Late Palaeozoic Ultramafic Lavas in Yunnan, SW China, and their Geodynamic Significance

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INTRODUCTION

Ultramafic lavas that may be termed komatiites or high-magnesian picrites are widespread in Late Palaeozoic marine sequences within several orogenic belts in Yunnan, SW China (Figs 1 and 2; Fang et al., 1996). These lavas have been interpreted to be oceanic plateaux or seamount eruptive rocks associated with mantle plumes or hotspots in the Palaeo-Tethys ocean basin. The plateau lavas have been interpreted to be oceanic plateaux or seamount eruptive rocks associated with mantle plumes or hotspots in the Palaeo-Tethys ocean basin. The plateau lavas are thought to have been accreted onto the existing continents as a result of continental collision during the long and complex evolutionary history of the Tethys ocean basins before the ultimate amalgamation of Eurasia and Gondwana in the Tertiary (Fang et al., 1996). Given the fact that ultramafic lavas (i.e. komatiites or high-magnesian picrites) are very high temperature mantle melts that are common in the Archaean, but rare in the Phanerozoic (Arndt & Nisbet, 1982), except for those of Cretaceous age found on Gorgona Island (e.g. Echeverria, 1982; Kerr et al., 1996; Arndt et al., 1997; Révillon et al., 2000), it is important that these Late Palaeozoic ultramafic lavas in SW China are carefully examined. The ultramafic lavas appear to have been erupted under submarine conditions and exhibit well-preserved pillow structures (Fig. 3). Despite the widespread occurrence of the picrites (Fig. 1), the outcrops are rather sparse because of neotectonic complications (e.g. effects of India–Eurasia collision and the uplift of the Tibetan plateau) and because of the extensive vegetation in the region. In this contribution, we discuss the petrography, mineral compositions, and whole-rock major and trace element geochemistry of seven representative samples: six ultramafic lavas and one basaltic lava. We also discuss briefly their petrogenesis and geochemical implications. It is our intention that this short paper will draw the attention of

KEY WORDS: komatiites; picrites; China; mantle plumes

We report petrological and geochemical data on ultramafic pillow lavas from Late Palaeozoic marine sequences in Yunnan, SW China. These lavas have >26 wt % MgO, euhedral to subhedral olivine phenocrysts and acicular or quench clinopyroxene crystals with or without microlitic plagioclase in a devitrified and altered glassy matrix. These ultramafic lavas are compositionally komatiitic (>18 wt % MgO), but we term them high-Mg picrites because they lack spinifex-textured olivine. Although olivines in these picrites are cumulate crystals, causing the high MgO contents of the bulk rocks, the high forsterite content of these olivines, $Fo = 0.902 \pm 0.011$, suggests that the primitive magmas parental to the picrites would have had $\sim 17$–19% MgO, which is similar to the estimates for primary magmas of the Cretaceous Gorgona komatiites in the literature. The calculated liquidus temperature of the primitive magmas parental to the Yunnan picrites is $\sim 1400 \pm 25^\circ$C, which would imply a mantle potential temperature of $\sim 1540 \pm 30^\circ$C. This is inconsistent with magma generation beneath ocean ridges or in the mantle wedge above a subduction zone, but is consistent with a mantle plume origin, which is fully supported by the trace element characteristics of the magmas.
Fig. 1. Outcrops of ultramafic lavas in Yunnan, SW China, with regional tectonic framework shown by several orogenic belts (after Fang et al., 1996). Each indicated 'outcrop' represents a cluster of many smaller individual outcrops. Type I and Type II picrites, which both are from the southernmost 'outcrop', are in fact from two tectonic slices separated by a fault zone marked by the Nanlei river (too small to show on the map). The inset (after Wang & Mo, 1995) shows the study area in the context of a geological sketch of mainland China, in which distinct tectonic blocks (abbreviated letters) are separated by complex orogenic belts marked by bold discontinuous lines. TB, Tarim Block (Tarim basin); JB, Junggar Basin; QB, Qaidam Block; NCB, North China Block; LB, Lhasa Block; SGC, Songpan–Ganzi Complex; YB, Yangzi Block; SCB, South China Block.

the international community to these rocks and encourage more detailed research in the context of global tectonics and the Earth’s thermal evolution.

SAMPLES AND BRIEF PETROGRAPHY

The samples studied were taken from outcrops near Menglian (Fig. 1), where both ultramafic and basaltic pillow lavas are abundant. These lavas are locally intercalated with radiolarian cherts and stratigraphically overlain by shallow-water limestones (Fig. 2). Radiolaria in the intercalated cherts of Menglian and from other outcrops in the region (Fig. 1) suggest eruption ages varying from early to late Carboniferous, about a 50–60 Myr time span (Fig. 2; Fang et al., 1996). It is clear that not all these ultramafic lavas are related to a single magmatic event although we recognize that many mantle plumes are long lived (e.g. >80 Myr for Hawaii and >60 Myr for Iceland). Obviously, high-precision geochronology is required to place good time constraints.

