The Mantle Source of Thermal Plumes: Trace and Minor Elements in Olivine & Major Oxides of Primitive Liquids (And Why the Olivine Compositions Don’t matter)

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ABSTRACT

We estimate the mantle source compositions for mantle plumes, and by implication Earth’s lower mantle, by: (a) measuring trace (e.g, Sc, V, Cu) and minor (e.g., Ca, Mn, Ni) element concentrations of high forsterite olivine grains from several plume localities, (b) estimating the parent liquid compositions from which they crystallized, (c) calculating mantle potential temperatures and degrees of partial melting and (d) estimating trace element compositions of depleted and enriched mantle sources. Our sample set includes two continental flood basalt provinces (Emeishan and Deccan), a flood basalt that erupted in a continental rift setting (Baffin Island), our type example of a thermal mantle plume (Hawaii) and lavas from the Siqueiros Transform at the East Pacific Rise, which represent the mid-ocean ridge system. We also present olivine compositions for the peridotite xenoliths from Kilbourne Hole, New Mexico, USA, which are commonly used as primary and secondary analytical standards. We find that trace elements in lava-hosted olivine grains are too far removed from their mantle source to provided anything but greatly hindered views of such. Olivine compositions reflect not only evolving liquid compositions (including partial melting conditions and later fractionation), but also evolving Ol+liq partition coefficients, which mostly increase with decreasing T during crystallization. Mantle compositions, delimited by maximum forsterite contents and estimates of parental magmas (and experimentally determined partition coefficients) indicate that our selected plumes reflect some combination of (1) a depleted mantle source that is quite similar to that obtained by other methods, and (2) a variably enriched plume source that is more enriched than current estimates of pyrolite. The enriched plume mantle sources can be explained remarkably well as a mixture of subducted mid-ocean ridge basalt (MORB; Gale et al. 2013) and depleted MORB mantle (DM; Salters and Stracke 2004), with MORB:DM ratios of 1:5 to 1:4. These ratios are most sensitive to
estimates of melt fraction where plume parental magmas are last equilibrated with their mantle source, but are nonetheless consistent across a wide range of chemically very different elements, and estimates of MORB and DM obtained by very different means. Baffin Island is of particular interest. Like prior studies, we verify a high mantle potential temperature ($T_p$) of 1630$^\circ$C (compared to $T_p = 1320-1420^\circ$C for MORB from Cottrell and Kelley 2011 for Ol of Fo89.3-91.4). The Baffin source is also within error the same as DM with respect to trace elements, although still isotopically distinct; Baffin appears to be sourced in something that is akin to DM that lies at the base of the mantle, where plumes acquire their excess heat. Thus while part of our analysis supports the concept of a “slab graveyard” at the bottom of the lower mantle (e.g., Wyession 1996), that cemetery is by no means ubiquitous at the CMB: subducted slabs are either unevenly interred, or efficiently excavated by later upwellings.

INTRODUCTION

An enduring obscurity concerns the composition and mineralogy of Earth’s lower mantle—we may indeed have a better understanding of Pluto’s surface (Moore et al. 2016) than Earth’s lower reaches. As to the upper mantle, mantle xenoliths are a key source of information, since they are just one step removed (they are often residues of prior melt extraction) from the mantle source that gives rise to basalts (e.g., McDonough and Sun 1995; Salters and Stracke 2004; Workman and Hart 2005). Basalts, if sufficiently primitive, are also just one step removed from a pre-melt extraction mantle, and their compositions have been used to infer, for example, that subducted crust may be admixed into the sources of MORB (Hirschmann and Stolper, 1996; Waters et al. 2011) and ocean island basalts (OIB) (e.g., Hawkesworth et al. 1979; Hofmann and White 1982; Prytulak and Elliott 2007; Jackson et al. 2008). OIB are in turn thought to derive as deep-seated thermal plumes from the core-mantle boundary (Morgan 1972), and so their sources may provide our most direct view of the lower mantle.

Olivine (Ol) phenocrysts have been offered as an additional, perhaps less biased, view of MORB and OIB mantle sources (e.g., Sobolev et al. 2007). One obvious advantage is that primitive Ol grains are highly resistant to the mixing processes that homogenize
magmatic liquids, and so might preserve what is otherwise lost to magma mixing.

Clearly, diffusion may later homogenize phenocrysts (Thomson and Maclennan 2013), but the diversity of disequilibrium Ol grains demonstrates that the process is quite incomplete. As a test, we present new analyses of trace (Ti, V, Cr, Cu, etc.) and minor elements (Ni, Ca, Mn, etc.; for simplicity, herein referred to as “trace” elements) in olivine grains from several plume localities, and a MORB from the East Pacific Rise. Our data show that olivine compositions provide a rather opaque view of mantle composition, especially compared to their host lavas. For some elements (Ni and Cr) olivine compositions reveal quite little about mantle source regions (instead recording how their parent magmas were generated, i.e., at high \( P \) or \( T \) or high melt fraction), while for others (Sc and Ti, and possibly Ca) signatures of the mantle source(s) may be preserved, but through a connection that is not perfectly clear.

