Chemical heterogeneity of the Emeishan mantle plume: evidence from highly siderophile element abundances in picrites

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Abstract

Highly magnesian lavas or picrites have the potential to preserve important information about the origin and thermochemical state of the mantle source(s) of large igneous provinces. We have conducted a comprehensive study of highly siderophile element (HSE) concentrations in picrites from the ca. 260 Ma Emeishan large igneous province. We show that HSE abundances in the Emeishan picrites are greater than those in mid-ocean ridge basalts (MORB) and parental melts of Hawaiian picrites, but are similar to those in komatiites. The picrites have two types of C1-normalized HSE patterns: (a) type 1, as represented by the Muli picrites is similar to that of the primitive upper mantle; (b) type 2, as represented by the Dali picrites resembles East Greenland and Iceland picrites. Pt/Ir and Pd/Ir ratios in the type 2 picrites are higher than those in type 1 picrites. The primary melt compositions of the studied samples have been estimated by back-addition of equilibrium olivine. The calculated HSE abundances of the parental liquids of the Dali and Muli picrites are higher than those of the parental melts to Hawaiian picrites. Along with previously published isotopic data, our study provides further evidence for chemical heterogeneity of the Emeishan mantle plume.

Key words: Emeishan large igneous province; picrite; highly siderophile elements; primary melt; mantle plume; chemical heterogeneity

1. Introduction.

Continental flood basalts (CFBs) are produced during short-lived and highly productive magmatic events and are characterized by basalts derived, in part, from an anomalously hot and enriched mantle reservoir (Bryan and Ernst, 2008; Coffin and Eldholm, 1992; Campbell and Griffiths, 1990; Richards et al., 1989). Although the mantle plume model has become a ‘paradigm’ for understanding the formation of CFBs over past three decades, other mechanisms have also been proposed for the formation of CFBs that do not invoke the presence of mantle plumes (Anderson et al., 2005; Foulger et al., 2005; McHone, 2000). Plumes are thought to be generated through heat transfer across the core-mantle boundary, which causes a thermal instability resulting in diapiric ascent of a large buoyant mass of hot mantle material (Campbell, 2007; Campbell and Griffiths, 1990). CFBs may provide a window into the deep Earth that can reveal the chemical and physical properties of the mantle plumes. However, the chemical and isotopic signatures of mantle plumes are difficult to identify, due to the magmas assimilating materials from the lithospheric mantle, continental crust, and volcanic edifices along with the superimposed effects of fractional crystallization. Highly magnesian lavas are generally a minor component of CFBs, but perhaps provide the most important information about the primary melts of CFB provinces (Herzberg and Gazel, 2009; Putirka et al., 2007)

The geochemistry of continental flood basalts in the Emeishan large igneous province (ELIP) has been interpreted as resulting from complex interactions between a mantle plume and heated lithospheric and asthenospheric mantle (Ali et al., 2005; Chung and Jahn, 1995; Hanski et al., 2004, 2010; Li et al., 2010; Song et al., 2008; Xu et al., 2001, 2004; Zhang et al., 2008, 2009). Although the Emeishan basalts are generally considered to be related to a mantle plume, the origin and chemical structure of the Emeishan plume is still a matter of debate. Some studies have suggested that the Emeishan mantle plume originated at the core-mantle boundary (CMB) as in the case of the Siberian CFBs (e.g., Li et al., 2010; Hanski et al., 2004; Lo et al., 2002). However, others studies consider that the Emeishan mantle plume originated from the upper-lower mantle boundary (e.g., Zhang et al., 2008). Abundances of highly siderophile elements (HSE) are useful for characterizing the geochemical history of mantle reservoirs (e.g., Chazey Iii and Neal, 2005; Dale et al., 2008; Ireland et al., 2009; Jamais et al., 2008; Maier et al., 2009; Puchtel and Humayun, 2001). The siderophile and chalcophile nature of HSE, including the platinum-group elements (PGE), indicates that they should be highly enriched in Earth's core and significantly depleted in the mantle (e.g., Barnes et al., 1985; Walker, 2000). Thus, integrated studies of HSE abundances and Re-Os isotopes can potentially reveal the effect of core-mantle interaction on the chemical heterogeneity of mantle plume (e.g., Brandon et al., 1999; McDonough, 2003; Brandon and Walker, 2005; Ireland et al., 2011; Walker et al., 1995).

The absolute and relative abundances of HSE have been determined in a number of previous studies measured HSE abundances in evolved lavas with MgO <7% and proposed that the observed fractionations of HSE resulted from the crystallization of olivine, chromite and a trace alloy with the latter being incorporated in olivine and/or chromite (Li et al., 2012; Qi and Zhou, 2008; Wang et al., 2007, 2011). Based on a small dataset, Wang et al. (2007) suggested that the diversity of HSE geochemistry in Emeishan CFBs was produced by crustal contamination. Wang et al. (2011) determined HSE concentration in a suite of intrusive rocks and low-magnesian lavas, and concluded that fractionation crystallization under either sulfur-undersaturated or sulfur-saturated conditions controlled the HSE behaviour. However, there have been few systematic studies of the HSE in highly magnesian lavas from the ELIP (i.e., MgO > 12 wt.%; Li et al., 2012).

To better understand the HSE systematics of the ELIP parental melts, we collected picrites (MgO >12 wt.%) and related tholeiitic basalts (MgO= 9-11 wt. %) from in the eastern part of the ELIP (Fig. 1). Compared with less primitive basalts, these highly magnesian lavas have the potential to provide more direct information about the thermochemical state of their source mantle (Herzberg et al., 2007; Herzberg and Gazel, 2009; Putirka, 2005; Wang et al., 2007, 2012). As such, these primitive picrites and basalts may be particularly useful in constraining the HSE content of the mantle source of the Emeishan mantle plume, which is the primary objective of our study

2. Geological setting and samples

The ELIP forms a massive Permian–Triassic succession of volcanic rocks along the western margin of the Yangtze Craton (Ali et al., 2005; Chung et al., 1995; Xu et al., 2001, 2004; He et al., 2003). These volcanic rocks cover an area of >2.5 × 10^5 km^2, with a diameter of ~500 km (Chung and Jahn, 1995; Xu et al., 2004; Ali et al., 2005). The ELIP comprises a succession of tholeiites, with minor picritic and rhyolitic/trachytic lava flows. In addition to the extrusive rocks, mafic–ultramafic layered complexes, dikes, sills, and syenitic and other alkaline intrusions form part of the ELIP. Prior to the eruption of the ELIP, He et al. (2003) argued that large-scale lithospheric uplift occurred in the region, although this point is disputed by Utskins-Peate and Bryan. (2008) and Sun et al. (2010). The ELIP was formed during the Late Permian, but differing views still exist on the exact timing of the volcanism and its potential relationship to mass extinction events. SHRIMP zircon U–Pb dating of mafic intrusions, dikes, and volcanic rocks has produced ages of 257–263 Ma (Zhong et al., 2006; He et al., 2007; Zhou et al., 2008; Fan et al., 2008; Shellnutt and Jahn, 2011), whereas $^{40}Ar/^{39}Ar$ dating of volcanic and intrusive rocks has yielded ages of 254 ± 5 Ma (Boven et al., 2002) and 251–253 Ma (Lo et al., 2002). More precise zircon U-Pb age determinations of mafic and silicic intrusive rocks from the ELIP have yielded a narrow range of ages between 257 Ma and 260 Ma (Shellnutt et al., 2012). Consequently, it is now accepted that the Emeishan CFBs were erupted at ca. 260 Ma.

The samples analyzed in this study were collected from the Dali and Muli areas (Fig. 1). Details about the samples, including their specific locations and whole-rock geochemistry, have been published elsewhere (Xu et al., 2001; Li et al., 2010; Hanski et al., 2010). The picrites from the Muli area are strongly altered and, apart from a few fresh clinopyroxene crystals, all primary magmatic minerals have been replaced by serpentine, talc, and chlorite.

Fresh olivine has not been found in these rocks, but the presence of olivine pseudomorphs indicates that olivine was abundant when the picrites were erupted. Fresh diopsidic clinopyroxene is present either as phenocrysts or in the matrix. Most of the Dali picrites are highly porphyritic (>25 vol.% phenocrysts) and contain abundant phenocrysts of forsteritic olivine, along with minor amounts of clinopyroxene ± orthopyroxene. Olivine phenocrysts are generally subhedral to rounded, occasionally embayed or partly resorbed, and are partially serpentinized along grain cracks and margins. Some olivine crystals host equant, euhedral to rounded Cr-spinel crystals that are a few tens of microns in diameter. Cr-spinel is also present as isolated grains in the groundmass. The groundmass consists principally of very fine-grained, intergrown clinopyroxene and plagioclase, as well as some devitrified glass.

3. Analytical techniques

For major and trace element analyses, volcanic rock samples were first split into small chips, and then soaked in 2 N hydrochloric acid for 1 h to remove alteration minerals. The rock chips were then powdered in an alumina ceramic shatter box. Major elements were determined by X-ray fluorescence (XRF) spectrometry on fused glass disks, whereas trace element were measured with a Perkin Elmer Elan 6000 inductively coupled plasma-mass spectrometer (ICP–MS) at the Guangzhou Institute of Geochemistry, Chinese Academy of Science (GIG-CAS). Analytical uncertainties are ±1%–2% for major elements, ±5% for rare-earth elements, ±5%–10% for other trace elements. Full details of the analytical procedures are described by Chen et al, (2010).

For PGE and rhenium concentration measurements, rock samples were first split into small chips using a hammer wrapped in paper to avoid contamination. All PGE abundances were determined by isotope dilution techniques. Approximately 2 g of whole rock powder was combined with a mixed PGE spike (^{190}Os, ^{191}Ir, ^{99}Ru, ^{194}Pt, ^{105}Pd and ^{185}Re) and attacked for

24 h at 240 ℃ in Carius tubes with reverse aqua regia (3 ml concentrated HCl+ 9 ml concentrated HNO_3) (Shirey and Walker, 1995). Osmium was extracted from the Re- and PGE-bearing solution as OsO_4 into carbontetrachloride (CCl_4) and back-extracted into HBr (Cohen and Waters, 1996). Final purification of the Os was achieved by microdistillation. Osmium abundances were measured using a Thermo-Finnigan TRITON® thermal ionization mass spectrometer (TIMS) in negative ion detection mode (Creaser et al., 1991; Volkening et al., 1991) at GIG-CAS.

Rhenium, Ir, Ru, Pt, and Pd were separated from aqua regia by cation exchange chromatography using pre-cleaned Bio-Rad AG 50W-X8 resin (100–200 mesh). To eliminate Cr-based polyatomic interferences on ^{101}Ru, which may result in erroneously elevated Ru abundances if measurements are performed by ICP-MS (Meisel et al., 2008), 1 mL of 30% H_2O_2 was added to reduce Cr (VI) to Cr (III) before loading onto the cation exchange column. Rhenium, Ir, Ru, Pt and Pd were eluted with 30 mL of 0.5 N HCl. However, the PGE fractions after cation exchange chemistry still contain significant amounts of impurities such as Mo, Zr and Hf whose oxide species can interfere on PGE masses. As such, a clean-up procedure using Amberchrom CG-71m resin coated with N-benzoyl-N-phenylhydroxylamine (BPHA) was carried out to eliminate Mo, Zr and Hf (Li et al., 2013). Rhenium, Ir, Ru, Pt and Pd are not absorbed onto the resin and were eluted with 7 mL of 0.5 N HCl into the same fraction. The eluted solution was evaporated to near dryness and dissolved in 0.3 N HNO_3 for ICP-MS analysis.