Figure 4 shows photomicrographs of representative samples of the Yunnan ultramafic lavas. The samples are all altered to various extents with loss on ignition varying from 5·2 to 10·8 wt %. Texturally, the six ultramafic lavas can be grouped into two types. These two types occur in close geographical proximity, separated by a small river, the Nanlei River, interpreted to be a local fault zone. Type I picrites (YN14a, YN14b and YN16 from west of the Nanlei River) are somewhat altered. The primary mineralogy is dominated by anhedral (most) or subhedral (some) olivine phenocrysts of variable size (0·5–3 mm) with abundant fractures filled with serpentine, chlorite and other alteration products. Clinopyroxene occurs mostly as quench blades or elongated prisms of up to 2 mm in length. Quench plagioclase needles or blades are also present in all thin sections up to 1·5 mm
Fig. 2. Simplified stratigraphic columns for the two sample sites. The intercalated chert in Type I picrite site (samples YN14a, YN14b, YN16) contains radiolarians (Pseudolabellula annulata Ishiga, Provisocyntra pokemonsi Nazarov et Ormiston, Archocyrtium commasaemile Won, Robotium sp.) that give a Late Carboniferous age. The intercalated chert in Type II picrite site (samples YN17, MXE441, MXE01 and also basalt YN18) contains radiolarians (Albaillella deflandrei Gourmelon, A. paradoxa Deflandre, Entactinia vugaris Won) that give an Early Carboniferous age. It should be noted that shallow-water limestones stratigraphically above the columns are not shown.

Fig. 3. Photographs of ultramafic pillows along road cuts south of Menglian (Fig. 1, Type I picrite site). Bottom two panels are close-ups, in which the dashed black lines mark the outlines of the pillows. The scales are denoted by the marker pen (14 cm long, middle) and geological hammer (29 cm long, bottom).

long. The least abundant are euhedral or subhedral spinel crystals. The groundmass, which is interpreted to be devitrified glass, is volumetrically <30%, and is mostly made up of secondary chlorite and minor actinolite–tremolite and serpentine. Vesicles of up to 3 mm in diameter are present in all thin sections, suggesting volatile-rich melts or eruption in shallow water depth.

Type II picrites (YN17, MXE441 and MXE01 from east of the Nanlei River) are also altered. The primary mineralogy is dominated by euhedral olivine phenocrysts of variable size (0.5–3 mm). The olivine crystals are less fractured than Type I olivines, but altered to various extents to chlorite with fresh cores preserved. Clinopyroxene occurs as quench needles or blades or rarely as small (<0.5 mm) euhedral–subhedral crystals, some displaying spinifex texture. No plagioclase quench crystals are observed in Type II picrites. The groundmass is devitrified glass replaced mostly by chlorite, and to a lesser extent by tremolite and serpentine. Small euhedral–subhedral spinel crystals are present. Vesicles are also
Fig. 4. Photomicrographs of representative Type I and Type II picrite lavas, all taken under cross-polarized light. Ol, olivine phenocrysts; Cpx, clinopyroxene quench crystals; Plag, plagioclase quench microlites; Sp, spinel.

present in Type II picrites. It should be noted that the two textural types also differ in geochemistry (see below).

ANALYTICAL METHODS AND DATA

Major and minor element compositions (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, Cr and Ni) of phenocryst olivine, quench clinopyroxene, quench plagioclase and small spinel phenocrysts of the Yunnan picrites were analysed on polished thin sections using a JEOL Superprobe JXA-8800L at The University of Queensland. Analytical conditions were optimized for standard silicates and oxides at 15 kV accelerating voltage with a 20 nA focused electron beam for all the elements with the exception of Na and K, for which a broader beam (10 mm) was used. Routine analyses were obtained by counting for 30 s at peak and 5 s on background. Repeated analysis of natural and synthetic mineral standards yielded precisions better than 2% for elements with abundances >5 wt %, and better than 5% for those <5 wt %. Instrumental drift was negligible during the session of the analysis. Averages and standard deviations of major element compositions of phenocryst olivine, quench clinopyroxene, quench plagioclase and small spinel phenocrysts of the picrites are given in Table 1.

Major element oxides (SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO, CaO, Na₂O, K₂O and P₂O₅) for whole-rock samples were analysed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Perkin Elmer Optima 3300 DV system at The University of Queensland following the procedure of Kwiecien (1990). Precision (1σ) for most elements based on US Geological Survey (USGS) rock standards (BCR-1, BIR-1, AGV-1 and G2) is better than 1% with the exception of TiO₂ (~1·5%) and P₂O₅ (~2·0%). Loss on ignition (LOI) was
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Type I picrite</th>
<th>Type II picrite</th>
<th>Type I picrite</th>
<th>Type II picrite</th>
<th>Type I picrite</th>
<th>Type II picrite</th>
<th>Type I picrite</th>
<th>Type II picrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ol</td>
<td>40.02</td>
<td>40.22</td>
<td>40.01</td>
<td>40.01</td>
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<td>40.01</td>
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<tr>
<td>Cpx</td>
<td>54.90</td>
<td>54.95</td>
<td>54.95</td>
<td>54.90</td>
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<td>54.95</td>
<td>54.90</td>
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<tr>
<td>Plag</td>
<td>4.90</td>
<td>4.95</td>
<td>4.95</td>
<td>4.95</td>
<td>4.90</td>
<td>4.95</td>
<td>4.95</td>
<td>4.95</td>
</tr>
</tbody>
</table>