We first review some crucial, perhaps under-appreciated, controls on oceanic volcanic compositions, and how olivine compositions respond to \( T \) and liquid composition. Our analysis, which includes some new estimates of mantle-equilibrated parental magmas and the mantle potential temperatures at which they were formed, indicate that the lower mantle contains a depleted component similar to depleted MORB mantle, which is herein noted as DMM [“DM” in Stracke and Salters (2004) and “DMM” in Workman and Hart (2005) with further variations in Shimizu et al. 2016]. This finding is tentative to be sure, but not new, as the FOZO component of Hart et al. (1992) has near DMM-like \(^{87}\text{Sr}/^{86}\text{Sr} \) (0.70248) and \(^{143}\text{Nd}/^{144}\text{Nd} \) (0.5131) and so is clearly quite depleted. What remains clear is that progress will require us to resurrect a pan-periodic chart view of mantle-derived liquids (e.g., Stracke 2012; White 2015), and direct comparisons (e.g., MORB-
normalized, rather than the less-useful but habitual chondrite normalized trace element diagrams) of mantle sources, the latter of which are sorely lacking. Ultimately, we plan to show the efficacy of using combined rock composition, experimental and phase chemical data to better constrain mantle plume sources.

BACKGROUND

Approach & Motivation

Our new trace element analyses of high forsterite (Fo; Mg$_2$SiO$_4$) olivine phenocrysts (ca. Fo>85) derive from (1) our archetype of a mantle plume, Hawaii, (2) two continental flood basalt provinces, Deccan and Emeishan, (3) a flood basalt province at a rifted margin, Baffin Island, and (4) a “D-MORB” or “depleted MORB” (derived from an especially chemically depleted DMM, see Waters et al. 2011) from the Siqueiros Transform (Perfit et al. 1996; Putirka et al. 2011), which is part of the East Pacific Rise. We also present new data for olivine grains from Kilbourne Hole mantle xenoliths (often known as “KLB”), collected by the lead author, which we use as both an analytical and petrologic reference.

Our choice of samples is predicated on the idea that oceanic islands and flood basalts are created by thermal mantle plumes, that these plumes have excess heat (Herzberg 1995; Herzberg and Gazel 2009; Li et al. 2012; Putirka 2016), and that they gain much of this heat from the underlying core (e.g., Hess, 1962; Morgan 1971; Lay et al. 2008), or from U-, K- and Th- enriched regions of the lowermost mantle (Garnero et al. 2016). Flood basalts and OIB thus may entrain deep-seated mantle material (e.g., Kellogg et al.
In contrast, mid-ocean ridge basalts (MORB) derive from passive upwelling of shallow upper mantle (McKenzie 1967). A key motivating work is that of Sobolev et al. (2007), who observe that olivine grains from many plumes exhibit peculiarly high Ni contents; they suggest that high Ni-in-Ol requires parental liquids that formed by partial melting of a pyroxenite (rather than peridotite) source. Their pyroxenite source is putatively created by mixing ambient mantle peridotite with partial melts of deeply subducted crust; this reaction may convert a former peridotite source to a near olivine-free, pyroxene-rich lithology. Some dispute this interpretation (e.g., Matzen et al. 2009, 2013; Putirka et al. 2011), arguing that high Ni-in-Ol can be obtained by crystallization of mafic magmas over temperatures ranging from 1500°C for moderate Ni contents to 1375°C for the highest Ni-in-Ol (Putirka et al. 2011, their Fig. 5). Others suggest that high Ni-in-Ol reflects mass exchange between a mantle source and Earth’s Ni-rich core (Herzberg et al. 2013, but see also Herzberg et al. 2016 for a moderating view). Modeling efforts suggest that pyroxenite- and peridotite-derived partial melts may have similar major oxide compositions (Jennings et al. 2016; Lambart et al. 2016), and our tests indicate the same, although some pyroxenite-derived melts (e.g., Kogiso et al. 2001) range to very low Al₂O₃ (<12 wt. %, with SiO₂/Al₂O₃ ratios >4) and very high CaO (>13.8 wt. %), that are less than typical for peridotite partial melts (mostly >12% Al₂O₃, <14% CaO, SiO₂/Al₂O₃ < 5). And surely, Ol compositions derived from such liquids should inherit these characteristics. In addition, trace elements that feature significant contrasts in partitioning behavior between Ol and either of pyroxene or garnet should provide reliable tests. For example, a pyroxenite source should yield Sc-depleted liquids compared to a peridotite source, and Ol grains should inherit such a
mineralogy-dependent influence. In a similar manner, if high Ni contents derive from a core-contaminated mantle, then other (easily analyzed) siderophile elements, such as Co, Cr, Zn and P should also be enriched.

