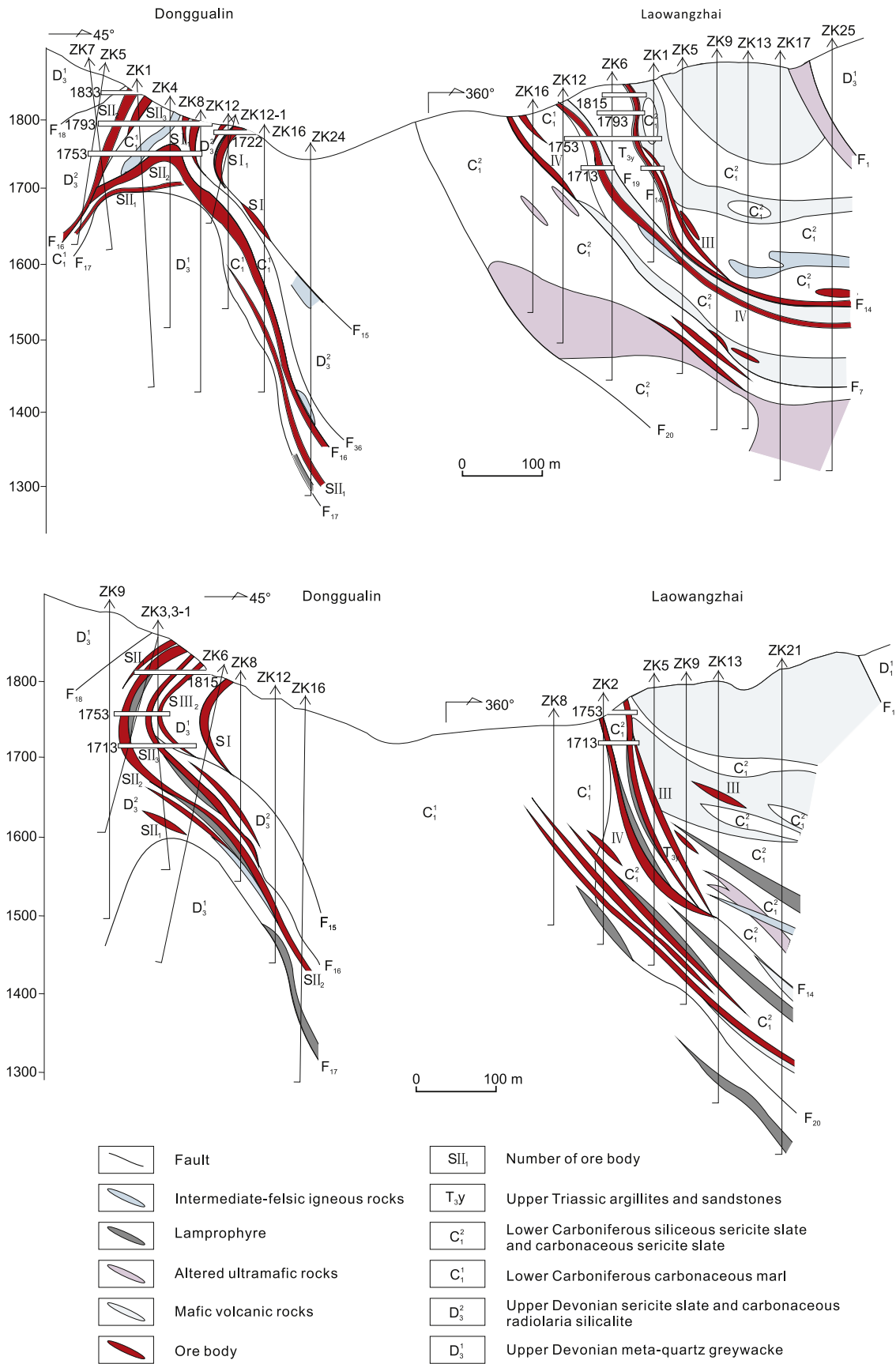


Fig. 2. Geological profiles of the Donggualin and Laowangzhai ore bodies at Zhenyuan, showing the close spatial relationship between the ore bodies and lamprophyres.

fission-track ages of the lamprophyres are 30.8–34.3 Ma (Wang et al., 2001b), 28.8–49.0 Ma (Hu et al., 1995), and 22.7–27.2 Ma (Huang et al., 1997), respectively, consistent with the timing of the Himalayan orogeny. Over 300 dikes make up a magmatic dike belt measuring ~5 km long and ~100–500 m wide, with single dikes being ~5–500 m long and ~0.3–3 m wide. The igneous rocks examined in the present study display petrographic characteristics that are typical of lamprophyres, including porphyritic textures, the presence of castellated phlogopite phenocrysts, and the absence of orthopyroxene, quartz, and feldspar phenocrysts. The phenocrysts comprise clinopyroxene (~10%), phlogopite (~10%), and minor olivine (0%–5%). The groundmass includes feldspar (~40%), mica (~15%), clinopyroxene (~10%), plagioclase (~5%), minor quartz (~1%), and carbonate (~1%; likely secondary). Accessory minerals in the groundmass include apatite, magnetite, and zircon. The rocks are dominated by minettes, which contain clinopyroxene (~20%), mica (~25%; mainly phlogopite and minor Mg-rich biotite), and K-feldspar (~40%). A few kersantites contain mainly clinopyroxene (~20%), mica (~25%), and plagioclase (~35%). Compositional zoning is common in the phlogopite phenocrysts (Fig. 3). The rocks have undergone varying degrees of carbonate, sericite, serpentine, and chlorite alteration, and some sulfur mineralization (producing, for example, pyrite, stibnite, and arsenopyrite).

Lamprophyre samples were collected from both the Laowangzhai and Donggualin ore bodies. To minimize later hydrothermal effects, the collected samples were fresh or weakly altered (grayish-black in color), with primary igneous textures and minerals preserved. Olivine and some pyroxene grains in the rocks were, however, altered to serpentine, chlorite, and carbonate. After detailed petrographic examination, the 30 least-altered samples were selected for geochemical and Os isotope analyses.