SiO₂: 40·49 40·46 40·30 40·32 40·31 40·39 40·49 40·46
TiO₂: 0·011 0·012 0·011 0·011 0·012 0·011 0·011 0·012
Al₂O₃: 0·101 0·086 0·078 0·061 0·051 0·045 0·101 0·086
FeO: 9·452 7·933 8·758 9·910 10·271 10·717 7·825 8·343
MgO: 49·11 50·37 49·52 48·71 51·37 51·37 51·37 51·37
CaO: 0·284 0·297 0·303 0·217 0·215 0·217 20·80 20·79
Na₂O: 0·004 0·007 0·008 0·004 0·008 0·012 0·321 0·325
K₂O: 0·004 0·007 0·005 0·006 0·001 0·004 0·002 0·003
P₂O₅: 0·005 0·007 0·005 0·013 0·014 0·015 0·016 0·017
NiO: 0·351 0·361 0·321 0·426 0·465 0·422 0·031 0·024
Cr₂O₃: 0·111 0·104 0·056 0·114 0·148 0·148 0·148 0·148

Mg-number: 0·903 0·919 0·910 0·910 0·910 0·910 0·910 0·910
Cr-number: 0·903 0·919 0·910 0·910 0·910 0·910 0·910 0·910
Ca-number: 0·903 0·919 0·910 0·910 0·910 0·910 0·910 0·910
determined by placing 1 g of samples in a furnace at 1000°C for several hours, cooling in a desiccator and reweighing. Trace and minor element (Li, Be, Sc, Ti, V, Cr, Co, Ni, Cu, Zn, Ga, Pb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Th and U) abundances in these same samples were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) on a Fisons PQ2+ system at The University of Queensland, with analytical conditions and procedures following Eggins et al. (1997) and Niu & Batiza (1997), except for sample digestion, which was carried out using high-pressure bombs to ensure complete digestion–dissolution. Precisions (1σ) are better than 1–2% for most elements, except for transition metals, for which precisions are better than 2–4% based on repeated analyses of highly depleted basaltic samples such as USGS reference rock standard BIR-1 [see Niu & Batiza (1997) for details]. The analytical data are given in Table 2.

DISCUSSION

Picrites vs komatiites

The ultramafic lavas have bulk-rock MgO contents >27.5 wt % (Table 2; analyses recalculated to 100% on an anhydrous basis), well in excess of the lower limit of 18 wt % for komatiites (e.g. Le Bas, 2000, 2001), and thus may be classified as komatiites on the basis of geochemistry. However, the lack of spinifex olivine disqualifies their being classified as komatiites (e.g. Arndt & Nisbet, 1982; Kerr & Arndt, 2001). We thus prefer the term ‘high-magnesian picrites’ in the subsequent discussion. On the other hand, although proper nomenclature is necessary for communication, and may reflect some physical aspect of the petrogenesis (e.g. the site or depth of crystallization, cooling rate, etc.), here we consider that understanding the composition and temperature of the primary mantle melts is the most important issue. This latter information is essential for evaluating mantle melting conditions and the Earth’s thermal evolution (e.g. Nisbet et al., 1993).

Composition and temperature of parental melts favour a mantle plume origin

Although Type II olivines tend to have lower MgO (but higher NiO) than Type I olivine, they are all on average ~Fo0 (Table 1). This highly magnesian olivine composition contrasts with the much lower Mg-number (0.6–0.82) of the quench clinopyroxene (cpx) and the low Ca-number (0.71–0.78) of quench plagioclase ( plag) in these samples. This observation suggests that the olivine crystals in these rocks are cumulate crystals that formed deep in a magma chamber at a high temperature before being brought to the surface by the eruption of more evolved melt with which the quench cpx and plag may be in closer equilibrium. The apparent zoning of the euhedral olivine crystals (Fig. 4) may suggest that their rims have lower Fo. However, it is not possible to examine the rims because of the alteration (Fig. 4). In any case, the cores of the olivine phenocrysts are likely to preserve the best record of the temperature of the parental melts (e.g. Nisbet et al., 1993).

The average composition of the olivine phenocrysts is Fo = 0.902 ± 0.011 (±1σ), which is close to the widely accepted mantle olivine composition (Dick, 1989; Herzberg & O’Hara, 1998, 2002; Griffin et al., 1999). Assuming that the cores of the olivine phenocrysts are magmatic (versus xenocrystal), this points to very primitive parental melts having Mg-number = 0.73 ± 0.02 (±1σ) by assuming Kj = [X_Mg/Fo1.5]/[X_Mg/Fo2.5] = 0.3 ± 0.03 (Roeder & Emslie, 1970). As the liquidus temperature is linearly related to the MgO content (not Mg-number) (e.g. Nisbet et al., 1993) of the melt, precise determination of the liquidus temperatures of the melts parental to the observed olivine crystals in the picritic lavas is not straightforward. Following the experimental and theoretical work of Beattie et al. (1991), Nisbet et al. (1993) developed an empirical relationship between olivine Fo content and the MgO content in weight percent of the melt in equilibrium with the olivine. This Fo4–MgO relationship, which can be described by a power-law equation of the form MgO (wt %) = 55 × Fo11.5 [derived from the work of Nisbet et al. (1993) assuming oxygen fugacity close to QFM (quartz–fayalite–magnetite)] is described by the curve in Fig. 5a. The Yunnan picrite whole-rock data, given their olivine discussion, deviate far from the equilibrium curve towards very high MgO contents. This deviation corroborates the petrographic inference that the olivine crystals are of cumulate origin, formed at a high temperature deep in a magma chamber before eruption. Therefore, the temperature information contained in the olivine phenocrysts does not reflect eruption temperatures, but the temperatures at which the olivine crystallized from the parental melts with MgO contents indicated by the open arrows in Fig. 5a.