Essential Contrasts Between OIB and MORB: The Influences of Pressures and Temperatures on Partial Melting

A long-observed truth (e.g., Langmuir and Hanson 1980) is that primitive OIB have higher FeO compared to MORB (Fig. 1A). This fact has necessary consequences. 1) Higher FeO in OIB almost certainly results from higher $P-T$ conditions of partial melting. It is experimentally well-verified that as $P$ increases, peridotite partial melts shift towards olivine in composition (Stolper 1980; Longhi 2002) and so liquids generated at higher $P-T$ conditions are enriched in elements compatible in olivine, such as FeO and MgO (see Langmuir and Hanson 1980), as well as Co and Ni, regardless of source composition. If MORB and OIB are generated from peridotites then major oxide compositions imply OIB genesis at $P = 20-50$ kbar (Fig. 1; Putirka et al. 2011), while MORB are generated at 8-15 kbar (Fig. 1). The necessary effect is that primitive OIBs—and their Ol phenocrysts—have higher Co, Fe and Ni contents relative to MORB as a consequence of partial melting of an olivine-bearing source. 2) Because FeO and other compatible elements are affected by the $P-T$ conditions of partial melting, seemingly anomalous ratios of Zn/Fe, Mn/Fe, Co/Fe etc., are as likely to reflect mantle melting conditions (e.g., low Zn/Fe = high melt fractions at high $P-T$ conditions, since these yield high FeO) and not necessarily source composition or mineralogy. Our review of peridotite partial melting experiments show that FeO/MnO
ratios are far from constant during partial melting, ranging from 45-60 at \( P = 40 \) to 70 kbar, and up to >85 at \( P = 20 \) to 35 kbar \( P \) (Fig. 1C), and new experiments by Matzen et al. (2017) yield the same result. Undoubtedly, FeO/MnO, and other such ratios also vary with source mineralogy (e.g., Humayun et al. 2004; Le Roux et al. 2010; Davis et al. 2013)—but only variance outside the ranges illustrated in Fig. 1C can disallow a peridotite source, and such variances are insufficiently explored—particularly for a pyroxenite source.

3) It is a grave error to assign an equal \( T \) or fractionation extent to olivine grains at an equivalent Fo content. Since OIB have greater FeO than MORB, their Ol grains can only reach an equivalent Fo (as Ol from MORB) when parent magmas have higher MgO, and consequently higher \( T \). The comparison of equivalent Fo contents is tempting, given our familiarity with simple systems (e.g., Bowen and Schairer 1935). But Green et al. (1999) incorrectly hypothesized that MORB and OIB derive from partial melting at equivalent \( T \) as both yield Fo91 olivine; their interpretation is flawed because Hawaiian magmas have greater FeO (FeO_{liq}) than MORB (Putirka 2005). For example, if we apply an Fe-Mg exchange coefficient, \( K_D(\text{Fe-Mg})_{\text{ol-liq}} \), of 0.30 (where \( K_D(\text{Fe-Mg})_{\text{ol-liq}} = \frac{X_{\text{FeO}}{\text{ol}} / X_{\text{MgO}}{\text{ol}}}{X_{\text{FeO}}{\text{liq}} / X_{\text{MgO}}{\text{liq}}} \), and \( X_i^j \) are mole fractions of \( i \) in the phase \( j \)), then to crystallize Fo91 olivine from a liquid with 8 wt. \% FeO_{liq} (typical of MORB) we must have 13.6\% MgO_{liq}. But a liquid with 11 wt. \% FeO (typical at Hawaii) must have 18.7\% MgO_{liq} to crystallize the very same olivine. Liquids with 13.6 and 18.7\% MgO can be produced from the same mantle, but only at very different \( P-T \) conditions and melt fractions (\( F \)), and the parent liquids (and their equilibrium Ol) will thus have very different trace element contents (Fig. 1).
These and other errors befall any analysis of olivine-compatible elements, as the $P-T$ conditions of partial melting are likely to exert a primary control.

**Methods**

We analyzed major oxides as well as trace elements in olivine that range from lithophile (Ca, Ti, Al, Na, Cu, Sc) to moderately siderophile (Mn, V, Cr, Zn, Co, Ni, P) (see Electronic Appendix 1). Olivine compositions were measured by LA-ICP-MS at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Guiyang, China; see Liu et al. (2008) for details of methods. In Fig. 2, elements are arranged in order of increasing Ol/(silicate)liq compatibility and metal/silicate compatibility, using Laubier et al. (2014), Le Roux et al. (2015), Siebert et al. (2011; their Table 6) and the GERM website ([https://earthref.org/GERM/](https://earthref.org/GERM/)).