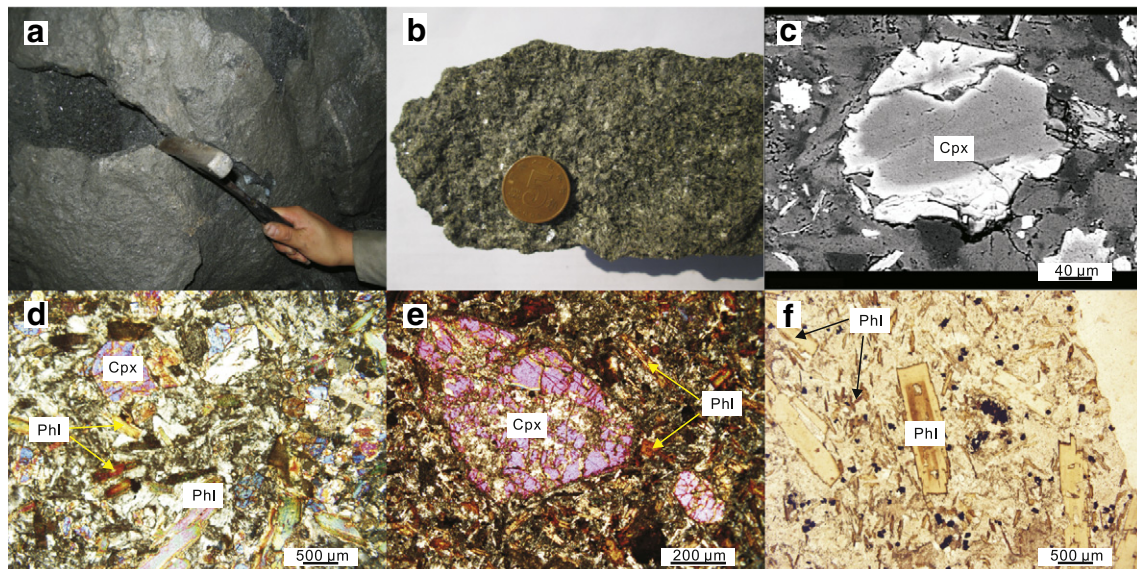
### 3. Analytical methods and calculations

Whole-rock major-element geochemical analyses were conducted by X-ray fluorescence (XRF) spectrometry at the ALS Chemex (Guangzhou, China), with analytical precision better than  $\pm 2\%$ . Trace-element geochemical and isotopic analyses were conducted at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS), Guiyang, China. Whole-rock trace-element concentrations were measured by inductively coupled plasma-mass spectrometry (ICP-MS; Perkin-Elmer ELAN DRC-e).

Powdered samples (50 mg) were dissolved in an HF/HNO<sub>3</sub> mixture in high-pressure Teflon bombs for 48 h at ~190 °C (Qi et al., 2000). An internal standard of 1 ml of 500 ppb Rh solution was added to monitor signal drift during analysis.

PGE concentrations were measured by isotope dilution and ICP-MS after treatment of samples using an improved digestion technique (Qi et al., 2011), as follows. Rock powder (~3 g) was carefully weighed into a 120 ml PTFE beaker. Water (~5 ml) was added to wet the powder, before 15–30 ml HF was added slowly (to avoid boiling due to the exothermic reaction). The acid was then evaporated to dryness to remove silicates before an appropriate volume of isotope-spike solution containing <sup>193</sup>Ir, <sup>101</sup>Ru, <sup>194</sup>Pt, and <sup>105</sup>Pd was added, together with 2 ml HF and 15 ml HNO<sub>3</sub>. The beaker was sealed in a stainless-steel pressure bomb, which was heated in an electric oven at 185 °C for 36 h. After cooling to room temperature, the beaker was opened, and 2.5 ml HCl added and evaporated to dryness. This acid-evaporation step was repeated three times to remove residual HF and HNO<sub>3</sub>. After the final drying, the residue was washed with water into a 50 ml centrifuge tube. After centrifuging, the residue was discarded, and PGEs pre-concentrated by Te-coprecipitation. The main interfering elements, including Cu, Ni, Zr, and Hf, were removed by ion-exchange chromatography, using a mixed-resin column containing Dowex 50WX8 cation-exchange resin and P507 Levetrel resin. The eluted solution was evaporated to a volume of 2–3 ml and transferred to a 15 ml centrifuge tube for ICP-MS analysis. Platinum, Pd, Ru, and Ir were measured by isotope dilution, while <sup>194</sup>Pt was used as an internal standard for determination of Rh (Qi et al., 2004). Analysis results for standards WGB-1, TDB-1, and UMT-1, and blank solutions, are listed in Supplementary Table 1. Results for the standards were in good agreement with their certified values, and total procedural Ir blanks ranged from 0.001 to 0.019 ng.

Osmium isotopes were measured using the above ICP-MS, following the procedure of Qi et al. (2007). A carefully weighed powder sample (~6 g) was loaded in a Carius tube with an appropriate volume of spike solution, 15 ml HNO<sub>3</sub>, and 5 ml HCl. The tube was sealed and heated in a stainless-steel pressure bomb at 140 °C for 12 h, then further heated to 180 °C for 24 h. After this digestion, the tube was transferred to a custom-made distillation system to separate the volatile Os, which was trapped in 5% HCl solution for measurement. The remaining solution was transferred to a clean beaker for Re separation, as follows. After drying, 2.5 ml HCl was added and evaporated to dryness. This procedure was repeated to remove any remaining HNO<sub>3</sub>, before HCl



**Fig. 3.** (a): Field photograph and (b) hand specimen photograph of the lamprophyre dikes at Zhenyuan. (c) Altered clinopyroxene phenocryst. (d) and (e) Typical lamprophyric texture, comprising clinopyroxene, plagioclase, and phlogopite. (f) Phlogopite phenocrysts showing composition zoning.

(7.5 ml) was added to the residue and the mixture transferred to a 50 ml centrifuge tube. After centrifuging, the solution was passed through an anion-exchange column (AG 1-X8) for ICP-MS measurement.

Regardless of the melting history of the mantle source of the Zhenyuan lamprophyres, we can calculate the residence time before a given lamprophyre source was isolated from the convecting mantle, based on when its Re/Os ratio became the same as the present-day ratio. Assuming the age to be 30 Ma, the time taken for the development of present-day  $^{187}\text{Os}/^{188}\text{Os}$  ratios (by the *in situ* ingrowth of  $^{187}\text{Os}$ ) can be determined by the Re-Os isochron equation (Eq. 1 in Supplementary Table 2 notes). Assuming also that the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of the convecting mantle (0.124; Widom et al., 2003) was the initial ratio, the residence time can be calculated (Eq. 2 in Supplementary Table 2 notes).

## 4. Results

### 4.1. Major and trace elements

Results of all elemental and Re-Os isotopic analyses, and calculations of residence time for the Zhenyuan lamprophyres, are given in Supplementary Table 2. Major-element contents were recalculated on an anhydrous basis for the discussion below.