Rhenium, Ir, Ru, Pd and Pt abundances were measured by isotope dilution on a Thermo-Scientific XSERIES-2 ICP-MS. The sample was introduced to the plasma with a conventional Scott-type glass spray chamber. We measured the following isotope masses for PGE and Re concentration calculations: ^{99}Ru, ^{100}Ru, ^{101}Ru, ^{105}Pd, ^{106}Pd, ^{108}Pd, ^{185}Re, ^{187}Re, ^{191}Ir, ^{193}Ir, ^{194}Pt, and ^{195}Pt. Isotope masses of ^{90}Zr, ^{95}Mo, ^{111}Cd, ^{178}Hf and ^{192}Os were also monitored to allow isobaric interference corrections to be made where necessary. Interference corrections were typically negligible, and only an ^{106}Cd interferences on ^{106}Pd was significant (ca, 5% correction) in some samples. Oxide formation (CeO^+/Ce^+) was minimized by tuning to ≤1.5%. Instrumental mass fractionation was determined and corrected for by bracketing analyses of a 2 ng/g of PGE standard solution. The Pt blank over the period of this study ranged from 25 to 40 pg. Other PGE and Re blanks are generally ≤10 pg. All the presented concentration data have been blank corrected. The blank contributions to measured PGE contents were <2% for all samples, and for Re contents were <10 % for most samples.

Analytical results for standard reference materials, including BHVO-2 (basalt) and WPR-1 (peridotite) are presented in Table 1. The standard PGE and Re concentration data obtained here show good agreement with those reported by Meisel and Moser (2004). The poorer reproducibilities of PGE concentrations in BHVO-2 may reflect sample heterogeneity (i.e., the “nuggets effect”).

4. Results

Major and trace element data and HSE concentrations for picrites and related basalts are presented in Table 2 and 3. Picrites from the Muli and Dali area are characterized by high MgO (>12wt.%), Mg# (Mg# = Mg/[Mg + Fe^{2+}]; Mg# > 71; assuming Fe^{2+} = 0.9 × total Fe), Cr (610-2570 ppm) and Ni (320-1327 ppm). This indicates that these picrites are primitive samples and may represent, or be almost, primary melts. In contrast, four basaltic samples have relatively low compatible elements contents (Table 2). The Muli picrites hvae a large range of La/Yb (1.2-10.9) and Al_2O_3/TiO_2 ratios (5.6-10.1), whereas with the exception of one sample (RX-1), the Dali picrites have almost constant La/Yb (5.4-5.7 for the DL suite and 8.9-9.2 for the RX suite) and Al_2O_3/TiO_2 ratios (8.3-9.2 for the DL suite and 4.8-5.3 for the RX suite).

The absolute HSE abundances in all the picrites are greater than those in MORB and in the parental magmas of Hawaiian picrites, but are similar to those in komatiites (Figs. 2 and 3). The concentrations of I-group PGEs (Os, Ir, and Ru = 0.2–2.4 ppb) in all samples are less than estimates for primitive upper mantle (e.g., Becker et al., 2006), whereas concentrations of p-group PGEs (Pd and Pt, Pt concentrations range from 2.6 to 27.8 ppb) are comparable to estimate for PUM. With the exception of Re, HSE concentrations in the Emeishan picrites are generally similar to the abundances reported for the picrites from Hawaiian, Iceland and East Greenland (Fig. 3).

Chondrite-normalized HSE patterns of the Muli picrites are characterized by relatively uniform Pt/Ir (typically 7-10; average=9.3 ± 4.2) and Pd/Ir (typically 1.9-5.9; average of 4.3 ± 1.9). These rocks can be divided into two sub-types in terms of Re abundances. One type is strongly depleted in Re, with concentrations that are significantly lower than those in MORB. The other type is slightly depleted in Re with abundances comparable to Hawaiian picrites and MORB (Fig. 3). HSE patterns are similar to picrites from East Greenland with consistent Os-Ir-Ru pattern, but higher Pt and Pd abundances as compared with Iceland picrites and MORB (Fig. 3). The Dali picrites are characterized by more fractionated Pt/Ir (8-33; average =15.9 ± 8.4) and Pd/Ir (1.3-12.1; average= 6.6 ±3.0) ratios than the Muli picrites.

When considering data for the entire picrite suite, Os, Ir, Ru, Pt and Pd are negatively correlated with SiO_2 and Al_2O_3 (Fig. 4a and 4b). Osmium, Ir and Ru in the Muli picrites correlate positively with MgO (Fig. 5). Inflections appear at MgO contents of ca. 18 wt.% on plots of Os, Pt, Pd, and Re versus MgO (Fig. 5). At MgO contents <18 wt.%, Os, Pt, and Pd decrease with decreasing MgO, whereas at MgO contents >18 wt.%, these PGE increase with decreasing MgO. The Dali picrites exhibit a small range of MgO contents (17-23 wt.%) and display broad correlations on plots of Os-, Ir-, and Re versus MgO. PGE concentrations in the Muli picrites correlate strongly with Cr and Ni with inflections at Ni ≈ 700 ppm on the

Ni-MgO trend (Figs. 5 and 6b). PGE contents of the Dali picrites are highly variable, and do not show systematic trend with MgO contents (Figs. 6a and 6b).

5. Discussion

Highly siderophile elements in the Emeishan picrites exhibit a large range in absolute and relative abundances (Table 3; Figs. 2 and 3). These variations can be attributed to several factors, including volatile losses in subaerial and shallow submarine flows (e.g., Ireland et al., 2009; Lassiter, 2003; Norman et al., 2004; Sun et al., 2003), crystal-liquid fractionation, and crustal contamination processes (AFC) (e.g., Righter et al., 2004; Dale et al., 2008; Jamais et al., 2008; Qi and Zhou, 2008; Ireland et al., 2009; Wang et al., 2011; Zhong et al., 2011). Volatile loss can affect abundances of Re and perhaps Ir. Prior to using the HSE to characterize the mantle source of the Emeishan picrites, these potential secondary effects need to be considered.

5.1. Estimation of parental melt compositions

Estimation of a parental melt composition is essential in trying to deconvolve the effects of crystal-liquid fractionation on HSE abundances. The parental melt represents the most primitive magma that was produced directly by melting of the mantle source. Samples that have major element compositions approaching the estimated parental melt compositions are presumed to have experienced olivine fractionation following separation from their mantle sources (e.g., Herzberg et al., 2007; Herzberg and Gazel, 2009; Putirka, 2005, 2007). Consequently, these samples best preserve the HSE composition of the parental melt. Samples that deviate from the parental melt composition have likely experienced variable amounts of crystal-liquid fractionation and/or crustal contamination.

Parental melt compositions of basaltic rocks can be estimated by addition or subtraction of equilibrium olivine back into or from selected samples, that have experienced fractional crystallization or accumulation of only olivine (e.g., Danyushevsky et al., 2000; Putirka, 2005; Herzberg et al., 2007; Wang et al., 2012). Despite the fact that compatible element contents (e.g., MgO, Cr, and Ni) of the studied picrites are similar to those of melts derived directly from the mantle, the linear trends evident in Figs. 4-6 clearly show that variable proportions of olivine accumulation and removal have played an important role in the generation of these picrites. A series of olivine and basalt compositions were calculated from starting materials as follows: (1) the composition of equilibrium olivine was obtained using K_D $(Fe/Mg)^{oliv/liq}$ = 0.33 (Putirka, 2005), assuming that $Fe^{2+}/(Fe^{2+} + Fe^{3+}) = 0.90$ in the melt (Frost and McCammon, 2008); (2) a more primitive basalt composition was calculated as a mixture of the basalt and equilibrium olivine in a weight ratio of 99.9:0.1; (3) steps (1) and (2) were repeated using the calculated primitive basalt to progressively obtain more primitive basalt compositions (Wang et al., 2012). The calculated of olivine and basalt compositions were repeated until the calculated equilibrium olivine had a forsterite content of Fo_{91}. Mg-rich olivine phenocrysts in the Lijiang (Zhang et al., 2006) and Dali picrites (Hanski et al., 2010) of the western Emeishan CFB province, have Fo values up to 91.6 and 93.5, respectively. To minimize the effects of clinopyroxene fractionation and alteration, only samples with MgO ≥ 12 wt.%, CaO >9 wt.%, SiO_2 ≥ 44 wt.% and loss on ignition < 5 wt.% were chosen as starting materials. Six samples (ML-04-33 and DL08-5, -6, -7,-8, and -16) were chosen as starting materials to these calculations the parental melts. The estimated arental melts have 47-48 wt.% SiO_2, 17-19 wt.% MgO, 8.5-11 wt.% Al_2O_3, 9.0-10.5 wt.% FeO, and 9-11 wt.% CaO (Table 4). The uncertainties are mainly due to the variability of K_D $(Fe/Mg)^{oliv/liq}$ and Fe^{2+}/Fe^{total} (Putirka, 2005), which will result in uncertainties ca. 3% for MgO and ca. 1% for SiO_2, Al_2O_3 and CaO. Variability in the compositions of high-Mg olivine phenocrysts (Fo >

90) may also contribute to the uncertainties. Even considering these uncertainties, our estimates likely represent the minimum values of the major element compositions of the primary melts.

5. 2. Effects of volatile loss and alteration on PGE and Re abundances

Volatile loss has been demonstrated to play an important role in the Re depletion of basaltic rocks (Sun et al., 2003; Lassiter, 2003; Norman et al., 2004). This effect may cause fractionation of Re from the other HSE. The potential for Re loss is consistent with petrographic evidence that shows the Muli picrites are highly altered, but relatively less so in the case of the Dali picrites. In general, chondrite-normalized HSE patterns for picritic suites show marked Re enrichments (Ireland et al., 2009). However, in the Muli lavas that were erupted in a subaqueous or in a shallow marine environment, chondrite-normalized HSE patterns show relative depletions of Re, which is consistent with Re loss from the lava flows. Five Muli picrites (ML-32, ML04-17, ML04-19, ML-04-23, and ML-04-49) have chondrite normalized Re values of <0.001 and show a strong depletions in Re on chondrite-normalized HSE patterns (Fig. 3). The DL picrites with flat Pt-Pd-Re patterns do not show such obvious depletions in Re abundances, although these can be observed in RX samples (Fig. 3).

Good correlations between an immobile element and another selected element can be taken as evidence of immobile element behavior (Polat and Hofmann, 2003; Wang et al., 2008; Wang et al., 2010). Aluminum (Al) is the most immobile element during low-temperature alteration of highly magnesian lavas (i.e., Komatiites, P131-148). As shown in Fig. 4b, but with the exception of samples RX-12, ML04-33, and ML04-49, all samples show good correlations between PGE concentrations and Al_2O_3 contents. This suggests that all the PGE (apart from Re) have essentially been immobile during low-temperature alteration. Although the samples have a large range in PGE abundances, all the studied samples show uniform chondrite normalized patterns (with the exception of Re). This provides further evidence for the immobility of most PGE elements in our studied picrites. In contrast, there is no meaningful correlation between Re and Al_2O_3 (Fig. 4b), which suggests Re was mobile during alteration.

