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Geochemistry of the Yumen picrites-basalts from the Emeishan large igneous province: Implications for their mantle source, PGE behaviors, and petrogenesis

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ABSTRACT

Olivine compositions are often used to infer the source lithology of basaltic rocks, but the effect of source melting conditions on olivine chemistry remains poorly studied. Here we present mineral chemistry, whole-rock major and trace elements, Sr–Nd isotopes, and platinum-group element (PGE) concentrations for high-Ti picriticbasaltic rocks from Yumen area. These data provide new constraints on the source lithology and petrogenesis of these high-Ti rocks in the Emeishan large igneous province (ELIP). The picrites have primitive compositional features (e.g., high Mg[#] values, depleted Sr—Nd isotopic compositions, no PGE depletions and/or fractionations). Some basaltic rocks have negative Nb–Ta anomalies, enriched Sr–Nd isotopic compositions, and depleted and/or fractionated PGE contents, indicative of fractional crystallisation, variable degrees of crustal contamination, and magmatic sulfide segregation. Combined with published data for the ELIP, the compositions of the primitive magmas and 10000Zn/Fe and FC3MS (FeO/CaO $-3 \times$ MgO/SiO₂, all in wt%) values of the ELIP high-Ti picrites are similar to those of garnet peridotite-derived experimental melts. Based on the primitive magma compositions, the ELIP high-Ti melts could have been produced by mantle melting at 4.0–5.4 GPa and 1620–1660 ◦C, and started to crystallise olivine at 1410–1550 ◦C, based on the Al-in-olivine thermometer, which are higher temperatures than for mid-ocean ridge basalts and ELIP low-Ti magmas. The high-Ni and low-Mn olivine phenocrysts in the ELIP high-Ti samples crystallised from peridotite-derived, MgO-rich melts at high temperatures. Variations in the physicochemical source melting conditions was enough to explain the differences in olivine Ni and Mn contents in the ELIP high- and low-Ti picrites-basalts. Additionally, the almost constant Pd, Pt, and Rh contents with decreasing Mg^* values indicate intermediate partition behaviors in the ELIP magmas. No correlations exist between whole-rock 10,000 \times Pd/Yb and Mg[#], (Th/Nb)_N, and ε_{Nd} (t) values, implying that selective assimilation of crustal sulfur resulted in magmatic sulfide saturation. We propose that the ELIP high-Ti magmas were derived from a deep-sourced garnet peridotite, and experienced various igneous processes during ascent through the continental lithosphere to form different types of ELIP high-Ti basaltic rocks.

1. Introduction

Identifying the source lithology of picritic-basaltic rocks is important as it is a crucial factor to unravel their nature of mantle source and petrogenesis. Based on differences in bulk partition coefficients for some trace elements (e.g., Ni–Mn–Ca) between peridotite and pyroxenite,

[Sobolev et al. \(2007\)](#page-13-0) proposed that olivine crystallised from pyroxenitederived melts (e.g., Hawaiian shield-stage tholeiites) have higher Ni and lower Ca and Mn contents than those from peridotite-derived melts (e.g., mid-ocean ridge basalts [MORBs]). Subsequently, this approach has been widely used to discriminate between peridotitic and pyroxenitic mantle sources for basaltic rocks, and several studies have proposed that

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Available online 19 July 2021 0024-4937/© 2021 Elsevier B.V. All rights reserved. Received 22 April 2021; Received in revised form 12 July 2021; Accepted 12 July 2021 a pyroxenitic component could have an important role in the mantle source of some large igneous provinces (LIPs; e.g., Hawaii, Siberia, Karoo, and Emeishan; e.g., [Sobolev et al., 2007; Kamenetsky et al., 2012](#page-13-0); [Heinonen and Fusswinkel, 2017; Howarth and Harris, 2017](#page-13-0); [Ren et al.,](#page-13-0) [2017;](#page-13-0) [Hole, 2018\)](#page-13-0). However, the trace element contents of olivine phenocrysts are also affected by other factors, such as the pressure–temperature (*P*–*T*) conditions and degree of melting, and volatile $(H₂O$ and $CO₂)$ contents of the mantle source. The melt produced by high-degree melting of pyroxenite can have similar Mn/Fe ratios to peridotite-derived melts ([Herzberg, 2011\)](#page-13-0). The partition coefficients of Ni, Mn, and Ca in olivine can decrease with increasing *P*–*T*, melt MgO content, and volatile contents ($H₂O$ and $CO₂$), respectively (Gavrilenko [et al., 2016;](#page-13-0) [Li and Ripley, 2010](#page-13-0); [Matzen et al., 2013, 2017](#page-13-0); [Yao et al.,](#page-14-0) [2021\)](#page-14-0). Therefore, before evaluating the role of a pyroxenitic source on olivine composition, the physicochemical effects of source melting should first be considered.

The Emeishan LIP (ELIP) has been well studied and is thought to have a mantle plume origin (e.g., [Chung and Jahn, 1995](#page-13-0); [He et al., 2003](#page-13-0); [Xu et al., 2004](#page-14-0); [Zhong et al., 2011; Zhong and Zhu, 2006\)](#page-14-0). However, the mantle source lithology of the ELIP remains controversial (e.g.,

Fig. 1. (a) Schematic map showing the tectonic units of China and (b) the distribution of the Emeishan continental flood basalts and coeval mafic–ultramafic intrusions modified after [Li et al. \(2016\)](#page-13-0). (c) Distribution of picrites and basaltic rocks in the Yumen area, southwest China, showing the sampling locations (modified after [Yao et al., 2019\)](#page-14-0).