The Laowangzhai and Donggualin lamprophyres are classified as calc-alkaline lamprophyres (Rock, 1987) (Fig. 4). Their major-element contents are similar to each other, with  $\text{SiO}_2$  of 41.41–50.13 wt% and total alkali ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) of 1.17–7.56 wt%, mainly 3.03–7.56 wt%. Their REE and trace-element patterns are also similar to each other, being characterized by strong light rare earth element (LREE) enrichment and a lack of obvious Eu anomalies ( $\text{Eu}/\text{Eu}^* = 0.78\text{--}1.04$ ) (Fig. 5a), except for one sample, YD-20. Sample YD-20 is LREE-depleted, and unlike the other lamprophyres, may have been sourced from depleted mantle. It also displays Nb and P depletion, but no Ta and Ti depletion as in the other samples. This single sample is not discussed further. Lamprophyre  $\Sigma$  REE contents range from 111 to 326 ppm, and  $(\text{La}/\text{Yb})_N$  ratios are 7.5–36.5. These rocks also show significant enrichment in large-ion lithophile elements (LILEs; e.g., Ba and K) and depletion in high-field-strength elements (HFSEs; e.g., Nb, Ta, Ti) (Fig. 5b). They have trace-element characteristics that distinguish them from mid-ocean-ridge basalts (MORB), but there are similarities with ocean-island basalts (OIB) in terms of strong LREE enrichment, and with island-arc-related volcanic rocks in terms of LILE enrichment and HFSE depletion.

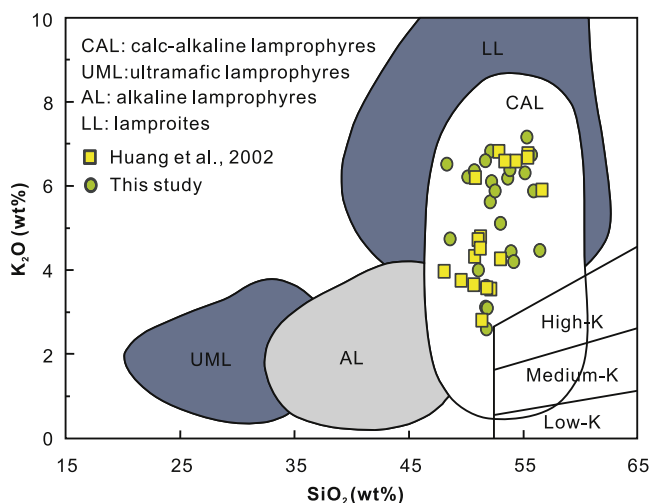


Fig. 4.  $\text{SiO}_2$  vs.  $\text{K}_2\text{O}$  classification diagram (after Rock, 1987) for the Zhenyuan lamprophyres. Green circles: this study; Yellow squares: Huang et al. (2002).

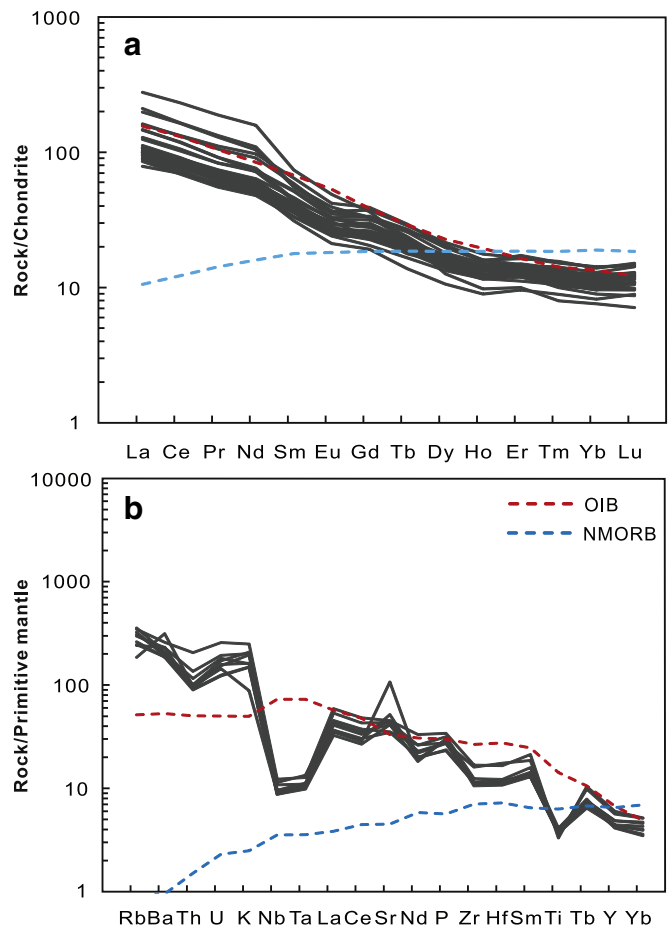


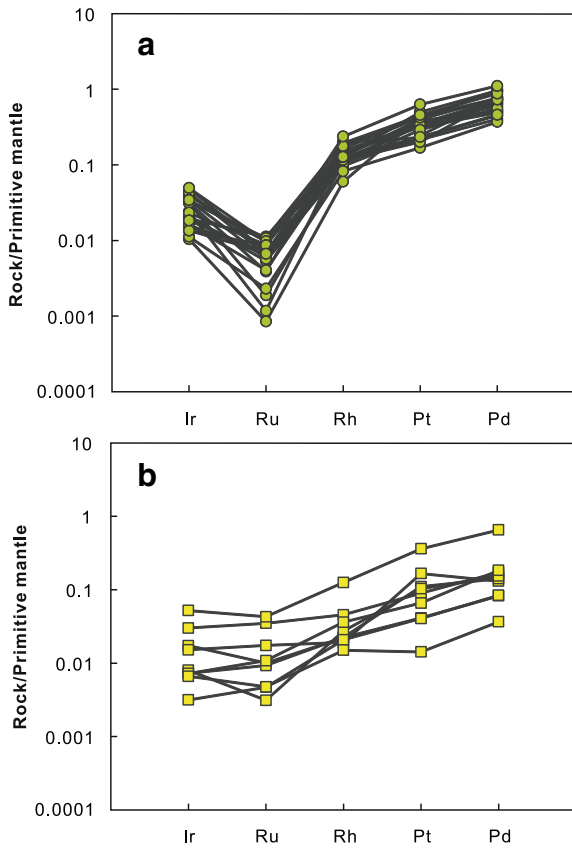
Fig. 5. (a) Chondrite-normalized REE patterns and (b) primitive-mantle-normalized multi-element diagram of the Zhenyuan lamprophyres. Average chondrite and primitive mantle compositions are from McDonough and Sun (1995); average N-MORB and OIB compositions are from Sun and McDonough (1989).