To understand the origin of our Ol compositions we consider how Ol saturated liquids may have evolved, by calculating Liquid and Crystal Lines of Descent (LLDs and CLDs respectively), which trace the evolution of co-existing liquid and crystal compositions (our high Fo Ol grains are from mafic lavas that are Ol saturated only). These curves are derived from olivine/liquid elemental partition coefficients. For the partitioning of Ni between olivine and liquid we use Matzen et al. (2013), supplemented by Jurewicz et al. (1993) and Taura et al. (1998); the latter two studies are mutually consistent with the high-precision work of Matzen et al. (2013) and allow calibration of $D_{Ni}^{ol-liq} = f(T)$ to be extended to both higher and lower temperatures (note that Herzberg et al. (2016) provide a precise model $D_{Ni}^{ol-liq} = f(D_{MgO}^{Ol-liq})$, but our key objective is to make the $T$-sensitivity of $D_{Ni}$ explicit). Using Jurewicz et al. (1993) only, we obtain:

$$D_{Ni}^{ol-liq} = e^{(3414T^{-4.9})}$$  \hspace{1cm} (1a)
Equation (1a) is calibrated over the range $T = 1140-1325^\circ$C at $P = 0.0001$ GPa, and MgO = 5-10 wt. %. It reproduces the calibration data (n=17) with a standard error of estimate of ±1.3, with $R^2$ of 0.82. Using Matzen et al. (2013) (0.0001-3 GPa; 1400-1600$^\circ$C), we obtain:

$$D_{\text{Ni}}^{\text{ol-liq}} = e^{(3349 \times 0.79)}$$  \hspace{1cm} (1b)

Combining the Matzen et al. (2013) and Jurewicz et al. (1993) we have:

$$D_{\text{Ni}}^{\text{ol-liq}} = e^{(4639 \times 1.71)}$$  \hspace{1cm} (1c)

which reproduces the calibration data (n=29) to ±1.2 with $R^2 = 0.85$. And combining Matzen et al. (2013), Jurewicz et al. (1993) and Taura et al. (1998) data (3.0-14.4 GPa; 1600-2000$^\circ$C) yields:

$$D_{\text{Ni}}^{\text{ol-liq}} = e^{(5853 \times 2.7)}$$  \hspace{1cm} (1d)

and reproduces the calibration data (n=40) to ±1.0 with $R^2 = 0.92$. Equation 1d is valid over the ranges $T = 1140-2000^\circ$C, $P = 1$ atm – 14.4 GPa, and MgO$_{\text{liq}}$ = 5.1-37.5 wt. %.

We also created models using Wang and Gaetani (2008; 0.0001 GPa; 1200-1325°C), whose eclogite liquid-equilibrated olivines yield very high $D_{\text{Ni}}^{\text{Ol-liq}}$ ($D_{\text{Ni}}^{\text{Ol-liq}} = 22$), as do some other experiments cited by Le Roux et al. (2015). But as we show below, $D_{\text{Ni}}$ from Jurewicz et al. (1993) (Eqn. 1a) appear to better explain certain of our observed plume Ni v. Fo trends.

Because $D_{\text{Ni}}$ is sensitive to T, it is possible to use $D_{\text{Ni}}$ to estimate T, which for statistical reasons requires a separate calibration. Using Matzen et al. (2013) and Jurewicz et al. (1993) we obtain:

$$T(\ ^\circ\text{C}) = (4.21 \times 10^4 + 1.87 \times 10^4[\ln(D_{\text{Ni}})])^{-1}$$  \hspace{1cm} (2)
which reproduces $T$ for the calibration data to $\pm 58^\circ C$ with $R^2 = 0.86$.

To facilitate the calculations of LLD and CLD curves, we also employ two additional empirical equations. First, from stoichiometric and mass balance constraints, we have:

$$Fo^{ol} = 23.55 + 1.3462MgO^{ol}$$ (3)

which reproduces Fo of olivine to $\pm 0.05$, with $R^2 = 1.0$. And to predict MgO in Ol we use:

$$MgO^{ol} = a \cdot \frac{b}{MgO^{liq}}$$ (4)

where $a = 55.45$ and $b = 106.1$, when FeOt$^{liq}$ (of the equilibrated liquid) is 11.5 wt. %.

Equation (4) is specific to FeOt$^{liq}$ content and reproduces MgO$^{Ol}$ to $\pm 0.1$ wt. % with $R^2 = 1.0$. For FeOt$^{liq} = 8\%$ (e.g., MORB), $a = 55.63$; $b = 75.78$; for FeOt$^{liq} = 13\%$ (high FeO OIB), $a = 55.45$; $b = 120.0$).

We also construct LLD and CLD curves for several of the other trace and minor elements in Ol (Ca, Ti, Al, Na, Cu, Sc, Mn, V, Cr, Zr, Co and P); these also make use of Eqns. (3) and (4), and olivine/melt partition coefficients from Laubier et al. (2014), Le Roux et al. (2015) and the GERM website (https://earthref.org/GERM/). While some of these elements quite likely have partition coefficients that are sensitive to $T$, only the partition coefficients for Mn, Ti and Cr are known with sufficient experimental precision to calibrate $D_i^{ol-liq} = f(T)$, and so for all other elements we use $D_i =$constant.