[Kamenetsky et al., 2012](#page-13-0); [Ren et al., 2017](#page-13-0); [Xiao et al., 2004](#page-13-0); [Xu et al.,](#page-13-0) [2001;](#page-13-0) [Xu et al., 2020](#page-14-0); [Yao et al., 2019](#page-14-0); [Yu et al., 2017](#page-14-0)). Compared with basalts, picrites have more primitive whole-rock and mineral compositions and are better for investigating the nature of the mantle source of LIPs (e.g., [Chung and Jahn, 1995](#page-13-0); [Ellam, 2006](#page-13-0); [Li et al., 2012](#page-13-0); [Schaefer](#page-13-0) [et al., 2000](#page-13-0); [Zhang et al., 2006\)](#page-14-0). Based on normal δ^{18} O values, and high Mn/Zn and low Zn/Fe ratios of olivine in Emeishan high-Ti picrites (Yumen, Maoniuping, Tanglanghe, Wuguijing, and Wulongba), [Yao](#page-14-0) [et al. \(2019\)](#page-14-0) proposed that these rocks were mainly derived from mantle peridotite. However, these olivines also have high Ni and low Mn contents that can be used to infer derivation from pyroxenite-derived melt (e.g., [Kamenetsky et al., 2012](#page-13-0); [Ren et al., 2017\)](#page-13-0). Therefore, there are two different explanations for the origins of high-Ni and low-Mn olivines in the Emeishan high-Ti rocks: (1) The effect of source melting conditions on the olivine composition that crystallised from peridotite-derived melts; and (2) the olivine crystallised in pyroxenite-derived melts. In this study, we present whole-rock major and trace element (including platinum-group element [PGE]), Sr–Nd isotope, and mineral chemistry (olivine, Cr-spinel, and clinopyroxene) data for picritic-basaltic lavas from Yumen, which is a newly discovered outcrop of ELIP high-Ti rocks. These and previously published data for ELIP picrites and basalts are used to: (1) determine the relationship between the Yumen picriticbasaltic lavas and the ELIP; (2) constrain the lithology of the mantle source, including the effects of source melting conditions on olivine phenocryst composition; and (3) investigate the PGE partitioning and the cause of magmatic sulfide saturation in the ELIP. Finally, we present a model for the formation of high-Ti picrites and basaltic rocks in the ELIP and propose that the method based on trace elements in olivine to distinguish peridotite- and pyroxenite-derived melts needs to be further refined, which has significant implications for the contribution of pyroxenitic components to LIPs.

2. Geological background

Voluminous Permian basaltic volcanic rocks and mafic–ultramafic intrusions occur over an area of *>*250,000 km2 in the western South China Block (i.e., the Yangtze and Cathaysia blocks that were amalgamated in the Neoproterozoic; [Ali et al., 2005;](#page-13-0) [Cawood et al., 2013](#page-13-0); [Shellnutt, 2014](#page-13-0)) from southwest China to northern Vietnam. These rocks form the ELIP ([Fig. 1](#page-1-0)). The study area is located along the western margin of the Yangtze Block, which is bounded by the Tibetan Plateau to the west and separated from the North China Craton to the north by the late Palaeozoic–early Mesozoic Qinling–Dabie orogenic belt. The basement of the Yangtze Block consists of Archaean crystalline and highgrade metamorphic rocks, which is covered by post-Archaean, lowgrade metamorphosed sedimentary sequences [\(Yan et al., 2003](#page-14-0)). In addition, abundant Neoproterozoic intrusive igneous rocks with granodioritic to mafic–ultramafic compositions are also widely distributed in this region (e.g., [Li et al., 2002;](#page-13-0) [Yao et al., 2018; Zhu et al., 2006,](#page-14-0) [2008\)](#page-14-0).

The thickness of the Permian flood basalt sequence in the ELIP varies from \sim 5000 m in the west to several hundred metres in the east (Anh [et al., 2011;](#page-13-0) [Chung and Jahn, 1995](#page-13-0); [Xiao et al., 2004](#page-13-0); [Xu et al., 2001](#page-13-0)). The flood basalts were erupted from 263 to 257 Ma [\(Shellnutt et al.,](#page-13-0) [2020;](#page-13-0) [Zhong et al., 2020](#page-14-0)) and rest unconformably on upper Permian limestones, and they are unconformably overlain by uppermost Permian sediments in the east and west and Upper Triassic or Jurassic sediments in the central part of the ELIP ([He et al., 2003](#page-13-0)). Some small mafic–ultramafic intrusions host magmatic Ni–Cu–PGE sulfide deposits, whereas world-class Fe–Ti–V oxide ore deposits are hosted by some large mafic intrusions (e.g., [Bai et al., 2019](#page-13-0); [Shellnutt et al., 2011;](#page-13-0) [Zhong](#page-14-0) [et al., 2002;](#page-14-0) [Zhou et al., 2008\)](#page-14-0). The ELIP basalts are divided into two geochemical groups: high-Ti (TiO2 *>* 2.5 wt% and Ti/Y *>* 500) and low-Ti (TiO2 *<* 2.5 wt% and Ti/Y *<* 500; [Xu et al., 2001, 2004; Xiao et al.,](#page-13-0) [2004\)](#page-13-0). Compared to low-Ti basalts, the ELIP high-Ti basalts are generally characterized by high whole-rock La/Sm and Sm/Yb ratios, and high Ni, low Mn contents in olivine. Many studies indicated that the ELIP high-Ti magmas maybe directly derived from low-degree partial melting of a deep mantle plume (e.g., [Kamenetsky et al., 2012;](#page-13-0) [Yao et al., 2019](#page-14-0); [Yu et al., 2017; Zhang et al., 2006](#page-14-0)). Considering the constant Pb isotope ratios in olivine-hosted melt inclusions with low-Ti to high-Ti compositions and some similar compositional features of major and trace elements to pyroxenite-derived melts, [Ren et al. \(2017\)](#page-13-0) obtained a view that all ELIP basalts originated from a mantle pyroxenite. In contrast, based on the high Os concentrations and unradiogenic Os isotopic sig-natures in high-Ti basalts, [Xu et al. \(2007\)](#page-14-0) suggested that the ELIP high-Ti magmas were likely derived from a sub-continental lithospheric mantle (SCLM). [Yao et al. \(2019\)](#page-14-0) proposed that the contribution of recycled component for the ELIP high-Ti magmas maybe limited owing to the normal mantle-like olivine O isotopes and the olivine Zn/Mn and Zn/Fe ratios consistent with these from mantle peridotite-derived melts.

Picrite samples in the ELIP have been reported from only a few locations, including Yumen, Dali, Lijiang, and Muli in the west, and Jinping–Song Da in the south. The picrites and basaltic rocks in Yumen are newly discovered outcrops [\(Yao et al., 2019](#page-14-0)). The footwall and hanging wall of this volcanic sequence in Yumen are similar to those of the ELIP in the west. A picritic lava flow with a thickness of \sim 5 m is interbedded within a basaltic sequence ([Fig. 1](#page-1-0)c). [Yao et al. \(2019\)](#page-14-0) studied olivine phenocrysts and olivine-hosted Cr-spinel in the Yumen picrites, but whole-rock data for these rocks have not yet been obtained.