The MgO contents of the corresponding melts parental to the olivine crystals are also plotted in Fig. 5b. It should be noted that the calculated MgO contents of the parental melts vary significantly from ~14.1 wt % to ~23.8 wt %, and are sensitive to small changes in olivine Fo content. We can use these calculated MgO contents of the parental melts to estimate their liquidus temperatures, which again vary significantly from one sample to another, and also vary depending on the model (Fig. 5c). Using the low-pressure MgO–T relationship of Nisbet (1982) and Renner (1989) for komatiites, and that of Niu et al. (2002a) for basalts based on high P–T experimental data (see
**Table 2: Major and trace element compositions of Late Palaeozoic ultramafic and mafic pillow lavas in Yunnan, SW China**

<table>
<thead>
<tr>
<th>Type</th>
<th>I picrite</th>
<th>II picrite</th>
<th>Basalt</th>
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<tbody>
<tr>
<td>YN14a</td>
<td>YN14b</td>
<td>YN16</td>
<td>YN17</td>
</tr>
<tr>
<td>wt %</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>SiO₂</td>
<td>41.03</td>
<td>42.00</td>
<td>42.45</td>
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<tr>
<td>TiO₂</td>
<td>0.532</td>
<td>0.548</td>
<td>0.565</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>7.479</td>
<td>7.817</td>
<td>8.793</td>
</tr>
<tr>
<td>FeOt</td>
<td>9.271</td>
<td>9.387</td>
<td>9.244</td>
</tr>
<tr>
<td>MnO</td>
<td>0.135</td>
<td>0.137</td>
<td>0.131</td>
</tr>
<tr>
<td>MgO</td>
<td>27.12</td>
<td>27.68</td>
<td>26.05</td>
</tr>
<tr>
<td>CaO</td>
<td>5.694</td>
<td>5.801</td>
<td>6.434</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.693</td>
<td>0.673</td>
<td>0.690</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.032</td>
<td>0.038</td>
<td>0.050</td>
</tr>
<tr>
<td>LOI (%)</td>
<td>7.477</td>
<td>5.596</td>
<td>5.213</td>
</tr>
</tbody>
</table>

Mg-no. = Mg/(Mg + Fe₂⁺) assuming 10% total Fe as Fe²⁺. The subscript CN stands for chondrite-normalized ratios.

Major element oxides determined by ICP-OES and trace elements determined by ICP-MS, at The University of Queensland. FeOt, total Fe expressed as FeO. Mg-number = Mg/(Mg + Fe²⁺) assuming 10% total Fe as Fe²⁺. The subscript CN stands for chondrite-normalized ratios.
liquidus temperatures of highly magnesian lavas from whole-rock compositions and olivine Fo contents (Fig. 6). Using this technique, the calculated primary magmas for the Yunnan picrites have a mean composition (corresponding to sample YN14a) of 18.6 wt % MgO, which is equivalent to a liquidus temperature of 1425°C (Herzberg & O’Hara, 2002). Both MgO content and liquidus temperature calculated this way are higher than conservative estimates based on empirical models (Fig. 5 and above). These results suggest that the Yunnan picrites are quite similar to the Cretaceous Gorgona komatiites (e.g. Kerr et al., 1996; Arndt et al., 1997; Herzberg & O’Hara, 1998, 2002; Revillon et al., 2000), and are thus consistent with a mantle plume origin. We also noted the report that melt inclusions in spinifex-textured olivine from the Gorgona komatiites have a lower MgO content of 14.29 ± 0.71 wt % (Sylvester et al., 2000).

The inferred MgO content (>17–19 wt %; see above) of the primary magmas for the Yunnan picrites is unusually high for mantle-derived magmas in any present-day tectonic setting. The inferred liquidus temperature (>1377–1425°C or 1400 ± 25°C) is higher than would be expected in the present-day mantle given a postulated present-day mantle potential temperature of 1280°C (McKenzie & Bickle, 1988) or 1350°C as we prefer (see Fig. 7 caption for details) derived from mid-ocean ridge basalts (MORB). Figure 7 shows the probable mantle potential temperature of 1540 ± 30°C for the petrogenesis of the Yunnan picrites. This latter temperature is even higher than model secular cooling curves for the upper mantle as suggested by Richter (1988) and others.

Fig. 5. (a) An empirical curve (MgO = 55 × Fo0.5) representing the equilibrium relationship between olivine forsterite content and MgO wt % in the melt. This curve is derived from the work of Nisbet et al. (1993), who used experimental data in the literature. Plotting of Yunnan ultramafic lavas using olivine Fo contents and whole-rock MgO indicates that the lavas are not true melt compositions, but possess excess cumulate olivine crystals. The MgO contents of the melt in equilibrium with the constituent olivine are indicated by the open arrows. (b) MgO contents of parental melts in equilibrium with olivine crystals calculated using curve in (a) are plotted. A mean value of 16.9 wt % MgO is indicated by the large black circle. (c) Liquidus temperatures for the parental melts. Although the model calculations may be large, and difficult to evaluate. For the purpose of discussion, we therefore, cautiously, use a mean MgO value of ~16.9 wt % to represent the parental magma composition, and a mean value of ~1377°C as the liquidus temperature for the parental melts in equilibrium with the olivine crystals observed in the Yunnan picrites.