Finally, we calculate mantle source compositions, and test whether such mantle sources were contaminated by a metallic core component. To calculate a mantle source, we use the approach of Putirka (2016) by using observed whole rock compositions (see Fig. 3, caption) as input, to predict an equilibrium Ol composition, and then test whether any such liquids can yield our observed maximum Fo contents observed at each volcanic
system (we assume \( f_{O_2} = \text{Ni-NiO} \); see Putirka 2016). Output from the Putirka (2016) models yields the degree of partial melting, \( F \), and the \( P-T \) conditions at which such melt is generated, and an \( \text{MgO}_{\text{liq}} \) for a mantle-equilibrated parental magma. The estimate of \( F \) is one of the least certain and yet most important variables when calculating a mantle source, and so we consider a range of predicted values of \( F \) in such calculations (see electronic supplements). We then infer the trace element contents of such a liquid from whole rock variation diagrams (see Fig. 3, caption for data). As an example, the concentration of Ni in a parental liquid, \( \text{Ni}_{\text{liq}} \), is the median concentration of Ni in whole rocks having the calculated values of \( \text{MgO}_{\text{liq}} \). Table 1 contains a summary of \( P-T \) and melt fraction estimates, and the predicted Fo contents of Ol (using Putirka 2016) for our calculated parental magma compositions (additional outputs are in electronic supplement 2). Finally, we use these trace element contents, our predicted \( T \) of melting (to estimate \( D_i \) when \( D_i = f(T) \)), our range of predicted values of \( F \), and \( D_i \) values from Putirka et al. (2011), updated with partition coefficients from Davis et al. (2013), Laubier et al. (2014), and Le Roux et al. (2015), to calculate a mantle source composition. Putirka et al. (2011) assume batch melting for this calculation, as the error associated with choice of melt model is deemed trivial compared to the errors on estimating a parental magma composition (e.g., Langmuir et al. 1992; Putirka et al. 2011).

**Results**

Table 1 summarizes our estimates for the \( P-T \) conditions of parental magma extraction from the mantle, the melt fraction at extraction, and mantle potential temperatures \( (T_p) \).
Melt fractions are slightly higher than in Putirka et al. (2011), as they are based on new models in Putirka (2016); $T_P$ estimates are slightly lower than in Putirka (2008) because a careful look at just the high precision data of Putirka et al. (2011) indicates slightly lower maximum $F_{o_2}$ contents for Ol phenocrysts (at Hawaii, $F_{o_2}90.5$ instead of $F_{o_2}91.3$ in Putirka et al.’s (2011) Table 3 and appendices), and these lower values are consistent with our new results ($F_{o_2}90.0$ for Hawaii; Table 1; electronic appendix 1).

Figure 2 provides a graphical summary of our trace element results. Here, our trace element analyses of Ol grains are compared at a constant value of $F_{o_2}89$ (the highest $F_{o_2}$ content common to all our analysis suites), with each plume locality normalized to the trace element contents of $F_{o_2}89$ Ol from our MORB sample (Siqueiros transform). To create Fig. 2, we find the trace element content of $F_{o_2}89$ Ol by taking the average of observed olivine compositions that fall (mostly) in the range $F_{o_2}87$-$F_{o_2}90$ (weighted to yield a mean of $F_{o_2}89$), or for Deccan (where all our Ol compositions are $<F_{o_2}89$), by projecting $M$ v. $F_{o_2}$ (where $M$ = a metal cation, such as Co, Na, Ti, etc.) trends back to $F_{o_2}89$, as Klein and Langmuir (1987) correct MORB compositions.

As we discuss below, these trace elements in olivine are controlled by both parent liquid compositions (in turn affected by $P-T$ conditions of partial melting), and the $P-T$ conditions of Ol crystallization, and can be divided along lines of partitioning behavior:

1) Elements highly incompatible in olivine ($D_{i_{ol-liq}}<<1$). For these (e.g., Ca, Ti, V, Al, Na, Sc), concentrations in Ol tend to be uncorrelated with $F_{o_2}$ contents, perhaps because of post-crystallization diffusion for at least some fast-diffusing elements (e.g., Thomson and Maclennan 2013), and because of this, they might not always reliably track liquid
compositions, or source composition. To give an example of the problem, consider that Prytulak and Elliott (2007) observe that plume lavas have elevated Ti relative to MORB—and our plume-derived Ol (except Baffin) are similarly enriched in Ti (Fig. 3A, B); so far, so good. Published experimental values of $D_{\text{Ti}}^{\text{Ol-liq}}$ range widely (0.003 to 0.21), and we find that only a very low and constant $D_{\text{Ti}}^{\text{Ol-liq}}$ ($=0.007$ in Fig. 3A, B) simultaneously yields a Liquid line of Descent (LLD) that reproduces whole rock MgO-TiO$_2$ trends (Fig. 3A) and a Crystal Line of Descent (or CLD, which tracks crystal compositions with fractionation; see Putirka et al. 2011) that approximates the mean Ti in olivine (but is otherwise insensitive to Fo content; Fig. 3B). So here, we capture the broader inter-suite Ti contents (Fig. 3A), but not at all the intra-suite variations of Ti-in-Ol (Fig. 3B), which suggests that Ti-in-Ol is not controlled by fractionation. And for Sc, we find that at Deccan, and especially Emeishan, Sc-in-Ol is quite high compared to Baffin or Hawaii, despite equivalent or lower Sc in corresponding whole rocks (Fig. 3C, D). This may require a greater $D_{\text{Sc}}^{\text{Ol-liq}}$ for our continental flood basalt samples, but may reflect non-equilibrium processes (e.g., Shea et al. 2015a, b) or sub-solidus equilibration of Sc-in-Ol with Sc-rich pyroxenitic cumulates. In either case, contrasts in Sc-in-Ol do not directly translate to equivalent contrasts in co-existing liquids, let alone corresponding mantle sources.