3. Sampling and analytical methods

3.1. Samples

In this study, seven picrites, six basalts, and five basaltic andesites (Hereafter, the term of "basaltic rocks" refers to the samples of basalts and basaltic andesites) were collected from the Yumen area, southwest China ([Fig. 1](#page-1-0)c). Detailed latitudes and longitudes of sampling locations are listed in Table S1. The picrite samples contain abundant olivine phenocrysts with grain sizes of *<*50 μm to *>*2 mm across and occasional clinopyroxene phenocrysts. Euhedral to rounded olivine phenocrysts are partially serpentinised along with cracks and grain margins. Cr-spinel crystals that are a few tens of microns in diameter are enclosed in olivine phenocrysts or occur as isolated grains in the groundmass. The basaltic rocks consist of small, subhedral grains of clinopyroxene and plagioclase and are aphyric (Fig. S1).

3.2. Analytical methods

The compositions of olivine-hosted Cr-spinel, olivine, and clinopyroxene were determined by wavelength dispersive analysis using a JXA-8100 electron microprobe at Chang'an University, Xi'an, China. The analytical conditions were: 15 kV accelerating voltage, 20 nA beam current, 1 μm beam diameter, and peak counting times of 20–40 s for major elements and 40–60 s for minor elements.

Whole-rock major element contents of the Yumen samples were determined by X-ray fluorescence spectrometry (XRF) at the ALS Chemex Co. Ltd., Guangzhou, China. The analytical precision was better ±5%. Whole-rock trace element contents were determined with a Perkin–Elmer Sciex ELAN DRC-e inductively coupled plasma mass spectrometer (ICP–MS) at the State Key Laboratory of Ore Deposit Geochemistry (SKLODG), Institute of Geochemistry, Chinese Academy of Sciences (IGCAS), Guiyang, China. Powdered samples (50 mg) were dissolved in HF + HNO₃ acid in high-pressure Teflon bombs at \sim 190 °C for 48 h. Rhodium was used as an internal standard to monitor signal drift. The analytical precisions for most trace elements are generally better than $+10%$.

Samples for whole-rock Sr–Nd isotope analysis were spiked and dissolved in Teflon bombs in a mixture of HF, $HNO₃$, and $HClO₄$ acid, and subjected to conventional two-step ion exchange chromatographic separation. The isotopic measurements were undertaken with a Thermo Scientific Triton Plus multi-collector thermal ionisation mass spectrometer at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), Beijing, China. The isotopic ratios were corrected for mass fractionation by normalising to $^{88}Sr/^{86}Sr = 8.375209$ and 146 Nd/¹⁴⁴Nd = 0.7219, respectively. The international standards NBS-987 and JNDI were analysed to evaluate data quality. The measured values for the NBS-987 Sr and JNDI Nd standards were ${}^{87}Sr/{}^{86}Sr$ = 0.710246 \pm 0.000015 (*n* = 5; 2 SD) and ${}^{143}Nd/{}^{144}Nd$ = 0.512114 \pm 0.000012 (n = 5; 2 SD), respectively. The United States Geological Survey standard BCR-2 yielded ${}^{87}Sr/{}^{86}Sr = 0.705042 \pm 13 (2\sigma)$ and ${}^{143}Nd/{}^{144}Nd = 0.512632 \pm 8 (2\sigma)$. These values are identical to the recommended values for this standard.

The concentrations of PGEs were determined by isotope dilution (ID)–ICP–MS using an improved digestion technique, whereby sealed beakers were placed in stainless steel pressure bombs. Powdered samples (8–10 g) were dissolved in HF acid in customised 120 mL PTFE beakers on a hotplate. The dried residues were then digested in HF + HNO₃ acid in stainless steel pressure bombs at 190 °C for \sim 48 h. The solutions were analysed with an ELAN DRC-e ICP–MS instrument. The detection limits are *<*0.02 ppb for Pt and Pd, and *<* 0.01 ppb for Ir, Ru, and Rh.

4. Results

4.1. Mineral chemistry

The chemical compositions of Cr-spinel inclusions and olivine and clinopyroxene phenocrysts in the Yumen and Wumulaka picrites are listed in Table S2. Based on the classification of Cr-spinel using Ti/Al ratios following [Yao et al. \(2019\),](#page-14-0) the picrites from the Yumen, Wumulaka, and Yongsheng areas are classified as being of the high-Ti group (molar 10Ti/Al *>* 0.5). Olivine phenocrysts in the Yumen picrites, along with olivine data from Yao et al. (2019) , have Fo = 77-92 $(Fo = 100 \text{ Mg/[Mg + Fe²⁺]})$, and higher Ni and lower Mn and Ca contents (1790–3590 ppm Ni, 850–2610 ppm Mn, and 1640–2540 ppm Ca) relative to ELIP low-Ti picrites (Dali and Binchuan areas). The data exhibit positive Ni–Fo, negative Mn–Fo, and no Ca–Fo correlations. Clinopyroxene phenocrysts in the Yumen picrites have compositions similar to augite with $Mg^* = 78-86$ (100 Mg/[Mg + Fe^T]), and have higher TiO₂ contents and lower Mg[#] values and CaO contents than those in the low-Ti picrites (Fig. S2).

4.2. Major and trace elements

Whole-rock major and trace element data for the Yumen volcanic rocks are listed in [Table 1.](#page-4-0) The studied volcanic rocks comprise three rock types: picrite, basalt, and basaltic andesite (Fig. 2). The picrites contain 19.7–21.6 wt% MgO, 8.1–8.6 wt% Al₂O₃, 1.8–2.1 wt% TiO₂, and 8.4–10.3 wt% CaO. The ELIP high-Ti picrites have lower Al_2O_3 and higher $TiO₂$ contents than the ELIP low-Ti picrites. The basalts contain 5.6–8.8 wt% MgO, 5.5–12.5 wt% Al_2O_3 , 2.2–3.6 wt% TiO₂, and 6.7–12.1 wt% CaO. With decreasing MgO contents, CaO decreases and Al2O3 increases. Whole-rock Ni contents of the Yumen basaltic rocks are lower than those in the picrites (Fig. S3).