5. 3. HSE characteristics of the parental melts

Given the linear trends evident in Figs. 4-6, the removal and accumulation of olivine can be assumed to have had a major effect on the absolute and relative HSE abundances in the studied picrites. This may be attributable to the co-precipitation of phases such as PGE alloys with the olivine phenocrysts (Ireland et al., 2009 and references therein). Combining the linear trend of HSE versus MgO and the estimated primary MgO contents can provide first-order constraints on the HSE composition of the parental melts for each picritic suite (Fig. 7). Osmium, Ir, and Ru contents of the Muli parental melt were estimated using this method to be: Os = 2.59 ± 0.30 ppb, Ir = 1.84 ± 0.45 ppb and Ru = 3.00 ± 0.69 ppb (all 2 SD). Platinum and Pd exhibit more a complex behavior and the estimates for Pt (16 ± 4 ppb) and Pd (10 ± 4 ppb) contents in the parental melts are based on the positive linear correlations defined by samples with MgO <20 wt.%. The Muli picrites do not display a linear correlation between Re and MgO, indicating that olivine fractionation and/or accumulation has had little effect on Re fractionation and concentrations. The Re concentration (0.25 ± 0.05 ppb) in the parental melts of the Muli picrites is derived from the average Re concentration for samples ML-28, ML04-20, ML04-45. Li et al. (2010) considered that these three samples were derived directly from the Emeishan mantle plume source with little or no lithospheric contamination.

In the Dali picrites, the DL samples defined good correlations between Os, Ir and Ru and MgO (Fig. 5). Osmium, Ir, and Ru contents of the DL parental melts were estimated as follows: Os = 0.88 ± 0.34 ppb, Ir = 0.80 ± 0.34 ppb, Ru = 1.90 ± 0.82 ppb. Platinum, Pd and Re do not display clear linear correlations with MgO in the DL suite, which indicates that olivine fractionation may have exerted little control on Pt, Pd and Re concentrations. The parental melt concentrations for these three elements can be constrained by the average of samples with MgO = 18–20 wt.% (Pt = 11.2 ± 1.5 ppb, Pd = 6.40 ± 0.97 ppb, Re = 0.45 ± 0.07 ppb). The RX samples do not display significant correlations between PGE concentrations and MgO content, perhaps due to their limited range and high values of MgO contents. PGE concentrations of the parental melts for the RX samples were constrained by the average values of these picrites (Os = 1.45 ± 0.74, Ir = 0.98 ± 0.38, Ru = 2.01 ± 0.26, Pt = 12.3 ± 6.5 and Pd = 3.42 ± 0.47 ppb).

The estimated HSE abundances of the parental melt for the Dali and Muli picrites are higher than the estimates for parental melts to Hawaiian picrites (Os =0.50-1.0, Ir = 0.38-0.50, Ru = 2.20-2.55, Pt = 2.20-2.25, Pd = 2.20 and Re = 0.30 -1.20 ppb; Ireland et al., 2009), and are consistent with previously published parental magma HSE concentrations for Emeishan picrites (Ir = 1.32, Ru = 1.96, Rh = 0.65, Pt = 5.79 and Pd = 7.93 ppb; Li et al., 2012).

5. 4. Estimated bulk distribution coefficients

Linear regressions between PGE concentrations and MgO contents can be used to estimate bulk solid-melt partition coefficients (i.e., D values; Ireland et al., 2009; Puchtel and Humayun, 2001). Applying the same method proposed by Ireland et al. (2009), we estimated the bulk HSE concentrations in the co-precipitating solid phases. In the Muli and DL picrites, estimated D values for Os (3.4 and 3.6, respectively), Ir (4.0 and 4.3) and Ru (1.7 and 1.8) indicate that these elements all behaved compatibly. Our estimated D values are similar to those for Hawaiian picrites (eg., D_{Os}= 2.2 -7.1, Ireland et al., 2009). Platinum and Pd normally behave incompatibly in mafic to ultramafic systems in the absence of sulfides (e.g., Maier et al., 2009; Puchtel et al., 2009), whereas Pt and Pd display a complex behavior in our picrites samples (Fig. 5). At MgO ≤ 19 wt.%, Pt and Pd are generally positively correlated positively with MgO, indicating that these two elements were behaving compatibly. At MgO >19 wt.%, Pt and Pd decrease with increasing MgO. These negative correlations may suggest that the PGE are hosted in chromite and sulfide inclusions present within the olivine grains, rather than structurally bound within the olivine lattice (e.g., Brenan et al., 2003, 2005; Ireland et al., 2009; Puchtel et al., 2001).

5.5. PGE and Re behavior during basalt petrogenesis

5.5.1 Lithosphere assimilation

Assimilation of lithosphere (crust and mantle) can also potentially affect the HSE characteristics and Os isotopic composition of a melt (e.g., Jamais et al., 2008). Assimilation of continental crust by the Emeishan CFBs has been suggested for highly evolved lavas from Guizhou (MgO< 8 wt.%) (Qi and Zhou, 2008). However, the Muli picrites with the most radiogenic Os isotope compositions also have high Os concentrations (> 1.8 ppb) (Li et al., 2010). Mass balance calculations demonstrated that assimilation of ca. 50-60% crust would be required to produce the radiogenic Os of the Muli picrites (Li et al., 2010). However, this is inconsistent with the major element chemistry of the picrites. Addition of more geologically realistic amounts of crust (<5%) would not result in resolvable variations of the HSE abundance. A hypothetical mixture of the Muli picrites, ingestion of 10% of upper continental crust component (0.02 ppb Os; $^{187}Os/^{188}Os$ =0.8, γ_{Os}= +540; Esser and Turekian, 1993) with 260 Ma picritic melts (1.2 ppb Os, $^{187}Os/^{188}Os$ = 0.1252, and γ_{Os}=0; Li et al., 2010) would result in a net change in the Os isotopic composition of the contaminated melt by only +0.9 γ unit. We therefore conclude that crustal contamination is unlikely to have significantly affected the HSE composition of our studied picrites.

Another mechanism to produce the observed HSE fractionations is silicate liquid immiscibility brought about by changes in the sulfur saturation state, and separation of an immiscible sulfur liquid and/or crystallization of sulfied minerals (Charlier et al., 2011). This requires that the highly magnesian volcanism was spatially and temporally associated with high-silica and high-iron melts (Jakobsen et al., 2005, 2011). However, the following lines of evidence rule out this possibility. Firstly, there are no high-silica igneous rocks spatially and temporally associated with the highly magnesium volcanism. Secondly, results from experimental studies that show that silicate liquid immiscibility in basaltic magma only starts at low temperatures and is limited to the final stages of magma crystallization (Jakobsen et al., 2011; references therein). In contrast, our studied samples are high-temperature and primitive magmas. Thirdly, the studied picrites defined a clear negative correlation between $Fe_2O_3^T$ and SiO_2 ($Fe_2O_3^T = -9.702 \times \ln (Fe_2O_3T) + 49.044$, $r^2 = 0.63$). This correlation is also inconsistent with the predicted effects of silicate liquid immiscibility.

Our currently available data cannot rule out assimilation of sub-continental lithospheric mantle during the ascent of the plume-derived melts through lithosphere. This is due to the fact that the Muli picrites have unradiogenic initial Os and Nd isotopic compositions with γOs (260 Ma) and εNd (260 Ma) values ranging from −4.2 to +11.5 and −5.5 to +6.4, respectively (Li et al., 2010).

5.5.2 Effects of partial melting and crystal-liquid fractionation

Partial melting is a potential controlling factor in producing HSE fractionations (e.g., Barnes et al., 1985; Shirey and Walker, 1998; Pearson et al., 2004; Ireland et al., 2009). The distinctive chondrite-normalized patterns, and relative and absolute contents of HSE are observed in different types of mantle-derived melts, such as some komatiites and typical MORB. Higher degree partial melts (>20%), such as some komatiites, have relatively flat chondrite-normalized HSE patterns that approach chondritic Pd/Ir ratios (Puchtel and Humayun, 2000, 2001b; Puchtel et al., 2004, 2005). In contrast, low-degree partial melts, such as typical MORB, are generally characterized by fractionated chondrite-normalized HSE patterns with high Pd/Ir and Pt/Ir ratios (Rehkamper et al., 1999; Bezos et al., 2005; Dale et al., 2008; Ireland et al., 2009).

Chondrite-normalized PGE patterns for the estimated Emeishan parental melts are comparable with those of komatiites and parental melts to Hawaiian picrites, which have been attributed to limited retention of I-PGE in their mantle sources due to saturation in Ir-(Os) alloys (e.g., Ireland et al., 2009; Fiorentini et al., 2011). Fractionation between I-PGE and P-PGE suggests the presence of residual sulfide in the plume source (Bennett et al., 2000).

The Muli and DL suite picrites exhibit positive correlations between I-PGE and MgO, Ni and Cr (Figs. 5 and 6). Although the RX samples do not show significant linear correlations, data for these samples largely fall on the trend defined by data for the DL picrites. This implies that early fractional crystallization of olivine, spinel and clinopyroxene is effective in removing the I-PGE from the magma. During the early stages of crystal fractionation, I-PGE may form laurite and Os–Ir–Ru alloys (e.g., Amosse et al., 1990; Capobianco and Drake, 1990; Qi and Zhou, 2008), which become trapped in early crystallizing phases, such as chromite and olivine (e.g., Puchtel and Humayun, 2000), and this effectively removes the I-PGE from the melt (Qi and Zhou, 2008).

The Muli picrites show a change in trends of Pt and Pd versus MgO diagram at MgO= ~ 19 wt.%. In plots of Pt and Pd versus Ni inflections also characterize the trends at Ni = 900 ppm. The Ni-MgO correlation in the Muli suite can be described by a regression where Ni (ppm) = 70.1× MgO (wt.%)-395. At MgO = 19 wt.% , this corresponds to Ni = 937 ppm for the parental melt. This suggests that the parental melts have the highest Pt and Pd values. The steep chondrite-normalized PGE patterns of the analyzed picrites clearly indicate fractionation between I-PGE and P-PGE (Fig. 3). A positive correlation between Os and Cr (Fig. 6a) thus suggests that the PGE variations may be partially attributed to early fractionation of olivine (± chromite).