Two Elements compatible in Ol ($D_{\text{i}}^{\text{Ol-liq}}>1$). Concentrations of some of these elements can closely track liquid compositions (e.g., Ni, Cr). Others (e.g., Mn, Zn) can change dramatically in Ol, even at high Fo contents, even as co-existing liquid compositions change little (Fig. 4A, B)—largely because the concentrations of elements like Mn and Zn in Ol are strongly controlled by temperature. For example, $D_{\text{Mn}}^{\text{Ol-liq}}$ and $D_{\text{Zn}}^{\text{Ol-liq}}$ are
close to unity (respectively ranging from 0.8–1.2 and 0.9–1.2; Davis et al. 2013),
becoming more compatible at lower $T$. This change towards increasing compatibility is
dealty evident as Ol crystals become more Mn- and Zn-rich with decreasing Fo (Fig. 4),
despite parent liquids having nearly identical and unchanging Mn and Zn contents at high
MgO; Figure 4 shows a calculated Ol-only LLD, demonstrating that during fractional
crystallization, the evolving, $T$-sensitive, $D_{\text{Mn}}^{\text{ol-liq}}$ and $D_{\text{Zn}}^{\text{ol-liq}}$ more greatly affect Ol than
coexisting liquids. Manganese is an interesting case as parental liquids at Baffin, Hawaii
and Emeishan have indistinguishable MnO contents at high MgO, but Ol grains from all
three plume localities yield distinct Mn-Fo arrays (Fig. 4B). Examining Ol compositions
alone, one could deduce a contrast in mantle source composition, but the whole rock data
belie such an interpretation; contrasts in Mn-in-Ol more likely reflect subtle contrasts in
crystallization environments. For instance, both the enriched (Emeishan) and depleted
(Hawaiian) Mn-in-Ol trends (Fig. 4B) can be produced from a liquid with 1317 ppm Mn
(or MnO = 0.17 wt. %), but applying a lower-$T$ ($1050$-$1280^\circ\text{C}$) model of $D_{\text{Mn}}^{\text{ol-liq}} = -3.6 +$
$4500/T(\circ\text{C})$ for the enriched trend, and a higher-$T$ ($1150$-$1400^\circ\text{C}$) model of $D_{\text{Mn}}^{\text{ol-liq}} = -6.2$
$+ 7800/T(\circ\text{C})$ for the depleted trend (higher $T$ yielding lower $D_{\text{Mn}}^{\text{ol-liq}}$). Other elements
change in more complex ways. Chromium, for example (Fig. 4E, F), is similarly
compatible as Mn and Zn ($D_{\text{Cr}}^{\text{ol-liq}} = 0.8$; Le Roux et al. 2015), but Cr-in-Ol decreases
with decreasing Fo, following parallel changes in liquid MgO-Cr values. Here, Cr
contents respond to a rapidly changing liquid composition. These liquids are likely
controlled by spinel, and so $\text{Cr}^{\text{liq}}$ is modeled empirically from whole rock compositions
and then Cr-in-Ol is predicted from $D_{\text{Cr}} = f(T)$, and $T = f(\text{MgO}^{\text{liq}})$, using: $\text{Cr}^{\text{liq}}(\text{ppm}) = -$
$118.1 + 56[\text{MgO wt. %}], \text{ and } \ln[D_{\text{Cr}}^{\text{ol-liq}}] = -2.51 + 3003.3/T(\circ\text{C})$, which describes the
mean of plume values with an error of ±0.31. Uncertainty on $D_{\text{Cr}}^{\text{ol-liq}}$ ($D_{\text{Cr}}^{\text{ol-liq}}$ varies from 1.3 to 2.2 at 1500-1525°C; Longhi 2002 and Salters and Longhi 1999) is alone sufficient to encompass all observed Cr-in-Ol values.

Discussion

Ni, Mn and Fe: Measures of Partial Melting Conditions, not Source Composition

The origin of high Ni in olivine from plume lavas has been accredited to a mantle pyroxenite mineralogy (Sobolev et al. 2007), a core-contaminated source at the base of the mantle (Herzberg et al. 2013), or Ni-enriched melts derived by pyroxene fractionation in the crust (Putirka et al. 2011). Our new data support none of these.