Chondrite-normalised rare earth element (REE) patterns of the Yumen volcanic rocks are shown in [Fig. 3a](#page-6-0). The samples have uniform, almost linear REE patterns with enrichments in light REEs relative to heavy REEs. The picrites have lower REE contents than the basalts and basaltic andesites, which can be explained by the latter having a more fractionated parental magma. Primitive-mantle-normalised patterns of some immobile incompatible trace elements are shown in [Fig. 3](#page-6-0)b. The Yumen picrites and basalts have ocean island basalt (OIB)-like patterns (e.g., enrichments in light REEs and small positive Nb–Ta anomalies), which are similar to other ELIP high-Ti picrites (e.g., Yongsheng). The high-Ti picrites have higher incompatible trace element contents and steeper patterns than the low-Ti picrites. Negative Nb–Ta anomalies are

Fig. 2. Total alkalis (Na₂O + K₂O)–silica (SiO₂) (TAS) diagram for the picrites and basaltic rocks in the Yumen area.

exhibited by some of the basaltic andesites from Yumen.

4.3. Sr–*Nd isotopes*

Whole-rock Sr–Nd isotope data for the Yumen volcanic rocks are listed in [Table 2](#page-7-0). Calculated initial $\varepsilon_{Nd}(t)$ ($t = 260$ Ma) values and $({}^{87}Sr/{}^{86}Sr)$ _i ratios for the Yumen picrites vary from +2.8 to +3.4 and from 0.70410 to 0.70445, respectively. Unlike the ELIP low-Ti picrites that have a wide range of Sr–Nd isotopic compositions (e.g., $\varepsilon_{Nd}(t) = -2.3$ to +7.0), the ELIP high-Ti picrites (Yumen, Wumulaka, and Yongsheng) have a limited range of Sr–Nd isotopic compositions (e. g., $\varepsilon_{Nd}(t) = +1.4$ to $+4.0$) and plot in the depleted mantle field. Initial $\varepsilon_{Nd}(t)$ and $({}^{87}\text{Sr}/{}^{86}\text{Sr})_i$ values of the Yumen basalts and basaltic andesites vary from -2.2 to $+2.0$ and from 0.70488 to 0.70573, respectively. The Sr–Nd isotope data for the Yumen basaltic rocks exhibit a negative correlation that trends towards the crust field [\(Fig. 4](#page-7-0)).

4.4. Cu, Ni, and PGE data

Whole-rock chalcophile element (Cu, Ni, and PGEs) concentrations of the Yumen volcanic rocks are listed in [Table 3.](#page-8-0) Primitive-mantlenormalised patterns for Ni–PGE–Cu of the Yumen volcanic rocks are shown in [Fig. 5.](#page-8-0) The Yumen picrites are characterized by unfractionated PGE patterns, but exhibit pronounced negative Ir anomalies relative to Ru. The Ni–PGE–Cu patterns are similar for the ELIP high- and low-Ti picrites. However, the Yumen basalts and basaltic andesites have fractionated PGE patterns with enrichments in PPGE (Pt and Pd) relative to IPGE (Ir and Ru), and some samples also exhibit negative Pt–Pd anomalies relative to Cu that are indicative of PGE depletion.

5. Discussion

To make best use of our new, but limited, geochemical data for the Yumen picrites and basalts, and constrain the mantle source and petrogenesis of the ELIP, we compiled whole-rock data for ELIP picrites and basalts with SiO2 *<* 52 wt% and MgO *>* 4 wt%. These samples were divided into high-Ti (whole-rock Ti/Y *>* 500) and low-Ti groups (wholerock Ti/Y *<* 500; Table S3).

5.1. Relationship between the Yumen picrites and basalts and the ELIP

The whole-rock major and trace element and Sr–Nd isotopic compositions, as well as the phenocrysts, of the Yumen picrites are similar to those of the ELIP high-Ti picrites (Figs. 3–4 and S2–S3). Their Sr–Nd

(*continued on next page*)

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Table 1 (*continued*)

(*continued on next page*)

Table 1 (*continued*)

Notes: oxides in wt%, trace elements in ppm.
a Expected data of the BHVO-2, BCR-2 are from http://georem.mpch-mainz.gwdg.de/sample_query_pref.asp

Fig. 3. (a) Chondrite-normalised REE and (b) primitive-mantle-normalised immobile trace element patterns of the Yumen volcanic rocks. The normalising values for chondrite and primitive mantle were taken from [Palme and O](#page-13-0)'Neill (2014). Data sources: Dali [\(Hanski et al., 2010\)](#page-13-0), Binchuan and Yongsheng ([Kamenetsky et al.,](#page-13-0) [2012\)](#page-13-0), Wumulaka [\(Tao et al., 2015](#page-13-0); this study), and Song Da [\(Li et al., 2012\)](#page-13-0).

Whole-rock Sr–Nd isotope data for the Yumen volcanic rocks.

Chondrite uniform reservoir (CHUR) values (${}^{87}Rb/{}^{86}Sr = 0.0847, {}^{87}Sr/{}^{86}Sr = 0.7045; {}^{147}Sm/{}^{144}Nd = 0.1967, {}^{143}Nd/{}^{144}Nd = 0.512638$) are used for the calculation. $\lambda_{\rm Rb} = 1.42 \times 10^{-11}$ year⁻¹ (Steiger and Jäger, 1977); $\lambda_{\rm Sm} = 6.54 \times 10^{-12}$ year⁻¹ ([Lugmair and Marti, 1978\)](#page-13-0). The (⁸⁷Sr/⁸⁶Sr)_i, (¹⁴³Nd/¹⁴⁴Nd)_i and $\epsilon_{\rm Nd}$ (t) of the Yumen

volcanic rocks were calculated using age of 260 Ma.