### 4.2. PGE geochemistry

The PGE contents of the Zhenyuan lamprophyres are as depleted as those of basalts from the Emeishan Large Igneous Province (ELIP) (Qi and Zhou, 2008; Song et al., 2009) (Supplementary Table 2). Primitive-mantle-normalized PGE patterns are presented in Fig. 6. According to these patterns, the Zhenyuan lamprophyres can be divided into two groups: Group A and Group B. Group A is characterized by strongly negative Ru anomalies and shows similar PGE patterns to many mafic rocks, the ELIP low-Ti basalts (Qi and Zhou, 2008; Song et al., 2009), mafic lavas from the Tonga arc (Dale et al., 2012), and spessartite (shoshonitic lamprophyre) from Weekend Dykes, Canada (Greenough et al., 1993). Group A samples have low IPGE and relatively high platinum-group PGE (PPGE; Rh, Pt, and Pd) contents, except for two samples that have relatively low PGE contents (YD-15 and YD-20). Group B displays slightly negative Ru anomalies and contains lower total PGE contents than Group A. In both groups the Pd, Pt, and Rh contents decrease rapidly with decreasing Ir (Fig. 7a–c).

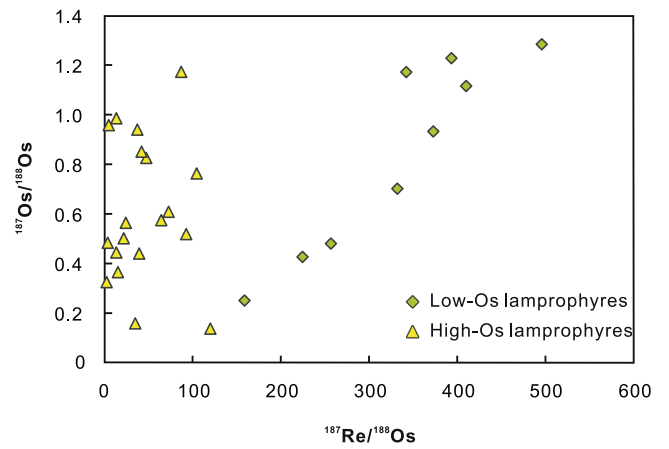
### 4.3. Re-Os isotopic compositions

The Zhenyuan lamprophyres exhibit extremely variable Os and Re concentrations, and can be classified into high- and low-Os types. The high-Os type contains Os concentrations of 0.030–1.8 ppb, and the low-Os type contains  $<0.030$  ppb. Re/Os ratios of the low-Os type are higher (159–496) than those of the high-Os type (2.8–121). For the



**Fig. 6.** Primitive-mantle-normalized PGE patterns of the two groups of Zhenyuan lamprophyres. Primitive mantle normalization values are from [McDonough and Sun \(1995\)](#). Green circles represent Group A in Fig. 6a, and yellow squares represent Group B in Fig. 6b.

low-Os lamprophyres, there is a positive linear correlation between  $^{187}\text{Re}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  (Fig. 8). The relation is likely due to mixing or contamination or metasomatism; if it were interpreted to be isochron, the age would be about 2.1 Ga. For the high-Os type, there is a positive correlation between Os content and calculated residence



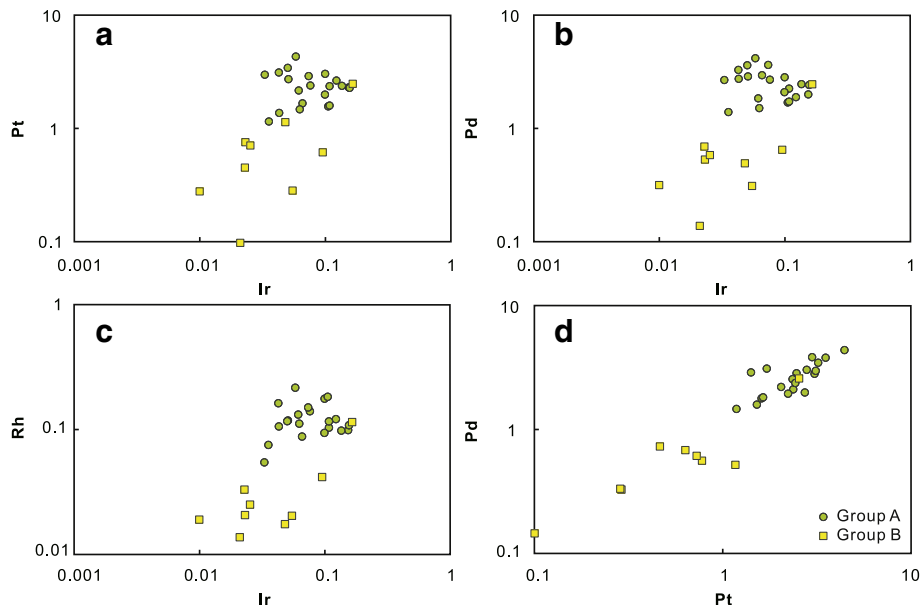
**Fig. 8.**  $^{187}\text{Os}/^{188}\text{Os}$  vs.  $^{187}\text{Re}/^{188}\text{Os}$  diagram for the Zhenyuan lamprophyres. One point with the lowest Os concentration and with  $^{187}\text{Re}/^{188}\text{Os} = 977$  seems to be due to an inaccurate Os concentration and is ignored.

time (Fig. 9), with results displaying two distinct peaks: one in the Precambrian and another in the Triassic – Cretaceous.

### 5. Discussion

#### 5.1. Mechanism of mantle metasomatism

The Zhenyuan lamprophyres have undergone serpentinization and other hydrothermal alteration. [Wang et al. \(2008\)](#) considered that hydrothermal fluids were also responsible for the release of PGEs from sulfides to precipitate platinum group minerals (PGMs) at low temperature. This is unlikely to be applicable to the Zhenyuan lamprophyres, however, because Ir does not readily leach from the source rocks and is not readily transported by hydrothermal fluids ([Keays, 1982](#)). In addition, the good correlations of Pt and Pd with Ir (Fig. 7a, b) indicate that the PGEs were originally concentrated by magmatic processes. In general, Pd is preferentially mobilized relative to other PGEs by hydrothermal alteration, leading to curve-flattening from Pt to Pd in primitive-mantle-normalized PGE patterns (Fig. 6) ([Barnes et al., 1985](#)). Most of the Zhenyuan samples display steep slopes from Pt to Pd, a narrow



**Fig. 7.** Binary plots for PGEs of the Zhenyuan lamprophyres.

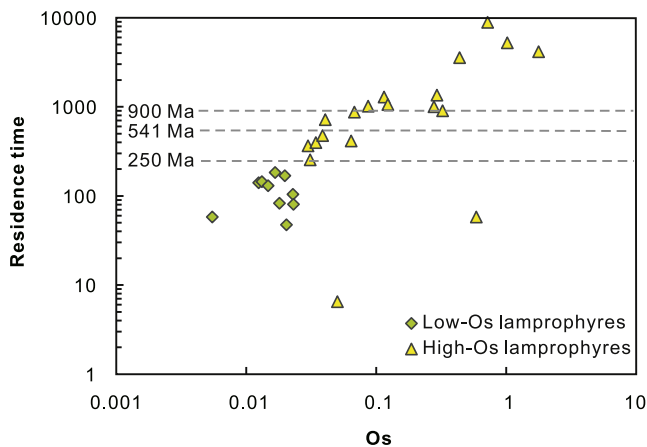


Fig. 9. Plot of Os vs calculated residence time of source mantle isolated from the convecting mantle, regardless of metasomatism history.