5.5.3 Source heterogeneities

Estimated PGE concentrations are highly variable in the primary melts of the Dali and Muli picrites. Due to the lack of systematic difference in partial melting processes in producing the Muli and Dali picrites, the large variations in absolute and relative HSE abundances most likely reflects source heterogeneity. Furthermore, the large range in Al_2O_3/TiO_2 and La/Yb ratios provides further evidence for source heterogeneity. Given that olivine fractionation or accumulation cannot fractionate these two ratios from their source values, the variations must reflect the crustal contamination and/or source heterogeneity. However, as crustal contamination was insignificant in generating the Dali and Muli picrites the large range in Al_2O_3/TiO_2 and La/Yb ratios suggests the Emeishan mantle plume was heterogeneous. The PGE contents in Muli picrites broadly correlate with Al_2O_3/TiO_2 and La/Yb ratios (apart from Re; Figs. 8 and 9), and, as such the PGE can be used to infer the source heterogeneity. This is consistent with Os-Nd-Sr isotope and elemental analyses of the Muli picrites (Li et al., 2010). Li et al., (2010) proposed that the generation of the Muli picrites involved at least three reservoirs, which were enriched and depleted plume source, and sub-continental lithospheric mantle. Plume-lithosphere interaction played an important role in producing the geochemical diversity of the Emeishan CFBs (e.g., Li et al., 2010; Xiao et al., 2004). The Muli picrites have a large range of initial Os isotopic compositions with γOs (260 Ma) = +11 to -5 (Li et al., 2010). These Os isotopic variations require long-term differences in the Re/Os ratios of the mantle sources. Previous studies have attributed the ^{187}Os/^{188}Os variations to the presence of recycled oceanic lithosphere and plume-lithosphere interaction (Li et al., 2010). The enrichment of ^{187}Os may reflect the contributions from a recycled oceanic lithospheric component or Earth's core (Li et al., 2010). Partial melting modeling shows that incorporation of a small proportion of outer core materials (ca. 0.1%) could explain the high PGE contents of the Muli picrites (Fig. 10). Other factors, such as the degree of partial melting, may also influence HSE concentrations, as a melt fraction which is just sufficient to exhaust sulfied in the source will produce a more HSE-rich melt than one resulting from a much higher degree of partial melting, where the HSE are further HSE-poorer melt. If this is correct, then correlations (and inflections) between HSE concentrations and La/Yb ratios in Fig. 9 are to be expected, because La/Yb ratios in a mafic to ultramafic magmas are directly related to the melt fraction. However, our data show no meaningful correlations between La/Yb and HSE concentrations and, as such we prefer the core-addition to explain the high HSE concentrations of the Emeishan picrites.

6. Conclusions

The Emeishan picrites are characterized by high absolute abundances of HSE. Chondrite -normalized HSE patterns of the picrites can be divided into two types: (a)Type-1, as represented by the Muli picrites, are similar to PUM with lower overall I-PGE abundances and lower relative and absolute Re abundances; (b) Type-2, as represented by the Dali picrites, are similar to those of East Greenland and Iceland picrites, which are characterized by more fractionated Pt/Ir (8.6–34.5; average = 15.9 ± 8.4) and Pd/Ir (1.3–12.1; average = 6.6 ±3.0) ratios relative to Type-1 picrites.

We estimated the major element compositions of parental melts for the picrites using back-addition of equilibrium olivine into selected whole-rock compositions. The estimated primary melts of the picrites have MgO contents of ca. 18-19 wt.%. The effects of crystal-liquid fractionation processes are evident in plots of HSE abundances versus MgO. For those plots that show broad linear trends between HSE and MgO regression of these trends provides a means to estimate the HSE composition of the parental melts for each picritic suite. The HSE concentrations at MgO = 19 wt.% on these regressions were used to define the primary HSE abundances of the parental melts. However, the primary abundances of some elements that do not correlate with MgO were estimated by the average compositions of the samples that have MgO contents similar to those estimated for primary melts. Estimated HSE concentrations for the Muli picrites are Os = 2.59 ± 0.30, Ir = 1.84 ± 0.45, Ru = 3.00 ± 0.69, Pt = 16 ± 4, Pd = 10 ± 4, and Re = 0.25 ± 0.05 ppb (±2SD). The estimated HSE concentrations for the DL picrites from the Dali suite are Os = 0.88 ± 0.34, Ir = 0.80 ± 0.34, Ru = 1.90 ± 0.82. Pt = 11.2 ± 1.5, Pd = 6.40 ± 0.97, and Re = 0.45 ± 0.07 ppb. The RX samples do not display significant correlations between PGE concentrations and MgO content, and so the HSE contents of parental melts for the RX samples were constrained by the average PGE values of these primitive picrites (MgO = 20–21 wt.%). The obtained average values are Os = 1.45 ± 0.74, Ir = 0.98 ± 0.38, Ru = 2.01 ± 0.26, Pt = 12.3 ± 6.5, and Pd = 3.42 ± 0.47 ppb. The estimated parental melt HSE abundances for the Dali and Muli picrites are generally similar to, but higher than, estimates for parental melts of Hawaiian picrites.

The HSE display a large range of absolute and relative abundances in the Emeishan picrites. Detailed consideration of the PGE geochemistry shows that this reflects the integrated effects of source heterogeneity, partial melting, plume–lithosphere interaction, and early fractionation of olivine (± chromite). Our estimated HSE abundances for primary melts of the Emeishan picrites, combined with previously published isotopic data, provide new evidence that the Emeishan mantle plume was chemically heterogeneous.

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Table captions

Table 1. Analytical data (in ng/g) for reference materials BHVO-2 (basalt) and WPR-1 (peridotite).

Table 2. Major and trace element concentrations of picrites from the Muli and Dali areas (ML = Muli area; RX and DL = Dali area).

Table 3. Highly siderophile element (HSE) concentrations of picrites from the Muli and Dali areas.

Table 4. Results of primary melt calculations using Herzberg modeling.

Figure captions

Fig. 1 Schematic illustration of the geological features of the Emeishan Large Igneous Province, also showing sample locations (modified after Xu et al., 2004).

Fig. 2 Total PGE contents plotted versus MgO. The reference fields are from Ely and Neal (2003) and data for the Emeishan basalts and picrites are from Li et al. (2012).

Fig. 3 CI-chondrite-normalized HSE patterns for (a) Muli and (b) Dali picrites. Primitive upper mantle (PUM) is considered to be representative of fertile peridotites prior to depletion of the upper mantle (Becker et al., 2006). The reference MORB field is modified after Dale et al. (2008). The primitive melt for Hawaiian picrites is an average of individual parental melts (Ireland et al., 2009). The chondrite normalizing values are from McDonough and Sun (1995). Data sources: east Greenland picrites — Momme et al. (1997, 2006); Iceland picrites — Momme et al. (2003); Hawaiian picrites — Bennett et al. (2000), Ireland et al. (2009), and Pitcher et al. (2009).

Fig. 4 PGE concentrations in the Muli and Dali picrites plotted versus (a) SiO_2 and (b) Al_2O_3. The dashed lines indicate the correlation between PGE contents and SiO_2 or Al_2O_3.

Fig. 5 PGE concentrations in the Muli and Dali picrites plotted versus MgO. Due to the narrow range of MgO contents in the Dali samples, the two picrite suites are shown separately on different plots.

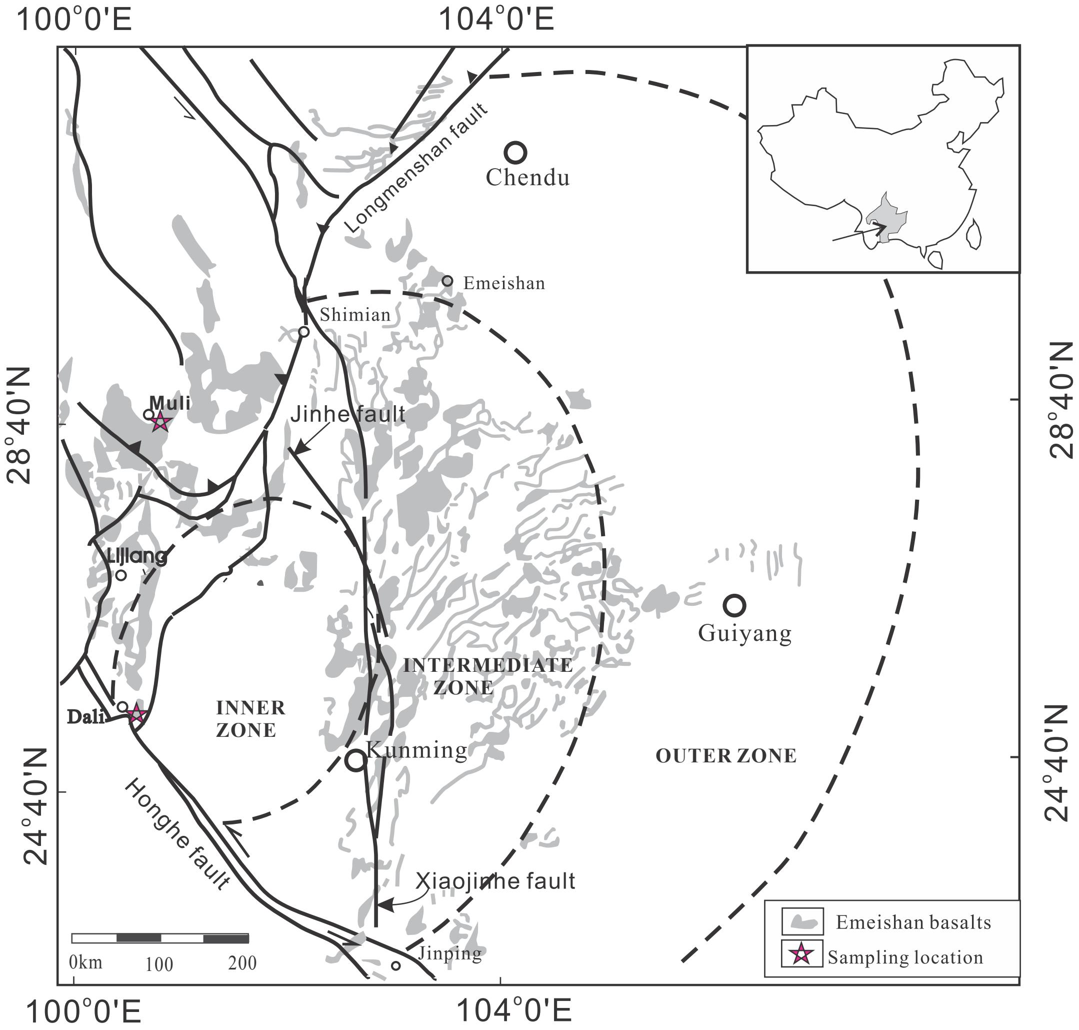
Fig. 6 PGE concentrations in Muli and Dali picrites plotted versus (a) Cr and (b) Ni contents.