To the extent that compatible elements in high Fo olivine might act as a proxy for a mantle source, the predicted patterns of enrichment (or depletion, since the core could just as well absorb siderophile elements from the base of the mantle) deriving from core-mantle equilibration are absent. Cobalt and Zn are nearly as siderophile as Ni (Siebert et al. 2011), but neither are enriched relative to MORB. Perhaps Co and Zn are depleted due to the existence of sulfide phases in evolved lavas, but Cu is enriched (Fig. 2) in our mafic samples, and high $T$ near-primary plume magmas are in any case not expected to be sulfide saturated. Meanwhile, mildly siderophile V and Mn, and highly siderophile P (Siebert et al. 2011), are depleted relative to MORB (Fig. 2). We suggest that Ni in plume-derived olivines reflects the high $P$-$T$ conditions of plume genesis, and Ol crystallization conditions, as can be discerned from Figs. 5A, B. The key observation is that OIB and MORB fall on the same Ni v. MgO trend (Fig. 5A,B), and so at a given MgO content, OIB and MORB have the same Ni contents. The Baffin plume seems to be
slightly depleted in Ni compared to Emeishan and Hawaii at >18% MgO, but the contrast is deceptive: at high MgO (>22 wt. %), whole rock Ni-MgO trends appear to be especially influenced by mixing, between high MgO magmas and olivine grains (Fig 5B), and so contrasts in whole rock Ni contents at high MgO are not necessarily reflective of contrasting mantle sources.

Can Any Whole Rocks be Proxies for Liquids?

The case for magma mixing at Hawaii, our type example of a mafic volcanic system, is long standing (e.g., Wright and Fiske 1971; Maaloe 1979; Rhodes and Vollinger 2004), but it does not obviate the need for considerable crystallization differentiation. And we can be near certain that liquids exist at nearly all points along the whole rock trend at MgO< 22%. The reason is that Ol compositions occur as a continuum, from Fo71.7 to Fo90.5 (Fig. 5C), requiring a corresponding continuum of liquids with 6.3%-20.8% MgO (Fig. 5D); to deny such is to argue that some fraction of observed Ol phenocrysts have no relationship to Hawaiian magmatism. But then where along the continuum of Fig. 5C does one draw a line to say that “these Ol compositions are irrelevant to Hawaiian magma genesis”?

This is not to say, however, that mixing is irrelevant. A range of Hawaiian Ol compositions can be generated by liquids that occupy any part of the gray shaded field in Fig 5D. But because most whole rocks are themselves mostly “liquid” (generally having <30% phenocrysts), it would be nearly impossible to create the observed whole rock trend if the liquids were quite different. And indeed, Hawaiian glass compositions overlap the whole rock trend, to at least 15% MgO (Fig. 5D). So why is the whole rock trend so linear? A large part of the reason is that Ol-only LLDs are quite linear (e.g., Figs.
397 3-5). And so mixing need do little work to straighten out what begin as rather straight
trends.

399 Rhodes and Vollinger (2004) further, and in our view correctly, recognize that mixing
is not restricted to two end-member compositions, such as one Ol composition, and a
single, low-MgO magma. Maaloe (1979) also appreciated this complexity, and
emphasized that Hawaiian whole rock trends do not intercept Ol compositional trends at
a consistent Fo content. For example, the Rhodes and Vollinger (2004) whole rock
compositions project to Fo82 for MgO versus Ni, Fo83.7 for MgO versus MnO, and
Fo87.2 for MgO versus FeO (using Putirka et al. 2011 Ol compositions). This
inconsistency is also visible at the thin-section scale: individual samples (Putirka et al.
2011) contain Ol phenocrysts with median and mean Fo contents ranging from at least
Fo81 to Fo89. The mixing vectors that produce any one particular sample are thus not
necessarily the same as the mixing vectors that produce a compositionally adjacent
sample.

411 Rhodes and Vollinger’s (2004) solution is to posit that evolved magmas (7% MgO)
mix with a range of magmas, having up to 40% MgO (Ol slurries), with liquids ranging
to 15% MgO. We would only add that liquids probably range to 21% MgO (to explain
high Fo olivine grains), and that the evolved end-member need not be fixed (so in our
view, anything can mix with anything). Nonetheless, Fo86 Ol grains are the most
common in our new dataset (Fig. 5C). These can be obtained from a liquid with 13.3%
MgO, which also is near the mean and median of Hawaiian whole rocks (Fig. 5D). Dry
Hawaiian liquids of this composition have densities of 2.8-2.9 g/cm³ (a little higher if
they carry crystals) and so are just the right density to be neutrally buoyant in Hawaii’s
middle crust, where thermobarometers place the majority of Hawaiian magma partial crystallization (Putirka 2017, their Fig. 1B). Olivines of Fo86 may be the most common because their equilibrium liquids are the most likely to be trapped in the middle crust. In any case, whole rocks appear to serve as accurate proxies for liquid compositions, up to some upper limit of MgO content, which falls near 21-22% at Hawaii, and which can be determined for any system based on whole rock FeOt values and maximum Fo contents of phenocrysts (see supplementary files for values inferred for the systems studied here and Putirka 2005 for the approach).