Pd/Pt range (0.70–1.25), and a positive Pt vs Pd correlation (Fig. 7d), indicating the coherent behavior of PGEs during magma evolution. PGE and Os isotope compositions of the Zhenyuan lamprophyres were thus controlled mainly by magmatic processes and the influence of post-magmatic hydrothermal alteration was minimal.

Lamprophyres in the western Yangtze Craton contain high concentrations of highly incompatible elements and volatile elements (Tuner et al., 1996), suggested by Lu et al. (2015) to indicate partial melting of metasomatized upper mantle. The presence of Nb-Ta and Ti anomalies (Fig. 4b) suggests an affinity with subduction processes (Sun and Kerrich, 1995; Thirlwall et al., 1994). The initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios of most samples, ranging from typical values of mantle to 1.1294, are much more radiogenic than that of upper mantle, with a  $\gamma_{\text{Os}}$  range of 10–787 (average 369).

#### 5.1.1. Crustal contamination

The Os isotopic composition of continental crust is highly radiogenic due to Os compatibility and Re incompatibility during partial melting (Shirey and Walker, 1998). Crustal contamination has been commonly cited as a mechanism for producing high initial Os isotopic compositions in arc lavas (Shirey and Walker, 1998; Woodhead and Brauns, 2004). The lack of correlations between  $^{187}\text{Os}/^{188}\text{Os}$  and MgO or  $\text{SiO}_2$  rules out significant influence by assimilation-fractional crystallization (AFC) processes (Alves et al., 1999). Compared with the average continental crust (Hofmann et al., 1986; Rudnick and Fountain, 1995), the Zhenyuan lamprophyres have much higher Ba (up to 2410 ppm) and Sr (up to 2310 ppm) concentrations, but much lower Nb/U ratios (1.4–2.3), suggesting their trace-element compositions were not obviously affected by crustal contamination. These rocks have high initial  $^{87}\text{Sr}/^{88}\text{Sr}$  ratios (0.707–0.709), negative  $\epsilon_{\text{Nd}}(t)$  (–3.07 to –1.43), and radiogenic lead ratios of  $^{207}\text{Pb}/^{204}\text{Pb} = 15.57\text{--}15.70$  and  $^{208}\text{Pb}/^{204}\text{Pb} = 38.70\text{--}39.06$  (Huang et al., 1999; Lu et al., 2015). The effect of crustal contamination on the magma evolution of the lamprophyres is therefore likely to have been limited. The petrogenetic modeling of Lu et al. (2015) also indicates that contamination by the upper or lower crust did not produce the enriched trace-element and isotopic signatures of Yunnan lamprophyres. Furthermore, the Os concentration in the crust is too low to significantly affect the  $^{187}\text{Os}/^{188}\text{Os}$  ratio in high-Os lamprophyres (although low-Os samples could have been affected).

#### 5.1.2. Subduction-related metasomatism of the mantle source

It has been suggested that Os is more mobile than Sr in slab-derived fluids (Widom et al., 2003). Terrigenous and pelagic sediments are generally characterized by highly radiogenic Os signatures ( $^{187}\text{Os}/^{188}\text{Os} \approx 1.0$ ) (Burton et al., 1999; Esser and Turekian, 1993; Sharma et al., 1999). The altered oceanic lithosphere can also be highly radiogenic in

Os, due to both the aging of high-Re/Os basaltic and gabbroic rocks, and interactions between seawater and crust (with the uppermost oceanic mantle) (Hart et al., 1999). Osmium isotopes in Java subduction-zone lavas may comprise a mixture of mantle-derived non-radiogenic Os and coexisting slab-derived radiogenic Os, with  $^{187}\text{Os}/^{188}\text{Os}$  ratios as high as 3.704 (Alves et al., 1999). It has been suggested that Os mobility in slab-derived fluids depends on oxygen fugacity and chlorine content (Brandon et al., 1996), and that significant Re-influx into the sub-arc mantle occurs, as indicated by studies of the Zermatt-Saas ophiolitic basalts in Switzerland (Dale et al., 2009). The positive correlation between  $^{187}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Re}/^{188}\text{Os}$  for low-Os lamprophyres (Fig. 8) implies that some Re entered the mantle wedge during slab-fluid metasomatism. Terrigenous and pelagic sediments and oceanic basalts may have high  $^{187}\text{Os}/^{188}\text{Os}$  ratios, but given their low Os concentrations compared with mantle rocks they are unlikely to raise mantle-source  $^{187}\text{Os}/^{188}\text{Os}$  ratios to ~10 times the normal mantle value, as observed here. Owing to the large partition coefficients for Os in sulfides (Hart and Ravizza, 1996), the formation of metasomatic sulfide melt is a potential mechanism for radiogenic slab-derived Os enrichment in the sub-arc mantle (Borg et al., 2000), especially if an eclogitic sulfide melt with  $^{187}\text{Os}/^{188}\text{Os}$  as high as 50 (Luguet et al., 2008) were involved. Another consequence of sulfide melt metasomatism and infiltration would be to raise the concentrations of chalcophile elements, consistent with the high-Os lamprophyres observed in this study. It is thus possible that the highly radiogenic signatures of the Zhenyuan lamprophyres were due mainly to subduction-related metasomatism, which also resulted in their depletion in Nb, Ta, and Hf (relative to U, La, and Sm, respectively) (Ayers, 1998; Hofmann et al., 1986; Ma et al., 2014a; Rudnick and Gao, 2003). The occurrence of such subduction-related metasomatism is further supported by the presence of phlogopite, which is a hydrous mineral phase (Beccaluva et al., 2004; Ionov et al., 1997).