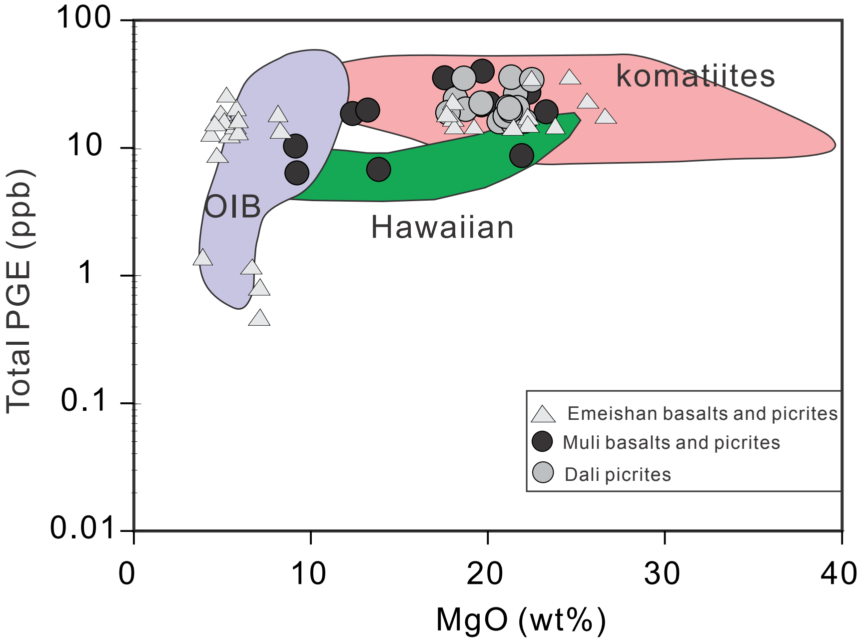
Fig. 7 Example of how the parental HSE melt contents were estimated using Os abundances from the Muli picrites. The parental melt was assumed to contain 19 wt.% MgO and its Os abundance was determined by linear regression through the data. Three samples do not plot on the regression trend.

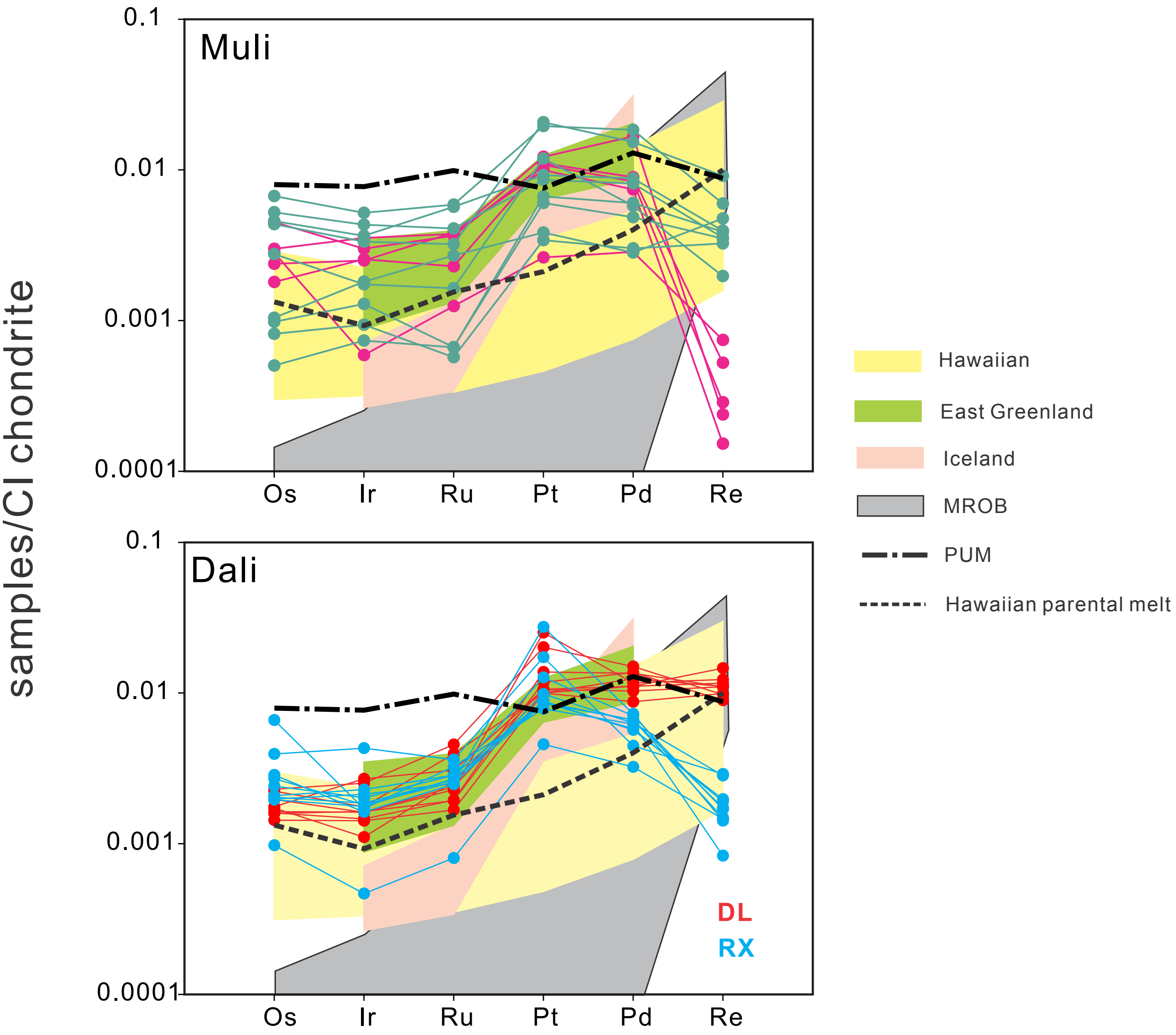
Fig. 8 PGE concentrations plotted versus Al_2O_3/TiO_2 ratios.

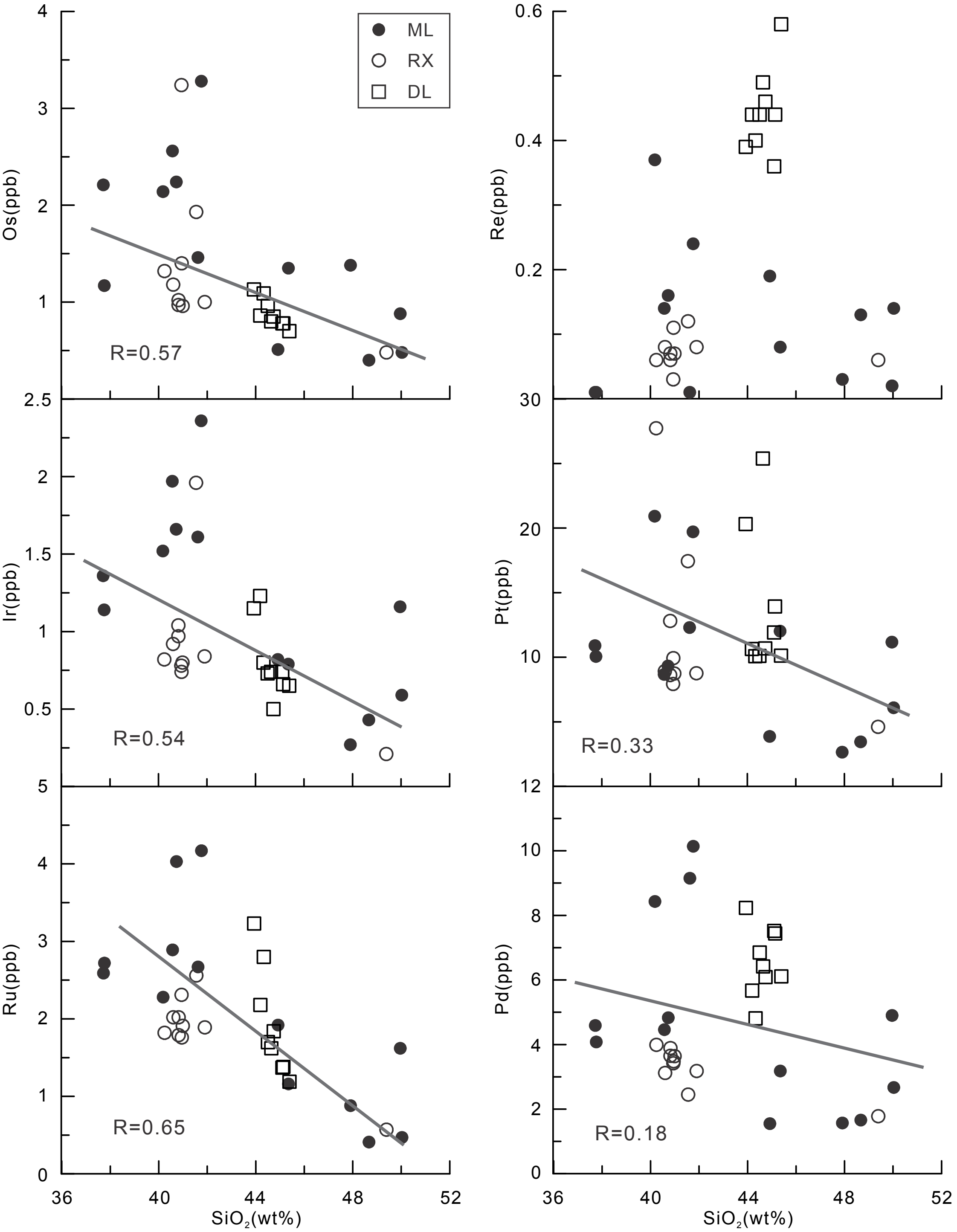
Fig. 9 PGE concentrations plotted versus La/Yb ratios.

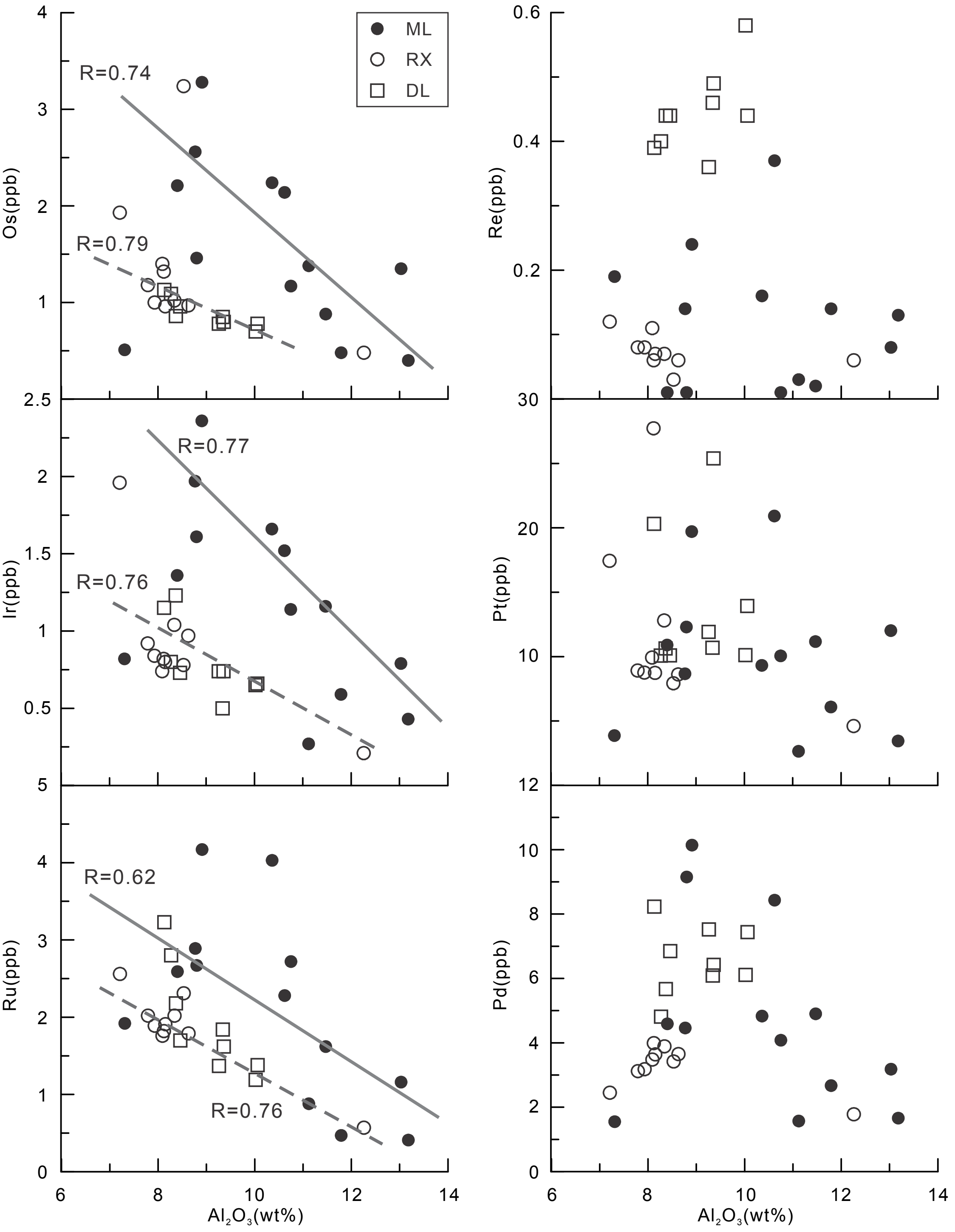
Fig. 10 Comparison of the estimated parental melts for the Muli, DL, and RX picrites with primary melts of the Hawaiian picrites (Ireland et al., 2009), komatiites (Puchtel and Humayun, 2000), PUM (Becker et al., 2006), and partial melts (black dashed lines) of a hybrid source comprising 99.9% primitive mantle and 0.1% outer core. The compositions of primitive mantle and outer core, and the bulk partition coefficients (D values), are from Puchtel and Humayun (2000). The normalizing values are from McDonough and Sun, (1995).