Herzberg & O’Hara (2002) have recently developed a new technique that allows more precise estimation of liquidus temperatures of highly magnesian lavas from whole-rock compositions and olivine Fo contents (Fig. 6). Using this technique, the calculated primary magmas for the Yunnan picrites have a mean composition (corresponding to sample YN14a) of 18.6 wt % MgO, which is equivalent to a liquidus temperature of 1425°C (Herzberg & O’Hara, 2002). Both MgO content and liquidus temperature calculated this way are higher than conservative estimates based on empirical models (Fig. 5 and above). These results suggest that the Yunnan picrites are quite similar to the Cretaceous Gorgona komatiites (e.g. Kerr et al., 1996; Arndt et al., 1997; Herzberg & O’Hara, 1998, 2002; Revillon et al., 2000), and are thus consistent with a mantle plume origin. We also noted the report that melt inclusions in spinifex-textured olivine from the Gorgona komatiites have a lower MgO content of 14.29 ± 0.71 wt % (Sylvester et al., 2000).

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Herzberg & O’Hara (2002) have recently developed a new technique that allows more precise estimation of
for the Late Palaeozoic. We therefore infer from these calculations that the Yunnan picrites are genetically associated with deep mantle melting, and are probably products of mantle plumes or hotspots in Late Palaeozoic time. The field lithological association further suggests that the Yunnan picrites may represent an ocean island or oceanic plateau setting (e.g. Fang et al., 1996). We note that Green et al. (2001) have suggested a present-day mantle potential temperature of 1430°C that is the same beneath ocean ridges and ocean islands.

Major and trace element data favour a mantle plume origin

The Yunnan picrite lavas have two compositionally distinct groups (Table 2 and Figs 8 and 9) that correspond to the two rock types identified petrographically: Type I picrites (YN14a, YN14b and YN16) are depleted in incompatible elements, whereas Type II picrites (YN17, MXE441 and MXE01) are enriched in incompatible elements. Panels in rows (a) and (b) of Fig. 8 show that the major elements are decoupled from the incompatible trace elements, but coupled with the compatible trace elements. This suggests that Type I and Type II picrites have different parental melts with different incompatible element abundances in the first place (e.g. the inverse Na$_2$O–La and FeO–Na$_2$O trends), and also reflects the fact that the compositions of the lavas do not represent true liquid composition, but contain cumulate minerals. As a result, cumulate olivine (plus some minor cumulate cpx) and quenched groundmass (quench cpx and plag and devitrified glass altered to chlorite, tremolite, etc.) determine the bulk-rock major element compositions. For example, the positive Na$_2$O–Al$_2$O$_3$–CaO correlations indicate that the parental magmas for Type I picrites (vs Type II) are enriched in these elements as reflected by the presence of quench plagioclase, which is absent in enriched Type II picrites. It should be noted that the significant inverse trends of Al$_2$O$_3$–Ni and CaO–Co result from differences in both parental melt compositions and modal mineralogy. Row (c) in Fig. 8 shows that the between-type distinctions also apply to mobile in incompatible elements (alkalis such as K, Rb and Cs plus Pb). These scattered, yet significant, positive trends between moderately incompatible–immobile elements such as TiO$_2$ and highly incompatible and mobile elements suggest that the post-magmatic alteration has not entirely erased the primary igneous signatures of these otherwise mobile elements (except for Sr, which is uncorrelated with any element of interest).

It is important to note the nearly perfect correlations [rows (d) and (e) of Fig. 8] between incompatible and
highly incompatible elements (e.g. La, Ce, Zr, Hf, Nb, Ta, Th, U) in the Yunnan picrites. (Note the similar abundances in depleted Type I lavas, but variable abundances in enriched Type II lavas for a given element.)

Given the fact that these lavas are rather altered and U would be fairly mobile during post-magmatic alteration under oxidizing conditions (i.e. in the form of $U^{6+}$), the systematic co-variation of U with all these immobile (e.g. La, Ce, Th, etc.) and highly immobile (Nb, Ta, Zr, Hf, etc.) elements demonstrates unequivocally that U was not mobile during the alteration. This suggests that elemental ratios involving U and other immobile elements in these rocks reflect primary igneous signatures. This is important because ratios such as Th/U, Nb/U and Nb/Th in mafic or ultramafic lavas have been widely used not only to identify the tectonic settings in which the melts have formed (e.g. Hofmann, 1988; Sun & McDonough, 1989; McDonough & Ireland, 1993; Pearce & Peate, 1995), but also to infer the nature and timescales of the Earth’s chemical differentiation and continental crust accretion (e.g. Hofmann, 1988; Niu & Batiza, 1997; Sylvester et al., 1997; Collerson & Kamber, 1999; Niu et al., 1999, 2002a; Campbell, 2001).