#### 5.1.3. Carbonate metasomatism

Previous studies of carbonatites (both oceanic and continental) indicated that they are characterized by low Os and relatively high Re concentrations (Pearson et al., 1995; Widom et al., 1999). Yaxley and Green (1996) inferred that deep slab-derived carbonate melts may be relatively evolved melts that have suffered Os loss through fractionation processes. In addition, PGE studies of some continental xenolithic suites (assumed to be carbonatite metasomatized) indicate that PGEs and Re are not significantly mobilized during subcontinental carbonatitic metasomatism (Handler et al., 1997; Hart et al., 1999; Lorand and Alard, 2001). Wood (1987) suggested, however, that in high- $f\text{O}_2$  and Cl-rich H-O-C fluids, decreasing  $f\text{H}_2\text{O}$  (and thus increasing  $\text{CO}_2$ ) would increase the solubility of PGEs. A combination of metasomatism and oxidation of the mantle wedge by carbonate-rich melts could thus provide an alternative explanation for the radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratios in low-Os lamprophyres. Concomitant isotopic exchange with, and scavenging of Os by, radiogenic and high- $f\text{O}_2$  carbonate-rich melts would produce both the radiogenic Os and relatively low Os abundances observed in the low-Os group. This is consistent with deeply derived carbonate-rich slab melts imparting stronger metasomatic signatures in the Re-Os isotope system than either hydrous slab fluids or adakitic slab melts (Widom et al., 2003).

#### 5.1.4. Evolution of lithospheric mantle beneath the western Yangtze Craton

The late Permian (ca. 260–250 Ma) Emeishan continental flood basalts are grouped as having either high or low Ti contents, and previous studies suggest these groups were generated from the mantle plume and continental lithospheric mantle, respectively (Xiao et al., 2004). Based on major- and trace-element geochemical characteristics, and Sr, Nb, and Pb isotopes, Lu et al. (2015) suggested that lamprophyres in the western Yangtze Craton were derived from the same metasomatized mantle source as the ELIP low-Ti basalts. We propose here that there may have been two metasomatism events along

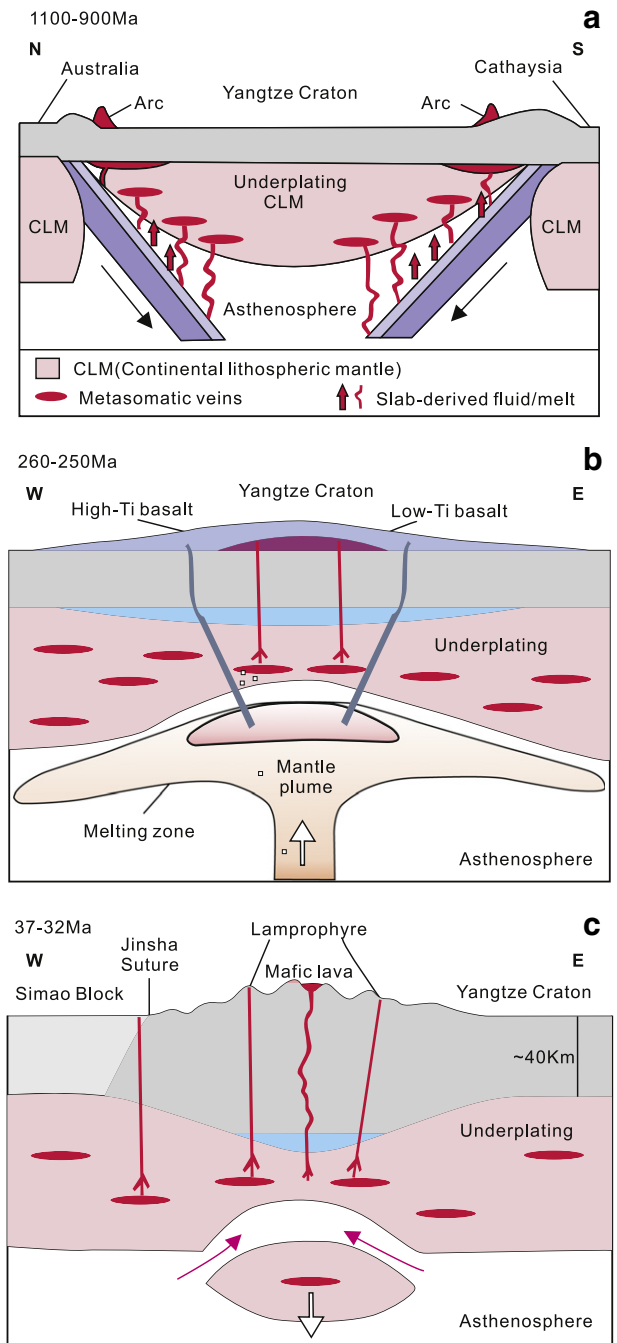
the western Yangtze Craton margin. The lithospheric mantle may first have been enriched during Proterozoic subduction (pre-900 Ma), followed by carbonate metasomatism during the ca. 260–250 Ma ELIP event. Residual metasomatic mantle domains were preserved and tapped by delamination of the over-thickened CLM (formed during the Paleogene Himalayan orogeny), forming the lamprophyres and (ultra)-potassic rocks in western Yunnan. This inference is supported by several lines of evidence, as outlined below.

The Zhenyuan lamprophyres have  $^{187}\text{Os}/^{188}\text{Os}$  signatures that are significantly more radiogenic than those of any continental mantle. Their mantle source would have had to evolve with a long history of suprachondritic Re/Os ratios in order to generate the observed  $^{187}\text{Os}/^{188}\text{Os}$  signatures (through the *in situ* ingrowth of  $^{187}\text{Os}$ ), without taking account of mantle melting history. Calculations using the lamprophyres with the most radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  (1.283) and  $^{187}\text{Re}/^{188}\text{Os}$  (496) ratios indicate that this mantle would have been isolated from the convecting mantle for ~142 Myr. Sample YD-11, however, with an  $^{187}\text{Os}/^{188}\text{Os}$  ratio of 0.957 and  $^{187}\text{Re}/^{188}\text{Os}$  ratio of 5.2, would require an ingrowth period of ~8900 Myr, which is not possible (as it exceeds the age of the Earth). The observed Os-isotope signatures could be accounted for by mantle metasomatism and later Re loss and radiogenic ingrowth, following Precambrian metasomatism. The Zhenyuan lamprophyres are characterized by high initial  $^{87}\text{Sr}/^{86}\text{Sr}$  and low initial  $^{143}\text{Nd}/^{144}\text{Nd}$ , as well as high  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{187}\text{Os}/^{188}\text{Os}$  ratios, compared with MORB (Lu et al., 2015; this study). This suggests long-term enrichment of Rb, LREEs, U, and Re in the subcontinental lithospheric mantle (Guo et al., 2005; this study). The enriched Sr, Nd, Pb, and Os isotopic compositions of the Zhenyuan lamprophyres thus reflect the time-integrated effect of LREE, Rb, U, and Re enrichment during Proterozoic subduction (Fig. 10a).