100°0'E
104°0'E
28°40'N
24°40'N
Chendu
Longmenshan fault
Emeishan
Shimian
Muli
Jinhe fault
Lijiang
Guiyang
INTERMEDIATE ZONE
INNER ZONE
Dali
Kunming
OUTER ZONE
Honghe fault
Xiaojinhe fault
Jinping
0km
100
200
Emeishan basalts
Sampling location

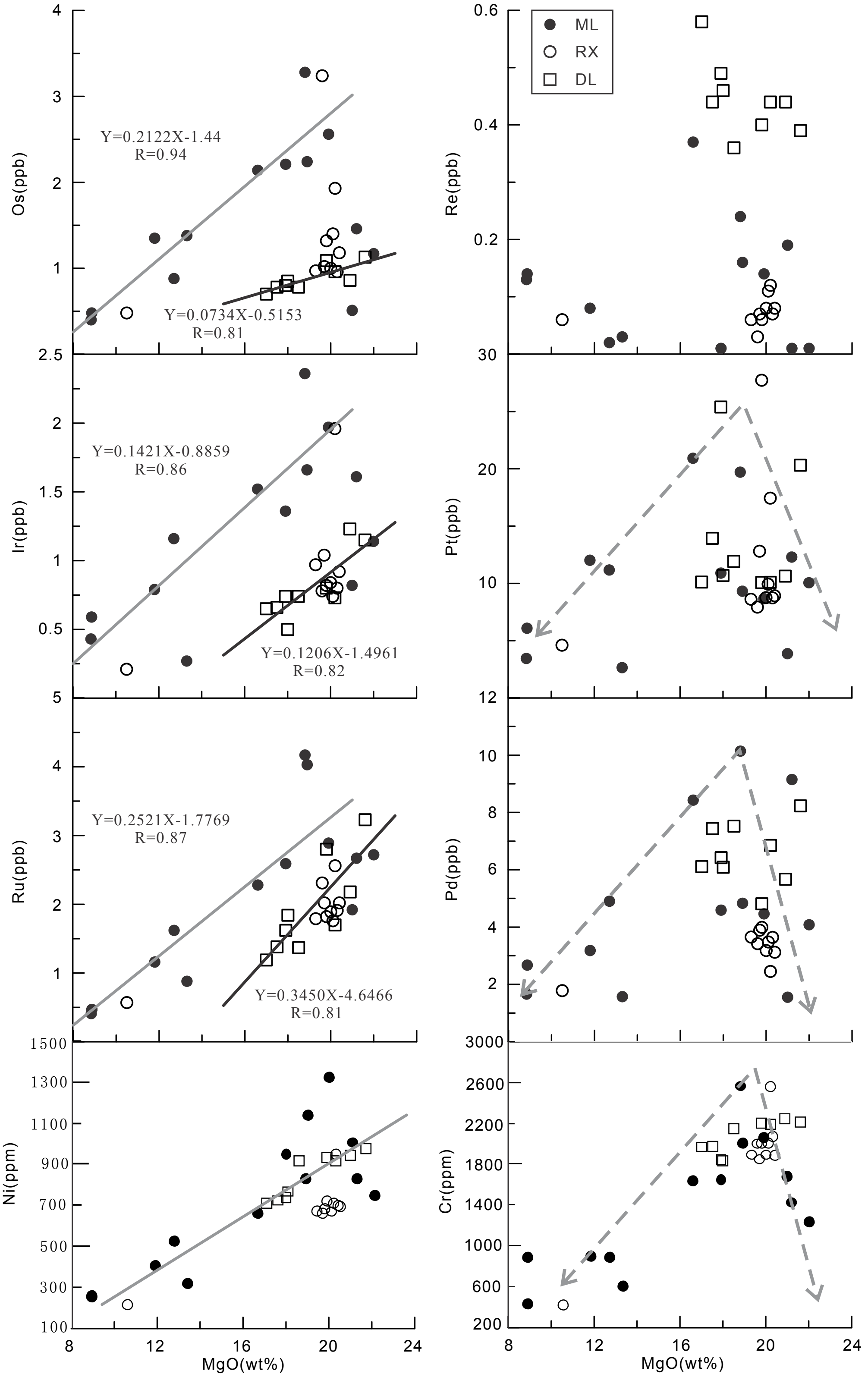

100
10
1
0.1
0.01
Total PGE (ppb)
0
10
20
30
40
MgO (wt%)
komatiites
OIB
Hawaiian
Emeishan basalts and picrites
Muli basalts and picrites
Dali picrites

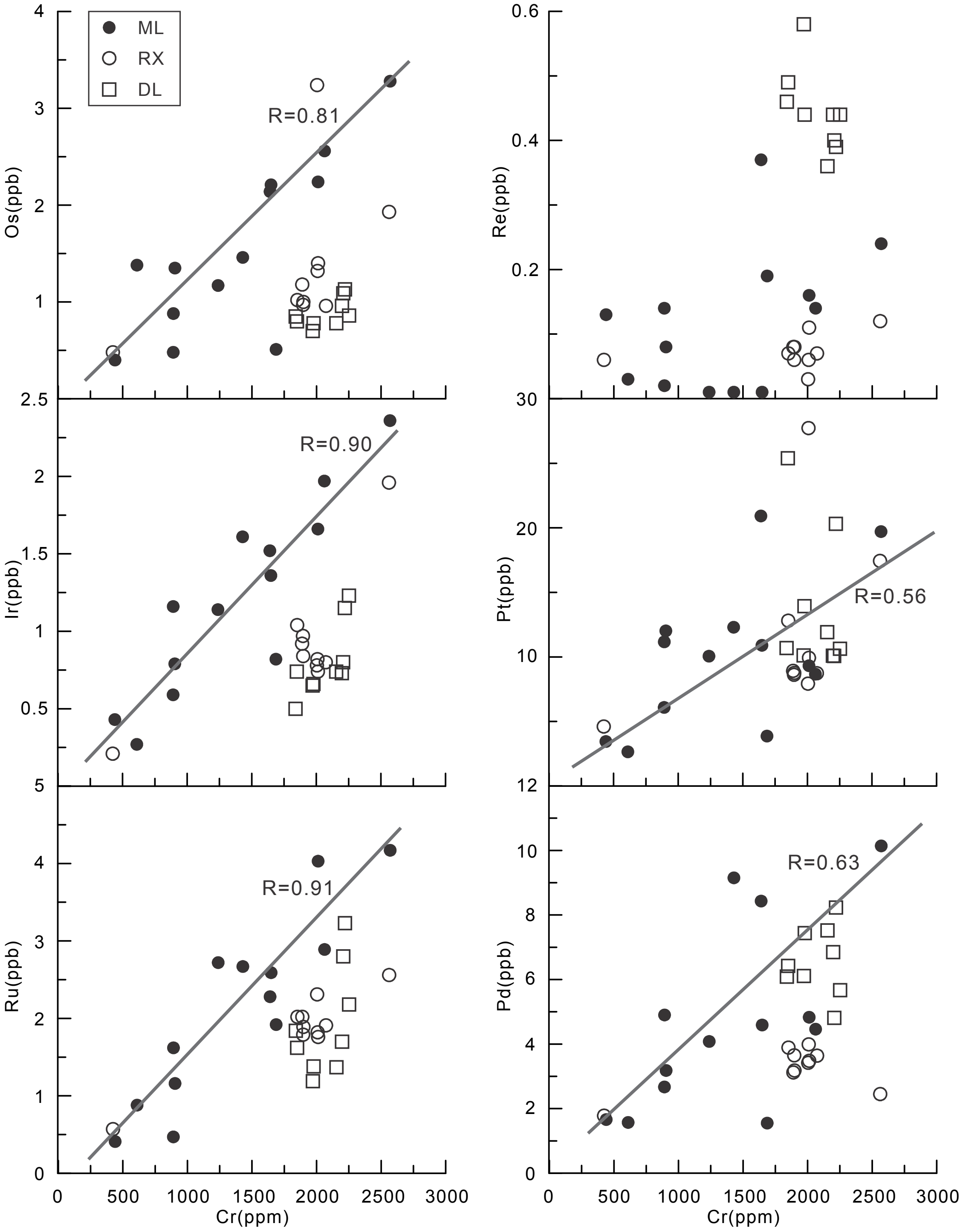

samples/CI chondrite
Muli
0.1
0.01
0.001
0.0001
Os
Ir
Ru
Pt
Pd
Re
Dali
0.1
0.01
0.001
0.0001
Os
Ir
Ru
Pt
Pd
Re
DL
RX
Hawaiian
East Greenland
Iceland
MROB
PUM
Hawaiian parental melt