^a Expected data of the NBS987 is from [Miyazaki and Shuto \(1998\).](#page-13-0)

^b Expected data of the JNdi-1 is from [Tanaka et al. \(2000\).](#page-13-0)

^c Expected data of the BCR-2 is fro

Fig. 4. Plots of initial $\varepsilon_{Nd}(t)$ vs. $({}^{87}\mathrm{Sr} / {}^{86}\mathrm{Sr})_i$ for the Yumen volcanic rocks. Data sources for the other picrites are the same as in [Fig. 3.](#page-6-0) The oceanic mantle array is from [Zindler and Hart \(1986\)](#page-14-0). The parameters of Nd (ppm), ε_{Nd} (260 Ma), Sr (ppm) and $({}^{87}\text{Sr/}^{86}\text{Sr})$ _i used in the mixing calculation are 20, 3.35, 180 and 0.7043 from Yumen picrites for the mantle-derived magma; 30.7, − 38.5, 304, 0.713 and 26.6, − 15, 273, 0.715 for the Yangtze lower and upper crust (referred from [Bai et al., 2019\)](#page-13-0).

isotopic compositions plot in the oceanic mantle field and have higher $\varepsilon_{\rm Nd}$ (260 Ma) and lower ($\rm ^{87}Sr/^{86}Sr)_{i}$ than the Yumen basaltic rocks, and no correlation between ε_{Nd} (260 Ma) and (⁸⁷Sr/⁸⁶Sr)_i (Fig. 4). This indicates that the Yumen picrites have not experienced obvious crustal contamination. However, ε_{Nd} (260 Ma) values of the Yumen basaltic rocks exhibit a negative correlation with $({}^{87}\mathrm{Sr} / {}^{86}\mathrm{Sr})_{\mathrm{i}},$ indicating crustal contamination (Fig. 4), because continental crust has higher ($^{87}\rm{Sr}/^{86}\rm{Sr})_i$

values than the mantle [\(Rudnick and Gao, 2014\)](#page-13-0). In the mixing modelling of Sr–Nd isotopes, because of the primitively compositional features, the average Sr and Nd concentrations of the Yumen picrites and the Sr–Nd isotope values of the most depleted picrite sample are used as the composition of primitive magma end-member [Sm: 20 ppm, ε_{Nd} (260 Ma): 3.35, Sr: 180 ppm, $({}^{87}Sr/{}^{86}Sr)$ _i: 0.7043]. The compositions of Yangtze lower and upper crust in which our samples outcrop are regard as the enriched end-member [Sm: 30.7 ppm, ε_{Nd} (260 Ma): -38.5, Sr: 304 ppm, $({}^{87}Sr/{}^{86}Sr)$; 0.713 for Yangtze lower crust; Sm: 26.6 ppm, ε_{Nd} (260 Ma): −15, Sr: 273 ppm, $({}^{87}Sr/{}^{86}Sr)_{i}$: 0.715 for Yangtze upper crust; [Bai et al., 2019\]](#page-13-0). The Sr–Nd isotopic compositions of the Yumen basaltic rocks can be explained by the less than 10% contamination of Yangtze crustal component. Crustal contamination can also account for the negative Nb–Ta anomalies of the Yumen basaltic rocks [\(Fig. 3](#page-6-0)b). The content of MgO from 8 wt% decrease to 5 wt%, whole-rock CaO contents of the Yumen basaltic samples decrease, but $Al₂O₃$ contents increase (Fig. S3). There is also no Eu depletion [\(Fig. 3a](#page-6-0)). These observations suggest that clinopyroxene started to crystallise at 8 wt% MgO, and that plagioclase crystallisation did not occur at MgO *>* 5 wt%. The low whole-rock Ni contents in the basaltic rocks are due to fractional crystallisation of olivine (Fig. S3f). These fractionations are consistent with the presence of clinopyroxene and olivine in the Yumen picritesbasalts and plagioclase phenocrysts in basaltic rocks (Fig. S1c–d). The Yumen picritic-basaltic lavas occur between overlying Lower Triassic sediments and underlying Permian limestones and have an interbedded contact relationship between them ([Fig. 1](#page-1-0)), indicating these picrites and basaltic rocks and ELIP are of the same age. Therefore, we suggest that the Yumen picritic-basaltic lavas are part of the ELIP high-Ti group, and were produced by variable assimilation–fractional crystallisation (AFC) of the ELIP high-Ti magmas.

Table 3

Whole-rock chalcophile element data for the Yumen volcanic rocks.

 $^{\rm a}$ Duplicate samples.
 b Expected data of the WGB-1 are from Qi et al., 2011

Fig. 5. Primitive-mantle-normalised Ni–PGE–Cu patterns for the Yumen volcanic rocks. Data sources for the fields of ELIP high- and low-Ti picrites are the same as in [Fig. 3](#page-6-0). The normalising values for primitive mantle were taken from [Palme and O](#page-13-0)'Neill (2014).

5.2. Peridotitic mantle source for high-Ti basalts in the ELIP

There are two contrasting views regarding the lithology of the mantle source of the ELIP high-Ti basalts (i.e., peridotite vs. pyroxenite; e.g., [Kamenetsky et al., 2012](#page-13-0); [Ren et al., 2017](#page-13-0); [Yao et al., 2019](#page-14-0)). To address this issue, primary magma compositions were calculated by adding/subtracting equilibrium olivine to the compositions of olivinehosted melt inclusions (MgO *>* 8 wt%; [Hanski et al., 2010;](#page-13-0) [Kamenet](#page-13-0)[sky et al., 2012](#page-13-0)) until the melt is in equilibrium with Fo93 olivine, using a $K_d^{\rm Fe/Mg}$ (olivine/melt) of 0.30 [\(Roeder and Emslie, 1970](#page-13-0)) and assumed Fe^{2+}/Fe^{T} ratio of 0.90 for the melt. Whole-rock MgO/FeO ratios of the Yumen picrites are in equilibrium with Fo92 olivine, meaning that the whole-rock compositions of the Yumen picrites approximate primary magma compositions. The MgO, $SiO₂$, $Al₂O₃$, and CaO contents of the Yumen picrites and ELIP high-Ti primitive magmas plot in the field of experimental melts of garnet peridotite [\(Fig. 6a](#page-9-0)–d). In addition to the involvement of recycled oceanic mafic crust, [Zhang et al. \(2019\)](#page-14-0) proposed that high-pressure melting in the mantle source of the ELIP highTi basalts could also explain their slightly higher $TiO₂$ contents than low-Ti basalts, because Ti in garnet is incompatible and the proportion of garnet in the mantle source increases with depth. [Yang and Zhou \(2013\)](#page-14-0) proposed that the FC3MS parameter (FeO/CaO – $3 \times$ MgO/SiO₂, all in wt%), which is unaffected by pressure–temperature, is a better indicator for distinguishing pyroxenite- and peridotite-derived melts, because modelling calculations show that FC3MS values of pyroxenite melts (*>*0.65) are higher than those of peridotite melts (*<*0.65). Calculated FC3MS values of the Yumen picrites and primitive magmas of the ELIP both plot in the peridotite-derived melt field ([Fig. 6e](#page-9-0)). Based on the lower bulk partition coefficient for Zn and lower $K_D^{Zn/Fe}$ in eclogite/pyroxenite relative to peridotite, [Le Roux et al. \(2010\)](#page-13-0) proposed that melts derived from eclogite/pyroxenite should have higher 10000Zn/Fe (*>*14) ratios than peridotite-derived melts (6–12.5). The 10000Zn/Fe ratios of the ELIP picrites plot in the field of peridotite-derived melts ([Fig. 6f](#page-9-0)). Therefore, these whole-rock geochemical features, along with the depleted Sr—Nd isotopic compositions ($\varepsilon_{Nd}(t) = +1.4$ to $+4.0$; $({}^{87}Sr/{}^{86}Sr)_{i} = 0.70410$ to 0.70515), indicate that the ELIP high-Ti basalts were derived from a depleted mantle source consisting of garnet peridotite.