As mentioned above, the Zhenyuan lamprophyres exhibit both high and low Os contents. They may also be sorted into two distinct groups based on calculated residence times, as indicated in Fig. 9. In addition to the mantle metasomatism events discussed above, we suggest that all the Zhenyuan samples experienced Precambrian subduction-related metasomatism, consistent with previous studies of regional mantle-metasomatism (Zhou et al., 2002, 2006). We suggest that carbonate metasomatism was related to the late Permian ELIP mantle-plume event (Fig. 10b), during which high-Ti basaltic magma ascent and emplacement may have influenced the mantle source by carbonatitic metasomatism, leaving residual carbonate globules (Fig. 10b). As in the case of the Jiaodong Peninsula in the North China Craton, two lamprophyre types (low-Ti and high-Ti) have been recognized (Ma et al., 2014a, 2014b, 2016). Furthermore, a mantle plume would have carried more radiogenic Os isotopes through entrainment of the lower mantle. Huang et al. (1999) reported the presence of carbonate globules in some Zhenyuan lamprophyres and suggested that fluids were derived from the dehydration of altered MORB, and deeply derived carbonates both being the most important materials in re-fertilizing the local lithospheric mantle. We therefore suggest that the Zhenyuan lamprophyre dikes may also have experienced carbonatitic metasomatism.

## 5.2. Crystal fractionation of lamprophyre

In mafic magma fractionation, PGEs may be considered as compatible IPGEs (Os, Ir, and Ru) or incompatible PPGEs (Rh, Pt, and Pd), based on melting points (Barnes et al., 1985; Naldrett et al., 1979). IPGEs are compatible during fractional crystallization (Barnes et al., 1985) as they mainly exist in mafic minerals and alloys in S-undersaturated magmas. The most distinctive PGE features of the Zhenyuan lamprophyres include: (1) low PGE contents compared with MORB; (2) fractionation of IPGEs and PPGEs; and (3) negative Ru anomalies. Several mechanisms may have led to such fractionation, including: (1) sulfide segregation (Amosse et al., 1990; Bockrath et al., 2004a; Handler et al., 1999); (2) separation of an Ir- and Ru-rich alloy (Fleet



**Fig. 10.** Schematic diagram showing the petrogenesis of the post-collisional Zhenyuan lamprophyre and the evolution of mantle lithosphere beneath the western Yangtze Craton (modified from Deng et al., 2014). (a) Metasomatism of the lower lithospheric mantle at ca. 1100–900 Ma. (b) In the late Permian (ca. 260–250 Ma) the Emeishan mantle plume ascended beneath the western Yangtze Craton, carrying small amounts of carbonates from the lower mantle. This resulted in the production of high-Ti and low-Ti basalts from the plume and continental lithospheric mantle, respectively (Xiao et al., 2004). (c) In the Paleogene the lithospheric mantle beneath the western Yangtze Craton was thickened during Indo-Asia collision, and the mantle eventually became delaminated at ca. 37–32 Ma. The ensuing asthenospheric upwelling may have caused the regional lamprophyres and eruption of mafic lava.

et al., 1996; Maier and Barnes, 1999; Peck et al., 1992; Tredoux et al., 1995); and (3) removal of Os, Ir, and Ru in, or with, early crystallized magmatic minerals such as olivine, pyroxene, and Cr-spinel (Barnes and Picard, 1993; Hart and Ravizza, 1996; Keays, 1982, 1995; Peach and Mathez, 1996). It seems, therefore, that both sulfide segregation



and mineral fractional crystallization occurred during the magmatic evolution of the Zhenyuan lamprophyres.

### 5.2.1. Sulfide precipitation

Sulfur and copper behave similarly during magmatic differentiation, meaning that Cu can serve as a proxy for sulfur. In addition, the sulfide-liquid/silicate partition coefficient of Pd is much greater than that of Cu ( $D_{\text{sulfide/melt}} = 3.5 \times 10^4$  for Pd, and  $\sim 10^3$  for Cu) (Barnes and Picard, 1993; Fleet et al., 1996; Peach et al., 1990). Sulfide precipitation would therefore significantly increase the Cu/Pd ratio (Qi and Zhou, 2008; Saha et al., 2015; Song et al., 2009), making this ratio a useful indicator of S-saturation (Vogel and Keays, 1997; Woodland et al., 2002). Platinum becomes incompatible when olivine and clinopyroxene are fractionated (Capobianco and Drake, 1990; Capobianco et al., 1991, 1994; Puchtel and Humayun, 2001; Richter et al., 2004), meaning that Pt/HFSE ratios would decrease during the fractional crystallization of S-undersaturated magmas, and be significantly lowered at S-saturation due to sulfide removal.

The Zhenyuan lamprophyres exhibit Pd depletion, reduced Pd/Cr and Pt/Y ratios, and significantly increased Cu/Pd ratios compared with the primitive mantle (Fig. 11), suggesting that the low PGE contents are due to sulfide segregation. There is also depletion in Ir, Pt, Pd, and Rh (Fig. 7a–c), possibly due to sulfide precipitation. These features are most evident with Group B lamprophyres dominate the trend in these figures, which may thus have experienced more sulfide removal than the Group A type, thereby explaining their relatively low total-PGE content.

### 5.2.2. Early mineral crystallization

Previous studies indicate that distribution coefficients for IPGEs between olivine and silicate fluid ( $D_{\text{olivine/melt}} \sim 2$ ) are considerably higher than for PPGEs ( $D_{\text{olivine/melt}} \leq 0.01$ ; Brenan et al., 2005). During

early fractional crystallization, IPGEs may form laurite and Os-Ir-Ru alloy (Amosse et al., 1990; Capobianco and Drake, 1990; Peck and Keays, 1990), which may occur as fine inclusions in early fractionating phases; e.g., in chromite and olivine (Stockman and Hlava, 1984; Tredoux et al., 1995; Zhou, 1994). Laurite typically contains more Ru and Os than Ir, and it (and other PGMs in general) is more refractory than base-metal sulfides (Bockrath et al., 2004b; Brenan and Andrews, 2001). Laurite is therefore more likely to be retained in the mantle during melting. Laurite-rich PGM assemblages have been observed in Cr-spinel-rich rocks from sub-arc ophiolitic mantle (Garuti et al., 1999; González-Jiménez et al., 2011), and in highly depleted harzburgite and lherzolite of the Lherz massif (French Pyrenees) (Lorand et al., 2010; Luguet et al., 2007). Fractionation of IPGEs and PPGEs may thus be attributed to early olivine fractionation, through the formation of laurite and/or Ru-Os-Ir alloy (Qi and Zhou, 2008). It has been found that Pt, Pd, and Re are depleted relative to Os, Ir, and Ru in subduction-related metamorphosed mafic oceanic crust, suggesting these elements may be transferred to the mantle wedge by slab-derived fluids (Dale et al., 2007, 2009), increasing the concentration of PPGEs relative to IPGEs. Fluid fluxes into the arc mantle may therefore have been important for PGE fractionation and may also explain the negative Ru anomalies.