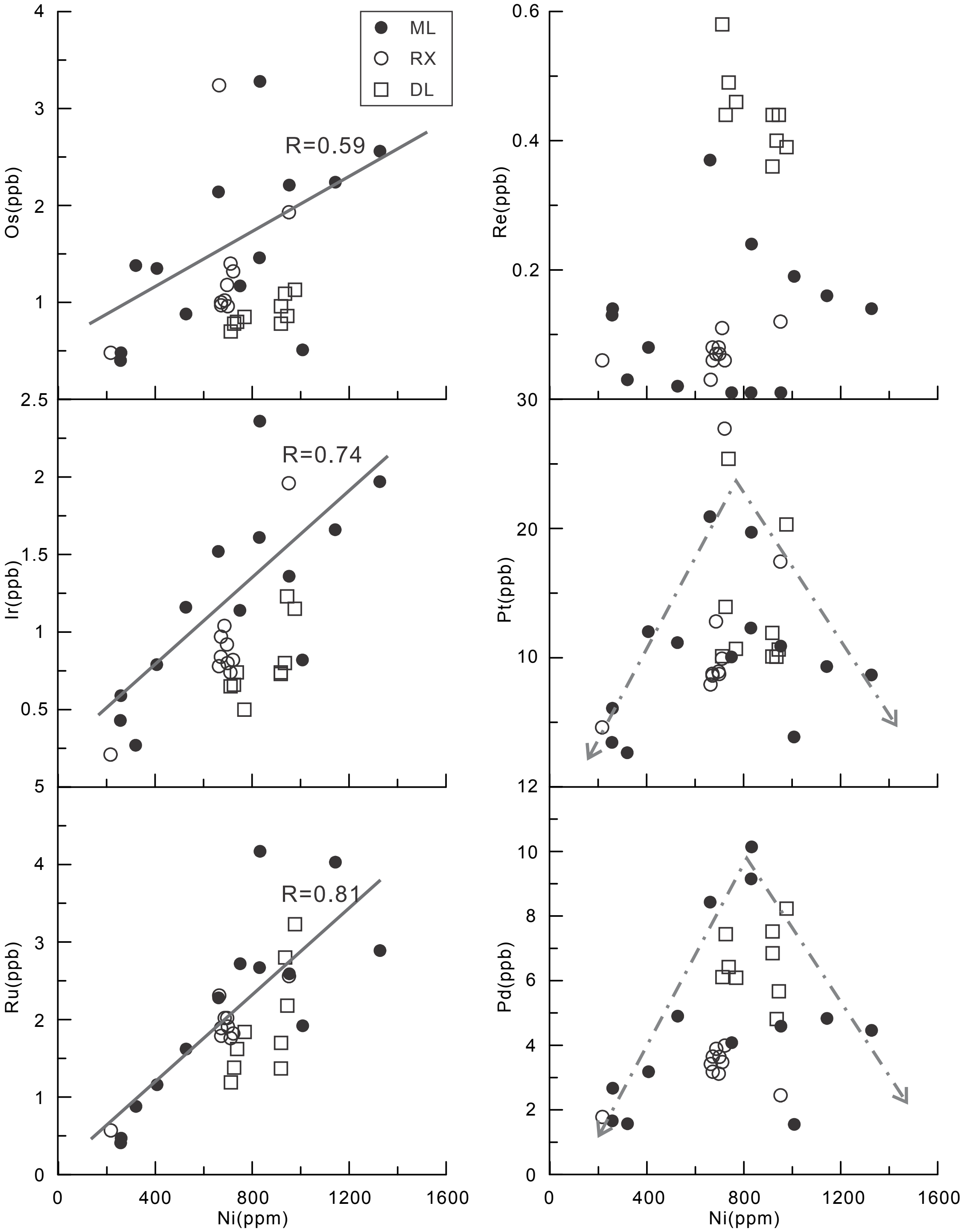

ML
RX
DL
Os(ppb)
4
3
2
1
R=0.57
Re(ppb)
0.6
0.4
0.2
Ir(ppb)
2.5
2
1.5
1
0.5
R=0.54
Pt(ppb)
30
20
10
R=0.33
Ru(ppb)
5
4
3
2
1
0
R=0.65
Pd(ppb)
12
10
8
6
4
2
0
R=0.18
36
40
44
48
52
SiO_2(wt%)
36
40
44
48
52
SiO_2(wt%)

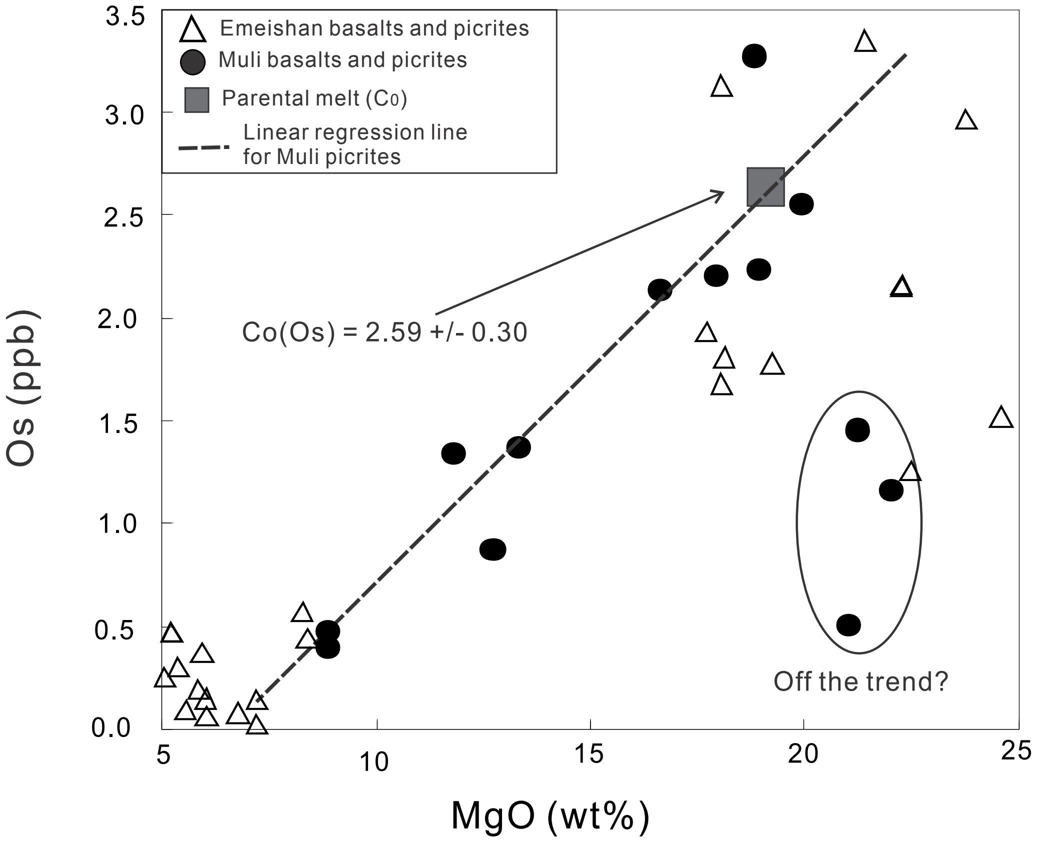


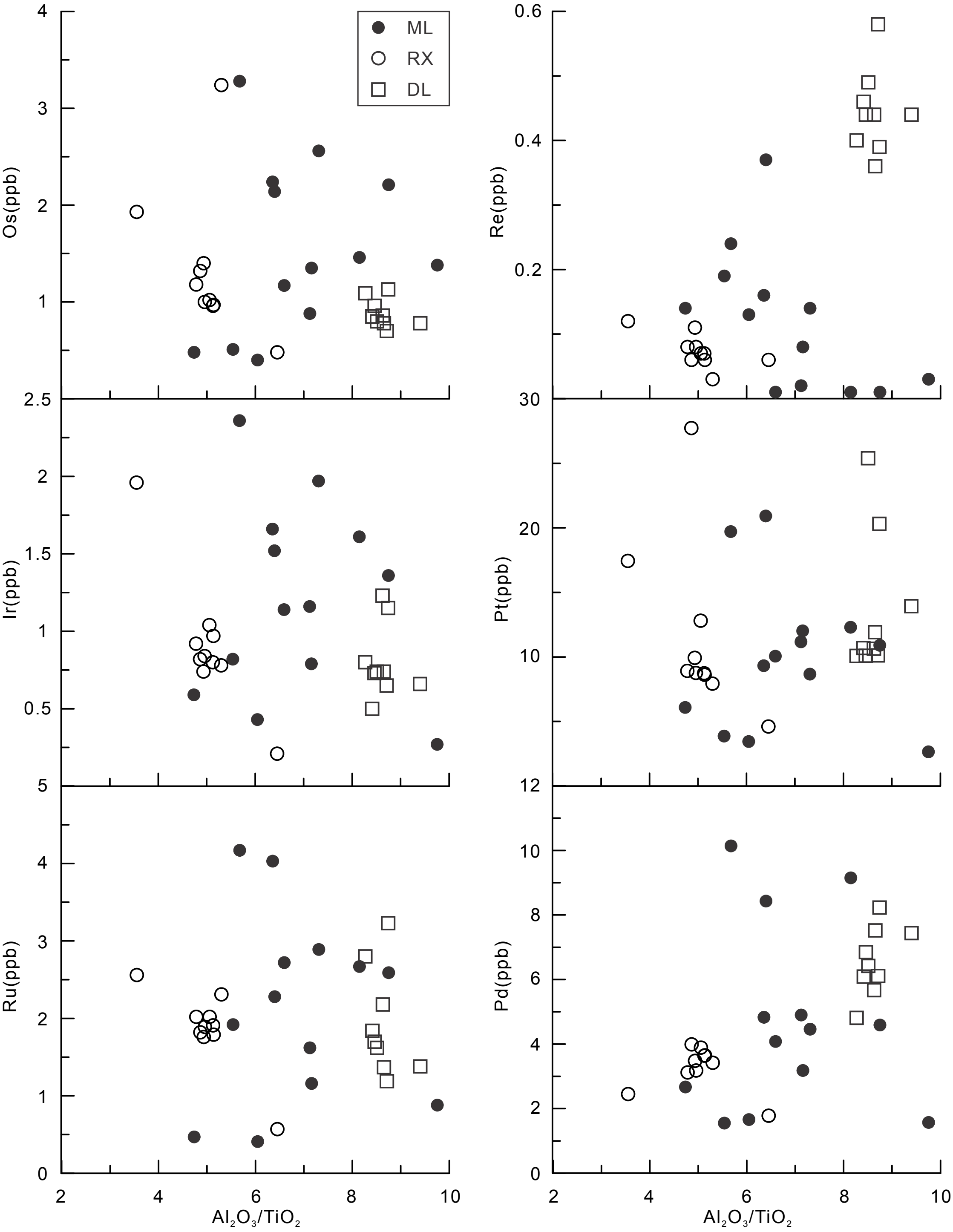
ML
RX
DL
Os(ppb)
R=0.74
R=0.79
4
3
2
1
Ir(ppb)
R=0.77
R=0.76
2.5
2
1.5
1
0.5
Ru(ppb)
R=0.62
R=0.76
5
4
3
2
1
0
6
8
10
12
14
Al$_2$O$_3$(wt%)
Re(ppb)
0.6
0.4
0.2
Pt(ppb)
30
20
10
Pd(ppb)
12
10
8
6
4
2
0
6
8
10
12
14
Al$_2$O$_3$(wt%)