Table 2 shows that both depleted (Type I) and enriched (Type II) Yunnan picrites together with a basalt from the Type II picrite site define a narrow range of Th/U = 3.62 ± 0.23, which is almost identical to chondritic ratio of 3.625, slightly lower than that of average ocean island basalts (OIB; ~3.92), primitive mantle (~4.00), and continental crust (~3.94), but significantly greater...
Fig. 8. Binary element–element plots for the Yunnan ultramafic lavas. ● Type I depleted picrites (YN14a, YN14b and YN16); ○, Type II enriched picrites (YN17, MXE441 and MXE01); □, alkali basalt (YN18) from Type II picrite site. Row (a) shows the good separation between the two types in both major and incompatible trace elements. The high Na₂O, Al₂O₃ and CaO in depleted Type I picrite are mostly controlled by the parental melts that are enriched in these elements as reflected by the quench microlites of plagioclase in these samples, which do not exist in Type II picrite. Row (b) also shows the distinction between the two types of lavas. Row (c) shows the scattered yet significant correlations between immobile–moderately incompatible TiO₂ and mobile and highly incompatible elements, which is unexpected for these highly altered lavas (note the up to 10% LOI in some samples). Rows (d) and (e) show almost perfect correlations among several important elements. It should be noted that the regression lines are derived from picrite lavas only, and the basalt (YN18) is plotted only for comparison.

than average mid-ocean ridge basalts (MORB; ~2–3), and island arc basalts (IAB; variable, but mostly <2 in arcs with limited terrigenous sediment input) (e.g. Hofmann, 1988; Sun & McDonough, 1989; Rudnick & Fountain, 1995; Niu & Batiza, 1997; Ewart et al., 1998; Niu et al., 1999; Y. Niu, unpublished data, 2002). The Th/U ratios alone suggest that the Yunnan picrites are of mantle plume origin. Although it may be argued that the elevated Th/U ratios could be due to continental crust assimilation, this argument is unsupported by other ratios, major element data, and the fact that the Th/U ratio is the same for both depleted and enriched lavas.

The distinctive between-type, but constant within-type Nb/U ratios (~26-5 for depleted Type I picrites; ~44-6 for enriched Type II picrites; 38-4 for the basalt) overlap MORB data (Niu & Batiza, 1997), but differ from average MORB and OIB (~40–50) (Hofmann, 1988; Sun & McDonough, 1989), and are significantly greater than that of IAB, which is variable but mostly <10 (Ewart et al., 1998; Y. Niu, unpublished data, 2002). It should be noted that Nb/U ~26-5 in Type I depleted picrites is lower than chondritic and primitive mantle ratios (~30–34). The distinctive between-type, but constant within-type Nb/Th ratios (~7-36 for depleted Type I
Fig. 9. Chondrite-normalized REE patterns of the Yunnan picrite and basalt lavas on the left and primitive mantle normalized trace element variation diagrams on the right. Average compositions of mantle-derived rocks are plotted in the bottom two panels for comparison. Chondritic and primitive mantle values, and average OIB compositions are from Sun & McDonough (1989). N- and E-MORB values are averages of high-quality ICP-MS analyses of MORB and East Pacific Rise near-ridge seamount samples from Niu & Batiza (1997) and Niu et al. (2002b). Arc tholeiites are average values of Ewart et al. (1998) and unpublished data (Y. Niu, 2002) for Tonga and Mariana arcs. It should be noted that the apparent positive Pb anomalies of the Type I picrites are real features.