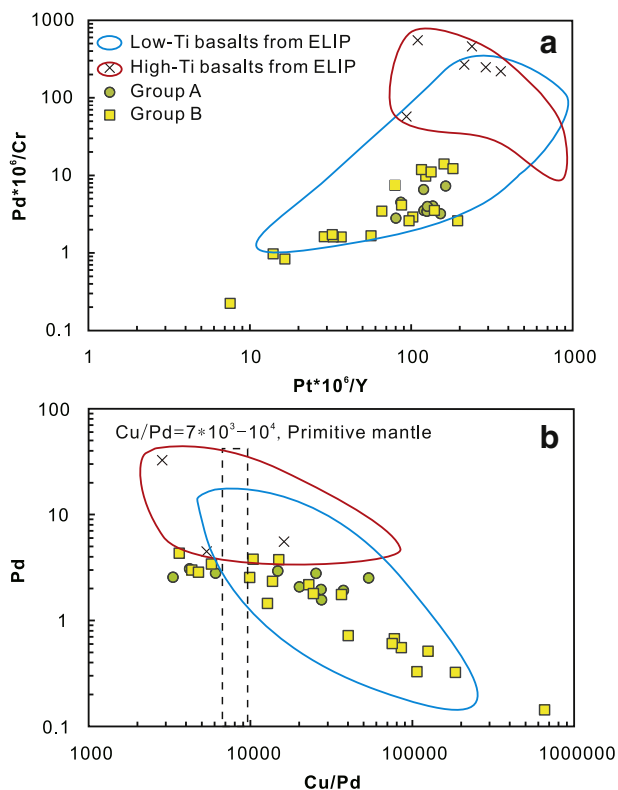
Qi and Zhou (2008) and Wang et al. (2010) reported negative Ru anomalies in ELIP basalts from Heishitou and Jinbaoshan, similar to those found in the Zhenyuan lamprophyres, and such anomalies have also been observed in subduction-related basalts (e.g., Park et al., 2012). This is consistent with our inference that the mantle source of the Zhenyuan lamprophyres has undergone subduction-related metasomatism. It is likely that the crystallization of major silicates, such as olivine, drove the precipitation of PGE-rich accessory phases (Burton et al., 2002; Zhang, 2015). Relative bulk-rock PGE partition coefficients decrease in the order: Ru > Ir = Os > Pt > Pd > Re (Dale et al., 2009), suggesting that Ru is more compatible than Os or Ir in Mg-rich samples (6–14 wt% MgO). Similar olivine/melt partitioning for Ru and Ir has been indicated in previous experimental studies (Brenan et al., 2003, 2005). We infer, therefore, that negative Ru anomalies in the Zhenyuan lamprophyres were caused by the crystallization of olivine.

### 5.2.3. Magmatic evolution of lamprophyres

Sulfur saturation clearly plays a key role in the evolution of arc rocks. As discussed above, we suggest that the magma has undergone both S-saturation and S-undersaturation. A two-stage mantle-evolution model is therefore proposed, as follows. Stage one involved S-saturation and sulfide removal, as indicated by increased Cu/Pd ratios. The reducing Pd/Cr and Pt/Y ratios, and increasing Cu/Pd ratio with decreasing Pd may have resulted from sulfide precipitation (Fig. 11b). The decrease in Ir, Rh, Pt, and Pd contents further indicates that the low PGE concentrations were caused by sulfide precipitation (Fig. 7a–c). It therefore seems that magma with a low degree of partial melting may have become S-saturated in the upper mantle, with the separation of immiscible sulfides, resulting in PGE depletions in order of increasing compatibility (Barnes et al., 1985; Keays, 1995; Vogel and Keays, 1997). With the fractionation of silicates and oxides, the sulfur content in the residual melt increased, as sulfur solubility increases with increasing  $fO_2$  due to the formation of  $SO_4^{2-}$  (Jugo, 2009). Stage two involved decompression during magma intrusion, possibly leading to S-undersaturation. Hence, the PGEs fractionated among each other in the Zhenyuan lamprophyres, due to the fractionation of olivine together with laurite and/or a Ru-Ir-Os alloy.

## 6. Conclusion

This study presents major- and trace-element and PGE concentrations and Os isotopic data of the lamprophyres from the Zhenyuan gold deposit. The Zhenyuan lamprophyres are calc-alkaline. Os concentrations in the lamprophyres range from MORB/OIB values to 1.8 ppb, and  $^{187}\text{Os}/^{188}\text{Os}$  ratios range from mantle values to 10 times higher.



**Fig. 11.** Plots of (a)  $\text{Pd} \times 10^6/\text{Cr}$  vs  $\text{Pt} \times 10^6/\text{Y}$  and (b) Pd vs Cu/Pd, indicating that low PGE contents of the Zhenyuan lamprophyres may have resulted from sulfide removal. Data of low- and high-Ti basalts from the ELIP are from Song et al. (2009). Range of Cu/Pd ratios of the primitive mantle is from Taylor and McLennan (1985) and Barnes and Maier (1999).

The highly radiogenic Os isotopic signatures suggest that the mantle source was Re-enriched through either Precambrian subduction-related metasomatism (during which the oxidized and Cl-rich slab-derived fluids transported PPGEs and Re from the subducted slab to the mantle wedge above), or late Permian ELIP mantle-plume activities (which contaminated the already re-fertilized subcontinental lithosphere with deeply derived carbonate, resulting in the lower Os contents and more radiogenic Os isotopic signatures).

The Zhenyuan lamprophyres can be grouped according to their mantle-normalized PGE patterns. We propose a two-stage model for the magma evolution of the Zhenyuan lamprophyres, with the first stage involving S-saturation and sulfide removal (which generated the characteristic low total-PGE concentrations), and the second stage involving S-undersaturation and early crystallization of mafic minerals (e.g., olivine) together with laurite and Ru-Ir-Os alloy, which fractionated the PGEs.

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## Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.lithos.2017.03.018>.

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