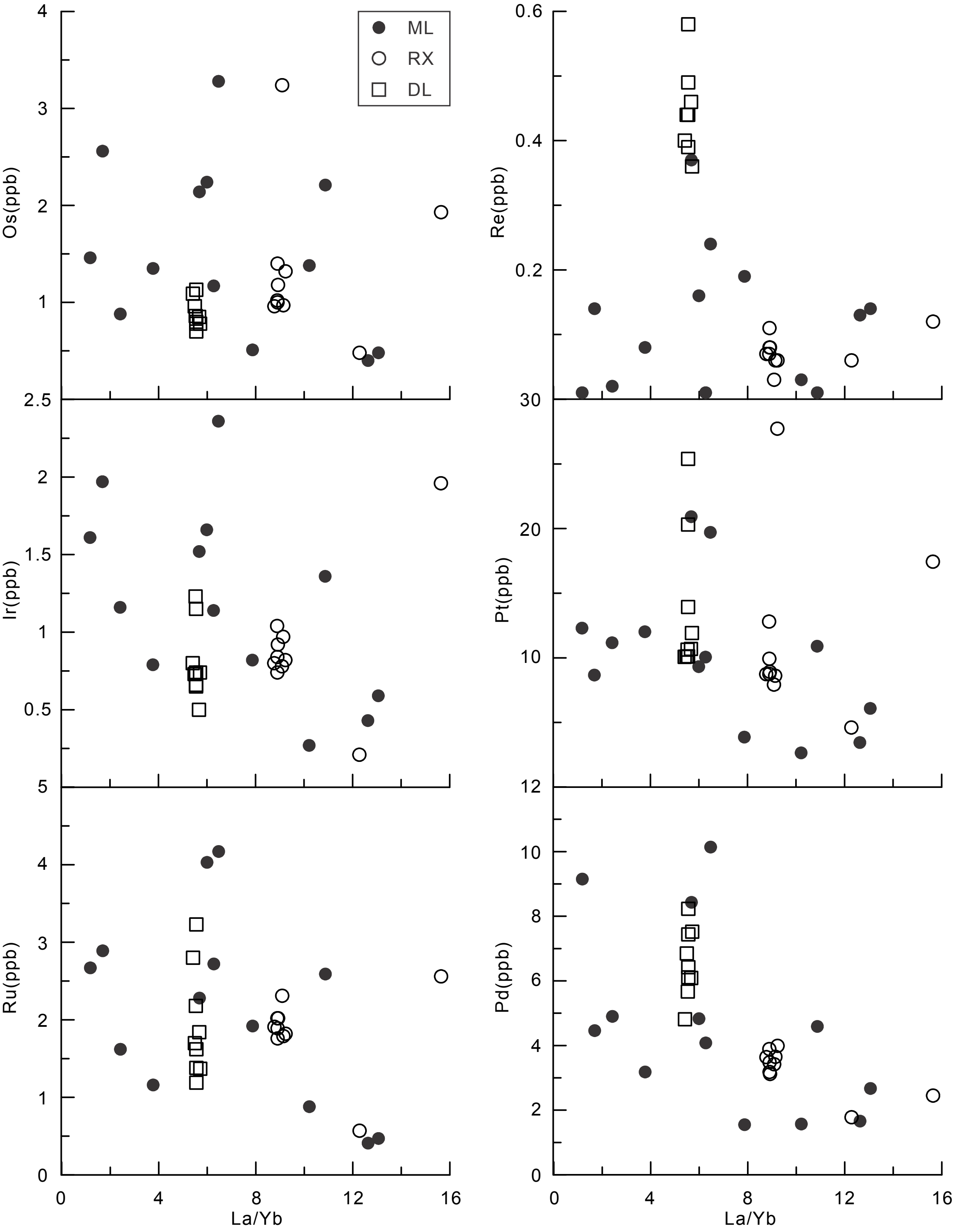

ML
RX
DL
Os(ppb)
Y=0.2122X-1.44
R=0.94
Y=0.0734X-0.5153
R=0.81
Re(ppb)
Ir(ppb)
Y=0.1421X-0.8859
R=0.86
Y=0.1206X-1.4961
R=0.82
Pt(ppb)
Ru(ppb)
Y=0.2521X-1.7769
R=0.87
Y=0.3450X-4.6466
R=0.81
Pd(ppb)
Ni(ppm)
Cr(ppm)
MgO(wt%)
MgO(wt%)
4
3
2
1
2.5
2
1.5
1
0.5
5
4
3
2
1
1500
1300
1100
900
700
500
300
100
0.6
0.4
0.2
30
20
10
12
10
8
6
4
2
3000
2600
2200
1800
1400
1000
600
200
8
12
16
20
24
8
12
16
20
24


ML
RX
DL
Os(ppb)
R=0.81
Re(ppb)
Ir(ppb)
R=0.90
Pt(ppb)
R=0.56
Ru(ppb)
R=0.91
Pd(ppb)
R=0.63
0
500
1000
1500
2000
2500
3000
Cr(ppm)
0
500
1000
1500
2000
2500
3000
Cr(ppm)

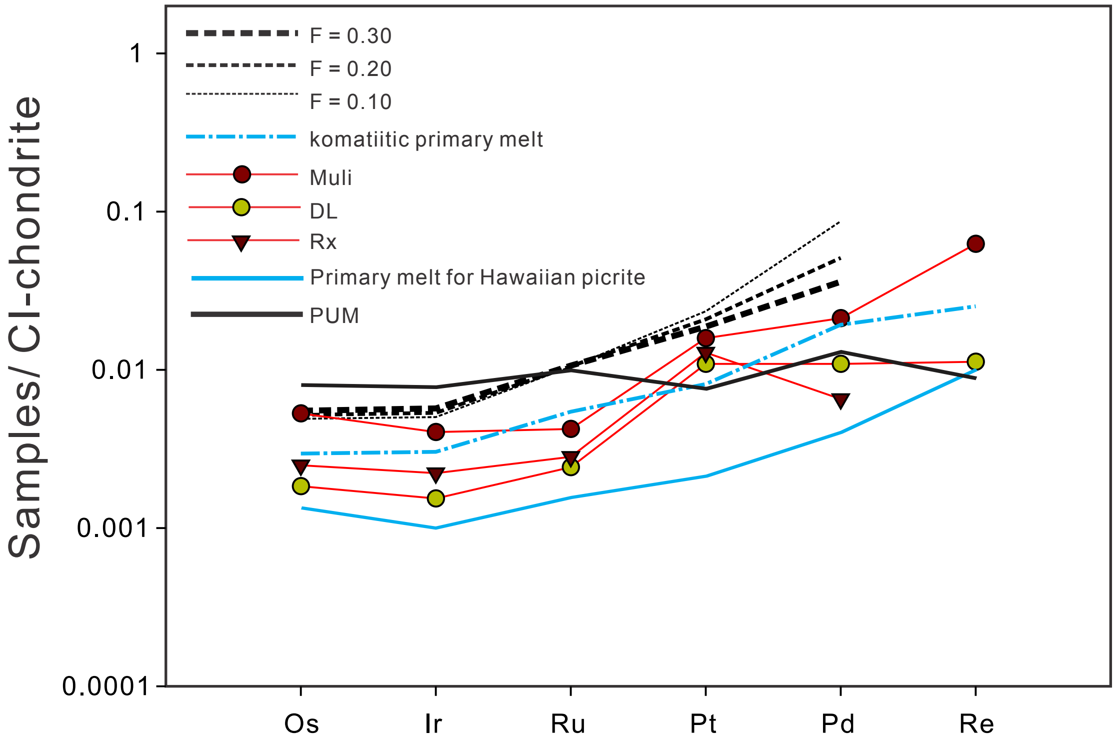

ML
RX
DL
R=0.59
R=0.74
R=0.81
Os(ppb)
Ir(ppb)
Ru(ppb)
Re(ppb)
Pt(ppb)
Pd(ppb)
Ni(ppm)
Ni(ppm)
4
3
2
1
2.5
2
1.5
1
0.5
5
4
3
2
1
0
0.6
0.4
0.2
30
20
10
12
10
8
6
4
2
0
0
400
800
1200
1600
0
400
800
1200
1600

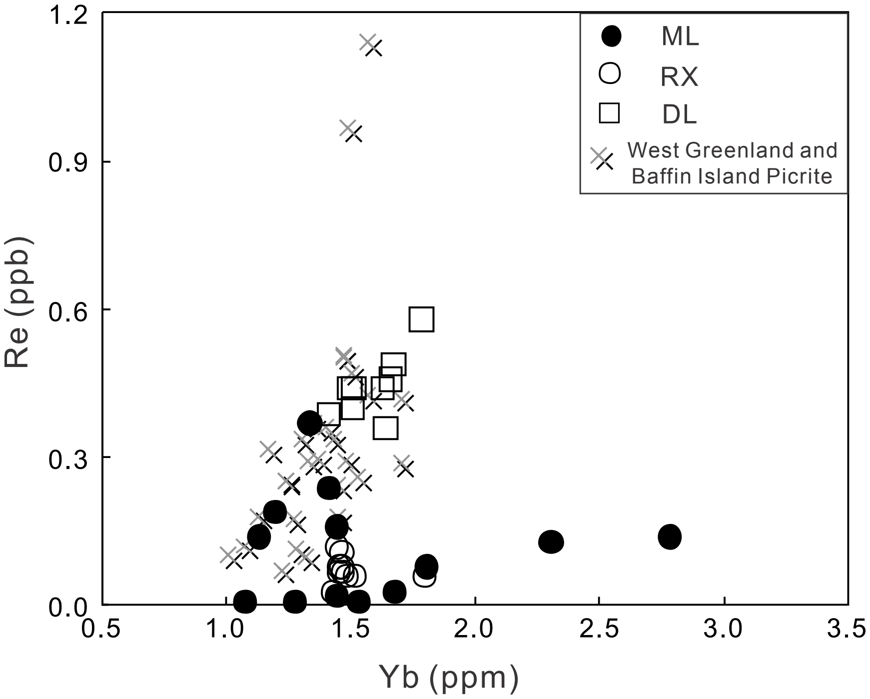

Emeishan basalts and picrites
Muli basalts and picrites
Parental melt (C0)
Linear regression line for Muli picrites
Co(Os) = 2.59 +/- 0.30
Off the trend?
Os (ppb)
MgO (wt%)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
5
10
15
20
25


● ML
○ RX
□ DL
Os(ppb)
Re(ppb)
Ir(ppb)
Pt(ppb)
Ru(ppb)
Pd(ppb)
Al_2O_3/TiO_2
Al_2O_3/TiO_2
4
3
2
1
0.6
0.4
0.2
2.5
2
1.5
1
0.5
30
20
10
5
4
3
2
1
0
12
10
8
6
4
2
0
2
4
6
8
10
2
4
6
8
10



ML
RX
DL
Os(ppb)
Re(ppb)
Ir(ppb)
Pt(ppb)
Ru(ppb)
Pd(ppb)
La/Yb
La/Yb
0
4
8
12
16
1
2
3
4
0.2
0.4
0.6
0.5
1
1.5
2
2.5
10
20
30
2
4
6
8
10
12
5


F = 0.30
F = 0.20
F = 0.10
komatiitic primary melt
Muli
DL
Rx
Primary melt for Hawaiian picrite
PUM
Samples/ CI-chondrite
1
0.1
0.01
0.001
0.0001
Os
Ir
Ru
Pt
Pd
Re


1.2
0.9
0.6
0.3
0.0
Re (ppb)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Yb (ppm)
ML
RX
DL
West Greenland and
Baffin Island Picrite