For the foregoing discussion and the detailed comparisons of the Yunnan picrites and basalt with average mantle-derived rocks in Fig. 9 (bottom panels) allow us to conclude that these rocks differ significantly from MORB, IAB and continental crust. We are thus left with the possibility that these lavas are indeed genetically associated with mantle plumes or hotspots. The variations of Nb/Th and Nb/U within these lavas with respect to ‘typical’ plume materials and the fact that mantle plume sources can both be enriched (e.g. [La/Sm] < 1) and depleted (e.g. [La/Sm] < 1) indeed reflect compositional heterogeneities in plume sources as expected in terms of mantle plume dynamics and as observed in plume products (e.g. Arndt et al., 1997; Fitton et al., 1997; Campbell, 1998). It is necessary to note that the Th/U ratio in both types of the Yunnan picrites, and the Nb/Th and Nb/U ratios in the depleted Type I Yunnan picrites resemble, to some extent, chondritic or values of the primitive mantle (e.g. Sun & McDonough, 1989).
The resemblance of the Yunnan picrites to the Cretaceous komatiites on Gorgona Island (see above) suggests that the Yunnan picrite data may contribute to the komatiite debate—whether the high-MgO Archaean komatiites resulted from hydrous melting at low temperatures in a convergent-margin setting (e.g. Parman et al., 1997; Stone et al., 1997; Grove et al., 1999) or anhydrous melting at very high temperatures associated with mantle plumes (e.g. Bickle, 1993; McDonough & Ireland, 1993; Nisbet et al., 1993; Arndt et al., 1998; Herzberg & O’Harra, 1998; Herzberg, 1999). Indeed, komatiite melts, at least some, must not be entirely dry as evidenced by the presence of some primary hydrous phases and primary vesicles (e.g. Stone et al., 1997). Primary vesicles are relatively abundant in the Yunnan picrites. Assuming komatiites were formed by high-degree melting of hydrous mantle at lower temperatures and shallower depths (e.g. Grove et al., 1999), then the first pertinent question is where in the global tectonic framework hydrous mantle may exist. The likely setting would be the mantle wedge above subduction zones where the mantle may become hydrous as the result of subducting slab dehydration. This is indeed the very environment in which the ‘wet komatiites’ were proposed to have originated from related evolutionary studies on the Barberton komatiites, the oldest (~3.49 Ga), and thought to be the hottest komatiite melts with highest MgO (up to 33 wt %) (e.g. Nisbet et al., 1993). This hydrous melting model assumes without elaboration that plate tectonics were already in operation 3-5 Gyr ago, which is not unlikely, but requires observational evidence. The hydrous melting model would also suggest that komatiites should have geochemical systematics that resemble IAB, i.e. enrichments in incompatible mobile elements such as K, Rb, Cs, Sr, Pb, U, etc. relative to incompatible–immobile elements such as Nb, Ta, Zr, Hf and, to a lesser extent, Th, and light REEs such as La, Ce, Pr, etc. These characteristics are not observed in komatiite melt inclusions (e.g. McDonough & Ireland, 1993). The geochemical signatures of Nb–Th–U in the Yunnan picrites discussed above (also see details in Fig. 9) do not in any way resemble IAB, but instead favour a mantle plume origin. It may be argued that in the Archaean U may behave as an immobile element as $U^{4+}$ during slab-dehydration reactions and mantle wedge melting because of the prevailing oxygen-poor atmosphere and hydrosphere (e.g. Sylvester et al., 1997; Collerson & Kamber, 1999), thus giving no U enrichments in the komatiite melts. However, the geochemical behaviour of Th ($4+$) is independent of oxygen fugacity, and we would expect Nb/Th < 4, Nb/U < 10 and Th/U < 2 in all Archaean komatiites as in present-day IAB, but this is not observed. If the Yunnan Late Palaeozoic picrites can be considered as a Phanerozoic analogy to Archaean komatiites, then these young ‘komatiites’ do not appear to be related in any manner to suprasubduction-zone hydrous mantle melting. In conclusion, komatiites may not be entirely dry, but they are not formed in mantle wedges above subduction zones. At least for the Yunnan picrites (or komatiites), the available data are most consistent with a mantle plume origin.

**Some remarks on the use and implication of Th/U, Nb/Th and Nb/U**

Th/U, Nb/U and Nb/Th ratios in mantle-derived rocks have been used to infer the nature and time scales of the Earth’s chemical differentiation and continental crust accretion (e.g. Hofmann, 1988; Sylvester et al., 1997; Collerson & Kamber, 1999; Campbell, 2001). Given the possible mobility of U during post-magmatic alteration under oxidizing conditions, U has been considered an unreliable element. Workers have used Th as a proxy for U (e.g. Johum et al., 1991). The discovery of the immobility of U in altered 2.7 Ga komatiites and basalts by Sylvester et al. (1997) suggests, however, that fairly reduced conditions may have existed by this time, reaffirming the usefulness of U. Taking a step forward, Collerson & Kamber (1999) constructed Th/U, Nb/U and Nb/Th variation curves using their selected data from the literature on komatiites, basalts, gabbros and tonalites as a function of time from ~3.8 Ga to the present as shown by the bold lines in Fig. 10. Assuming that all these selected basaltic and komatiitic rocks were derived from the depleted mantle, these workers interpreted these curves in terms of the evolution of the Earth’s atmosphere and continental crustal growth. For example, the steep increase in Nb/Th and Nb/U from ~3.0 Ga to ~2.0 Ga was interpreted as resulting from more effective removal of Th and U (via Nb) from the mantle to the continental crust through subduction-zone processes by implicitly assuming that continental crust accretion is purely through subduction-zone magmatic genesis. The continuous increase in Nb/Th from ~2.0 Ga onward was interpreted similarly, but at a slower rate. However, the decrease of Nb/U from ~2.0 Ga onward was interpreted to result from a sudden elevation of free oxygen in the atmosphere, which created a more oxidizing global environment, causing U to behave as $U^{6+}$, which is soluble in aqueous solutions, in rivers, and...
in the oceans. As a result, progressively more U was returned into the depleted mantle in the form of hydrous phases carried by subducting oceanic crust. Although this interpretation is interesting, it neglects the fact that $\text{U}^{6+}$ would be more mobile and more effectively transported to the continents via subduction-zone magma genesis. As a result less U would be returned to the depleted mantle. This latter argument is substantiated by the fact that average present-day IAB have $\text{Th}/\text{U} < 2$ in arcs with limited terrigenous sediment input, and have $\text{Nb}/\text{U} < 10$, suggesting that U is more effectively transported into the continents (vs Th and Nb) rather than recycled into the depleted mantle. $\text{Th}/\text{U}$ and $\text{Nb}/\text{U}$ ratios in IAB are lower than the documented ratios of any of the present-day mantle reservoirs, including the depleted MORB mantle. It should be noted that Collerson & Kamber (1999) chose E-type, not N-type MORB for the present-day MORB mantle. On this basis, both $\text{Th}/\text{U}$ and $\text{Nb}/\text{U}$ ratios should increase, not decrease, in the depleted mantle as opposed to the declining curves in Fig. 10 since 2 Gyr. There are two possibilities: (1) the secular variation curves of Collerson & Kamber (1999) are incorrect and more high-quality data on major and ultramafic rocks derived from the depleted mantle are needed to reconstruct the secular variation curves; (2) processes other than those proposed by Collerson & Kamber may have been operative in the last 2 Gyr.