5.3. Effects of source physicochemical melting conditions on olivine chemistry

In contrast to the high-Ni and low-Mn feature of olivine phenocrysts, the compositions of ELIP high-Ti primitive magmas calculated from olivine-hosted melt inclusions and whole-rock FC3MS and Zn/Fe values for the ELIP picrites are similar to peridotite-derived melts [\(Fig. 6\)](#page-9-0). [Yao](#page-14-0) [et al. \(2019\)](#page-14-0) noted that the high Mn/Zn and low Zn/Fe ratios of olivine phenocrysts with Fo *>* 85 in the ELIP picrites were similar to those from peridotite-derived melts. Recent experimental studies [\(Matzen et al.,](#page-13-0) [2013, 2017](#page-13-0)) have shown that the partition coefficients of Ni and Mn in olivine are mainly controlled by the source melting *P*–*T* conditions and MgO contents of the equilibrium melts, respectively. As such, Mg-rich melts derived from mantle peridotite at high *P*–*T* conditions can produce high-Ni and low-Mn olivine during low-pressure crystallisation. Hence, we estimated the effect of different *P*–*T* conditions on the composition of olivine phenocrysts in the ELIP.

Using the Al concentrations of primary olivine–Cr-spinel, the Al-inolivine thermometer of [Coogan et al. \(2014\)](#page-13-0) was used to estimate the

Fig. 6. Comparison of the Yumen picrites and primitive magmas with experimentally derived melts. MgO vs. (a) SiO₂, (b) CaO, (c) Al₂O₃, (d) TiO₂, and (e) FC3MS. The line separating peridotite- and pyroxenite-derived melts is from [Yang and Zhou \(2013\).](#page-14-0) (f) Mn/Zn vs. 10000Zn/Fe. The lines separating peridotite- and pyroxenite-derived melts are from [Le Roux et al. \(2010\)](#page-13-0). Data sources for the other picrites are the same as in [Fig. 3](#page-6-0). Melt sources: eclogite (Kogiso and Hirschmann, [2006;](#page-13-0) [Pertermann and Hirschmann, 2003\)](#page-13-0), garnet pyroxenite [\(Hirschmann et al., 2003](#page-13-0); [Keshav et al., 2004;](#page-13-0) [Kogiso et al., 2003\)](#page-13-0), spinel peridotite [\(Hirose and](#page-13-0) [Kushiro, 1993\)](#page-13-0), garnet peridotite ([Walter, 1998](#page-13-0)), and carbonated peridotite (3 GPa and 2.5 wt% CO₂; [Dasgupta et al., 2007\)](#page-13-0).

crystallisation temperatures of primary olivines (Fo *>* 86) in the Yumen high-Ti picrites. The crystallisation temperatures of olivine in the high-Ti magmas (1410–1550 °C; [Fig. 7](#page-10-0)a) are higher than those of the low-Ti magmas (1250–1360 ◦C; [Xu and Liu, 2016\)](#page-13-0). Using the method of [Lee](#page-13-0) [et al. \(2009\),](#page-13-0) the *P*–*T* conditions of mantle melting for the primitive high- and low-Ti magmas in the ELIP can be calculated from their primitive melt compositions. Given that the ELIP might have been derived from hydrous mantle [\(Liu et al., 2017](#page-13-0); [Xu et al., 2020\)](#page-14-0), the water contents of the ELIP primitive magmas were estimated from their Ce contents and the H₂O/Ce ratio (\sim 200) of least-degassed OIBs (Dixon [et al., 2002\)](#page-13-0). The Ce contents of the primary high- and low-Ti magmas can be calculated from the olivine-hosted melt inclusion data of [Kame](#page-13-0)[netsky et al. \(2012\)](#page-13-0) using the equation $Ce_{primitive\ magma} = Ce_{melt\ inclusion}$ \times (1 – X), where X is the proportion of added olivine. The estimated

water contents of the Yumen picrites and high- and low-Ti primitive magmas are 0.8, 1.3, and 0.25 wt%, respectively, which are similar to OIBs (0.2–1.6 wt% $H₂O$; [Herzberg and Asimow, 2008\)](#page-13-0). Although these estimated water contents have considerable uncertainty, it does not significantly affect the following discussion.

The ELIP high-Ti magmas were derived from mantle peridotite at higher mantle potential *P*–*T* conditions (4.0–5.4 GPa and 1620–1660 ◦C) than MORBs (\sim 1 GPa and \sim 1350 °C) and the ELIP low-Ti magmas (1.5–3.0 GPa and 1410–1530 $°C$; [Fig. 7b](#page-10-0)). Here our estimated mantle potential temperatures for the ELIP low-Ti magma are consistent with those calculated by primary melt composition of the ELIP low-Ti basalts (\sim 1400 to \sim 1550 °C; [Shellnutt and Pham, 2018\)](#page-13-0). Based on experimental results for the temperature effect on Ni partition coefficients in olivine, every 100 ◦C increase in the source melting temperature can

Fig. 7. (a) Olivine crystallisation temperatures of the Yumen picrites obtained by Al-in-olivine thermometry. The crystallisation temperatures for olivine in the ELIP low-Ti magmas are from [Xu and Liu \(2016\).](#page-13-0) (b) Pressure–temperature conditions of source melting for the Yumen picrites and ELIP low- and high-Ti magmas. The method used and MORB field are from [Lee et al. \(2009\).](#page-13-0) The solidus of dry and 1 wt% water lherzolite were taken from [Katz et al. \(2003\)](#page-13-0).

result in a decrease of \sim 455 ppm Ni in olivine ([Matzen et al., 2013](#page-13-0)). The difference in the source melting temperatures between the Yumen picrites and MORBs is \sim 250 °C. Thus, we can correct for the effect of melting temperature on the Ni content in olivine in the Yumen picrites using the equation: Ni_{corrected} = Ni_{olivine} $- 2.5 \times 455$. In a Fo–Ni plot, the corrected olivine data for the Yumen picrites plot in the field for olivine from MORBs (Fig. 8a). The partition coefficient for Mn between olivine–melt depends mainly on the melt MgO content and increases from 0.65 at 22 wt% MgO (i.e., a high-Ti primitive magma) to 0.8 at 16 wt% MgO (i.e., a low-Ti primitive magma; [Matzen et al., 2017\)](#page-13-0). The effect of the melt MgO content on the olivine Mn content in the Yumen picrites was corrected using the equation: $\text{Mn}_\text{corrected} = 0.8/0.65 \times \text{Mn}_\text{olivine}$. The corrected olivine Mn contents are similar to those of olivines in the ELIP low-Ti magmas and MORBs (Fig. 8b). These lines of evidence do not completely rule out a contribution from a pyroxenitic component to the ELIP, but demonstrate that variations in the physicochemical melting conditions can explain the different olivine Ni and Mn contents in the ELIP high- and low-Ti picrites and basalts.

5.4. PGE constraints on magma evolution in the ELIP

5.4.1. PGE partitioning

The partition coefficients for PGEs in sulfide liquids range up to $10^5\!$ and thus deviations from the trend lines in plots of $Mg^{\#}-PGEs$ ([Fig. 9\)](#page-11-0) for the basaltic samples indicate magmatic sulfide segregation. However, PGE partitioning in basaltic magmas is not fully understood. Based on negative correlations between whole-rock $(Pt/Ru)_N$ and $(Rh/Ru)_N$ vs. $Mg^{\#} (Mg/[Mg + Fe^{T}])$ and the approximately constant $(Pt/Rh)_{N}$, Li et al.

[\(2016\)](#page-13-0) suggested that Pt and Rh behaved incompatibly during magma differentiation in the ELIP. However, correlations between whole-rock $Mg^{\#}$ values and PGE contents may be a better way to investigate the PGE fractionations in the ELIP. Whole-rock PPGE (Pd, Pt, and Rh) contents of the ELIP Pd-undepleted samples show no obvious variations, whereas the IPGE (Ru and Ir) contents decrease significantly with decreasing whole-rock $Mg^{\#}$ values [\(Fig. 9a](#page-11-0)–e), indicating that the partition coefficients were close to one for Pd, Pt, and Rh, and that Ir and Ru were compatible. The obvious positive correlation between wholerock Cr and Ru contents at Cr *>* 300 ppm ([Fig. 9f](#page-11-0)) implies that Ru (Ir) is compatible in Cr-spinel, which is consistent with previous studies (e. g., [Arguin et al., 2016](#page-13-0); [Park et al., 2012; Righter et al., 2004\)](#page-13-0). Rhodium exhibits intermediate behaviour and its partition coefficient is influenced by temperature and the oxidation state ([Arguin et al., 2016](#page-13-0); [Brenan et al., 2003, 2012](#page-13-0)). We also propose that Pd and Pt could have such an intermediate behaviour in basaltic magma, but the reasons for this are unclear.

5.4.2. Cause of magmatic sulfide saturation

Due to the extremely high partition coefficients for PGEs in sulfide liquid relative to Ni, Cu, and lithophile elements (e.g., Yb), the ratio between these elements is highly sensitive to sulfide segregation. Given the possible addition of Cu during post-magmatic hydrothermal alter-ation, [Li et al. \(2016\)](#page-13-0) proposed that $10,000 \times$ Pd/Yb values of $>$ 100 can be used to infer Pd depletion and magmatic sulfide saturation and segregation. We used correlations between whole-rock $10,000 \times$ Pd/Yb and $Mg^{\#}$, (Th/Nb)_N, and ε_{Nd} (t) values to examine the factors responsible for sulfide saturation of the ELIP basaltic rocks ([Fig. 10\)](#page-12-0). No systematic

Fig. 8. Corrected Ni and Mn contents in olivine from the Yumen picrites, which accounts for the source melting conditions. Data sources: Dali [\(Hanski et al., 2010\)](#page-13-0), Binchuan and Yongsheng ([Kamenetsky et al., 2012](#page-13-0)), Wumulaka (this study), and Song Da [\(Li et al., 2016](#page-13-0)).

Fig. 9. Plots of whole-rock Mg[#] values (100 × Mg/[Mg + Fe^T]) vs. (a) Pd, (b) Pt, (c) Ru, (d) Rh, and (e) Ir, and (f) Cr vs. Ir, for the Yumen volcanic rocks. Data sources for the other ELIP samples are listed in Table S3.