Importantly, the apparent immobility of U in the altered Late Palaeozoic Yunnan picrites challenges the assumption that U has become mobile since 2 Gyr owing to the change from an anoxic to a free oxygen-bearing atmosphere since 2 Gyr. It is possible that the alteration of the Yunnan picrites may have taken place in a locally reduced environment, but the preservation of primary vesicles, intercalated cherts, and limestones altogether suggest that the alteration may have taken place in a system open to near-surface conditions. As discussed and concluded above and shown in Table 2 and Figs 8 and 9, the Yunnan picrites are of plume origin from a heterogeneous mantle source. The Type II picrites and the basalt are enriched in incompatible elements, but Type I picrites are depleted. We thus can assume that the depleted Type I picrite source may represent some portion of the depleted mantle entrained by the rising plume. Plotting the picrite data, in particular the depleted Type I data, onto the Collerson & Kamber plot in Fig. 10 reveals significant departures from the Collerson & Kamber curves in the Late Palaeozoic (assumed). This departure and the fact that we see from the altered Yunnan picrites no U mobility enforce the above suggestion that the secular variation of $\text{Th}/\text{U}$, $\text{Nb}/\text{Th}$ and $\text{Nb}/\text{U}$ in the depleted mantle must be reconstructed using high-quality data on samples that
truly reflect depleted mantle. Therefore, interpretations based on the existing curves must be reconsidered.

SUMMARY

(1) The ultramafic lavas (MgO >26 wt %) in the Late Palaeozoic marine sequences in Yunnan, SW China, represent an extremely rare case in the Phanerozoic, second to the Cretaceous Gorgona komatiites. Given the lack of the spinifex-textured olivine in the Yunnan ultramafic lavas, we prefer to term them high-magnesian picrites, not komatiites.

(2) Although the Yunnan picrites possess cumulate olivine, which leads to high bulk-rock MgO contents, the presence of phenocrystal olivine with Fo = 0.902 ± 0.011 suggests that their parental melts may have had MgO of 17–19 wt %, similar to those inferred from the spinifex-textured Gorgona komatiites. This suggests that the liquidus temperature of the primary magmas parental to the Yunnan picrites was about 1400 ± 25°C. Such liquidus temperatures imply a mantle potential temperature of ~1540 ± 30°C, which is inconsistent with melting beneath mid-ocean ridges or in the mantle wedge above a subduction zone, but consistent with a mantle plume origin. Their occurrence within the marine sequences suggests that the Yunnan picrites and associated basalts are best interpreted as components of an oceanic plateau developed in the Tethys ocean basin in the Late Palaeozoic. Trace element geochemical data for both the picrites and the basalt are consistent with a mantle plume origin.

(3) If the Yunnan picrites can be considered as a Phanerozoic analogy to the Archaean komatiites, the petrological and geochemical data for the Yunnan picrites would suggest that komatiites may not be entirely dry, but lack of geochemical characteristics typical of island arc basalts does not support models of komatiite formation by hydrous mantle melting in the mantle wedge above subduction zones.

(4) The Yunnan picrites studied fall into two distinct groups in terms of both petrography and bulk-rock major and trace element geochemistry. Type II picrites and the basalt are enriched in incompatible elements with [La/Sm]N >1, whereas Type I picrites are depleted in incompatible elements with [La/Sm]N <1, suggesting a compositionally heterogeneous plume source.

(5) Although all of the Yunnan picrites studied are altered with the glassy matrix devitrified and replaced by secondary chlorite, tremolite and other phases, U abundances vary coherently with other immobile and incompatible elements such as Nb, Ta, Zr, Hf, La and Ce. This demonstrates that U was immobile or unaffected by the alteration processes and preserves a primary igneous signature. This further suggests a fairly reduced condition of alteration, either locally or perhaps reflecting the typical situation in the Late Palaeozoic. The latter inference requires serious consideration because the results, whatever they may be, are of global tectonic significance.

(6) The Th/U, Nb/Th and Nb/U ratios in these altered picrites can be used to infer the involvement of a mantle plume source in the Late Palaeozoic. The incompatible element depleted Type I picrites should provide some relevant information on the Th/U, Nb/Th and Nb/U ratios of depleted mantle component at that time. The significant departure of these ratios in depleted Type I picrites from those secular curves constructed using selected data in the literature requires (a) revision of the curves with better quality data on samples truly representing the depleted mantle throughout the Earth’s history, and (b) reconsideration of the interpretations of the evolution of the Earth’s atmosphere and the inferred continental growth model based on those curves.

(7) Finally, we hope to draw the attention of the international community to the Yunnan ultramafic lavas for more comprehensive research. Detailed geo-chronological and regional tectonic studies are urgently required to place temporal and spatial constraints on proposed mantle plume activity in the context of the global tectonic evolution in the Late Palaeozoic.

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