PGE differences characterise the ELIP high- and low-Ti samples, and all the Pd-depleted samples are basaltic rocks. Similar to other ELIP basalts, the range of whole-rock Mg^* values of the Pd-depleted samples is similar to that of the Pd-undepleted Yumen basalt samples, indicating that fractional crystallisation was not the main cause of magmatic sulfide saturation in the ELIP [\(Fig. 10](#page-12-0)a). Furthermore, although the Pd-depleted Yumen basalt samples have relatively low $\varepsilon_{Nd}(t)$, there is no difference in $(Th/Nb)_N$ between the Pd-depleted and -undepleted samples ([Fig. 10](#page-12-0)b–c). This suggests that selective assimilation of crustal sulfide, rather than crustal silicate component, was the probable cause of sulfide saturation in the ELIP basaltic rocks. Sulfide saturation and segregation in basaltic magmas is key for the formation of magmatic Cu–Ni–PGE sulfide deposits in LIPs. [Zhou et al. \(2008\)](#page-14-0) suggested that, in the ELIP, the high-Ti magma was associated with the formation of giant Fe–Ti–V oxide ore deposits (e.g., Panzhihua and Baima), whereas the low-Ti magma was associated with the formation of Cu–Ni–PGE sulfide deposits (e.g., Jinbaoshan, Limahe, and Zhubu; [Fig. 1](#page-1-0)b). However, [Zhang](#page-14-0) [et al. \(2017\)](#page-14-0) investigated the parental magmas of the mafic–ultramafic intrusions hosting magmatic Cu–Ni–PGE sulfide deposits in the ELIP, including those at Nantianwan (1.03 wt% $TiO₂$ and 15.06 wt% MgO), Yangliuping (1.8 wt% TiO₂ and 10.08 wt% MgO), and Limahe (1.89 wt % TiO2 and 16.67 wt% MgO), and showed that these range from low- to high-Ti compositions. The high-Ti magma may have been more likely to produce Fe–Ti–V oxide ore deposits due to its high Ti and Fe concentrations [\(Zhou et al., 2008](#page-14-0)) or more oxidised mantle source ([Bai et al.,](#page-13-0) [2019\)](#page-13-0). However, the present study shows that the ELIP high-Ti magma also had the potential to form magmatic Cu–Ni–PGE sulfide deposits. Therefore, mafic–ultramafic rocks derived from high-Ti magmas should be targets for global Ni exploration in LIPs.

5.5. A petrogenetic model for the ELIP high-Ti picrites and basaltic rocks

Based on previously reported data for the ELIP and our new data for the Yumen picritic-basaltic samples, we suggest that the ELIP high-Ti magmas were generated by partial melting of a depleted, deep, garnet peridotite source, and then experienced variable fractional crystallisation and crustal contamination by different crustal components (e.g., silicates and sulfides), and sulfide liquid segregation. The petrogenetic model we propose for the ELIP high-Ti picrites and basaltic rocks involves: (1) ascent of the anomalously hot Emeishan mantle plume above the garnet peridotite solidus and melting at depths of \sim 140–160 km, which produced the Mg–Ti–Ni-rich primary magmas; (2) rapid ascent of

Fig. 10. Plots of whole-rock 10,000 \times Pd/Yb vs. Mg[#] values (100 \times Mg/ [Mg + Fe]), $\varepsilon_{Nd}(t)$, and $(Th/Nb)_N$ for the Yumen volcanic rocks. The Pd depletion boundary was taken from [Li et al. \(2016\).](#page-13-0) Data are from this study and sources listed in Table S3. The normalising values for primitive mantle (Th and Nb) were taken from [Palme and O](#page-13-0)'Neill (2014).

some primitive magmas to the surface, which experienced little fractional crystallisation of Cr-spinel and high-Ni and low-Mn olivine, thereby forming the ELIP high-Ti picrites; and (3) slow ascent of some primitive magmas to the surface, which experienced large amounts of fractional crystallisation and variable degrees of crustal contamination, thereby forming the ELIP high-Ti basaltic rocks. The variable degrees of fractional crystallisation and crustal contamination resulted in the formation of four types of ELIP high-Ti basaltic rocks: (1) high ε_{Nd} ($>$ 0) and Pd-undepleted (only experienced fractional crystallisation); (2) low ε_{Nd} (*<*0) and Pd-undepleted (experienced fractional crystallisation and contamination by a crustal silicate component); (3) high ε_{Nd} and Pddepleted (experienced fractional crystallisation and contamination by a crustal sulfide component); and (4) low ε_{Nd} and Pd-depleted (experienced fractional crystallisation and contamination by crustal silicate and sulfide components). Mafic–ultramafic intrusions formed at shallow crustal levels from Pd-depleted basaltic rocks have the potential to host magmatic Cu–Ni–PGE sulfide deposits.

Therefore, multiple garnet peridotite-derived magmas with different compositions were involved in the formation of the Yumen picrites and basaltic rocks, and interactions with the continental lithosphere were also significant. More importantly, this study shows that polybaric melting in a LIP can cause differences in olivine trace element contents, which were previously regarded to reflect different mantle source lithologies (i.e., peridotite vs. pyroxenite). This implies that olivine trace element contents should be used with caution when distinguishing peridotite- and pyroxenite-derived melts, and that contributions by pyroxenitic component may have been overestimated in other LIPs.

6. Conclusions

We present mineral compositional and whole-rock major and trace element, Sr–Nd isotope, and PGE concentration data for ELIP high-Ti picritic-basaltic samples from Yumen. These data and a compilation of previously published data for the ELIP allow us to draw the following conclusions:

- (1) The Yumen picritic-basaltic lavas have the same stratigraphy as the ELIP, and similar whole-rock and mineral compositions to the ELIP high-Ti picrites, which indicate they are part of the ELIP high-Ti group.
- (2) The compositions and FC3SM values of the primitive magmas, and 10000Zn/Fe values and Sr–Nd isotopic compositions of the ELIP high-Ti picrites indicate derivation from depleted garnet peridotite.
- (3) Differences in olivine Ni and Mn contents in the ELIP high- and low-Ti picrites can be explained by variations in the physicochemical source melting conditions rather than the nature of the mantle source lithology.
- (4) Correlations between whole-rock Mg^* values and PGE contents indicate that Ru and Ir behaved compatibly, and Pd, Pt, and Rh had partition coefficients of close to one in the ELIP basaltic magma system.
- (5) No correlations were observed between whole-rock $10,000 \times \text{Pd}/$ Yb and Mg[#], (Th/Nb)_N, and $\varepsilon_{Nd}(t)$ values, which indicate addition of crustal sulfur caused magmatic sulfide saturation in the ELIP. Variable degrees of fractional crystallisation and crustal contamination involving silicate and/or sulfide components by the high-Ti magmas resulted in the formation of different high-Ti basaltic rocks in the ELIP.

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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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