Plume-derived olivine grains, then, range to higher Ni compared to MORB because they crystallize from liquids (electronic appendix 2) that are generated at higher $F$, due to higher temperatures of partial melting. Their mantle sources have similar Ni (electronic appendix 3) but higher $F$ at plumes leads to greater Ni in the liquids (and their co-existing Ol) that are generated (Table 1). To illustrate, consider a liquid that falls on the Ni-MgO trend, having 20% MgO and 1050 ppm Ni (Fig. 6B); this point forms the “starting point” to the solid gray and black curves in Fig. 6B. To construct the CLDs (gray and black curves) in Fig. 6A and the LLDs (gray and black curves) in Fig. 6B, we use that starting composition and evaluate Eqns. (1a; gray curve) and (1b; black curve) by (i) calculating $T$ using the Helz and Thornber MgO-based thermometer (1987; 1416°C at 20% MgO); (ii) we then remove olivine in 2% increments, re-calculating $T$, and (iii) at each step, re-evaluating Eqns. (1a-b) to obtain $\text{Ni}^{\text{liq}}$, and using Eqns. (3) and (4), and mass balance to obtain $\text{MgO}^{\text{liq}}$, $\text{MgO}^{\text{Ol}}$ and Fo contents of Ol. Equation (1b) yields Ol with up to 4100 ppm Ni at Fo91, a CLD that reproduces the high-Fo portion of the Hawaiian array (Fig. 6A; black curve), and a LLD that nicely matches Hawaiian whole rocks (Fig. 6B; black
curve). Using Eqn. (1a), and the very same starting liquid, we obtain a flatter CLD that reproduces the Ni v. Fo trends at Hawaii, Deccan and Baffin (Fig. 6A; gray curves), and an LLD that reproduces some high Ni vs. MgO whole rock compositions at Hawaii (Fig. 6B; gray curves). Equation (1b) also yields a CLD and LLD that nicely reproduces MORB-derived high Fo crystals and whole rock compositions (Figs. 6A, B; blue curve), in this case using a starting liquid with 14.4% MgO_{liq}, Ni_{liq} = 500 ppm, and T = 1301°C. This begs the question of why MORB-derived magmas have lower Ni in the first place, and as we will show, it is because their parental magmas are produced at lower P-T conditions, at lower melt fractions, compared to OIB (Matzen et al. 2009; Putirka et al. 2011).

These data suggest that not only is the pyroxenite model unnecessary, it is untenable: Ni-enriched sources yield Ni-enriched liquids, which are unobserved (Fig. 6B), and a pyroxenite source predicts Cr-in-Ol that is >>2000 ppm, when Ni contents approach observed values (Fig. 6D). To take the Ni-enrichment case, we show a CLD derived using a parental liquid with 1500 ppm Ni at 20% MgO (from a pyroxenite, or Ni-enriched peridotite, it does not matter); this explains high Ni-in-Ol at Fo≤Fo88 deceptively well (red dashed CLD, Fig. 6A). But the suite of liquids implied by such a CLD have higher-than-observed Ni_{liq} compared to any known whole rock at any MgO (Fig. 6B) when we apply Eqn. 1b and the Helz and Thornber (1987) MgO_{liq} thermometer. Other combinations of thermometers and $D_{Ni}$ models fare no better (Figure 6C). Use of Eqn. 1c does not change the results perceptibly, and if we apply the MgO_{liq} thermometer of Putirka (2008; Eqn. 13), Ni_{liq} contents are further above observed values. If we instead apply Eqn. 1a and the Helz and Thornber (1987) thermometer we can use a parental
magma with just 1200 ppm Ni\textsuperscript{liq} (at 20% MgO) to predict Ni-in-Ol at Fo88, but this curve is still displaced to high Ni\textsuperscript{liq} (Fig 6C), and is worse still if the Putirka (2008) thermometer is applied, and does not even explain Ni-in-Ol patterns. The Cpx-dominated LLD of Putirka et al. (2011) fails more dramatically, for similar reasons, as it predicts liquids with remarkably high Ni contents at lower MgO (Figs. 6A, B, green dashed curves).

Perhaps an even more compelling reason to reject pyroxenite as a source is that Cr and Ni in olivine are very poorly predicted by such. To illustrate, we compare natural Cr and Ni in Ol crystals, to those that would precipitate from a pyroxenite, here using mineral-liquid partition coefficients of Le Roux et al. (2015) and each of the wide ranging pyroxenite mineralogies and melt fractions of Table S3 in Sobolev et al. (2007) (where partial melting ranges from 8 to 79%), as well as their bulk pyroxenite Cr and Ni contents for pyroxenite (e.g., 1710 and 1000 ppm respectively). The predicted Cr-in-Ol contents that would precipitate from pyroxenite-derived liquids are nearly 6 times greater than observed, and plot well off scale in Fig. 6D. If we instead assume that pyroxenites are subducted MORB, and so use the much lower bulk Cr and Ni contents for such (Cr = 296.1 ppm, Ni = 152 ppm; see Putirka et al. 2011), the liquids generated have much lower Cr, as do the equilibrated Ol, but Ni contents are too low (Fig. 6D). In contrast, Ol that precipitates from partial melts of a peridotite work quite well: using a mean bulk peridotite composition having Cr = 2617 ppm and Ni = 2198 ppm (Putirka et al. 2011), and allowing melt fraction to range as F = 0 to 0.3, yields Ol crystals that precisely match observed values (Fig. 6D).
Another issue involves the very high Ni-in-olivine at Hawaii at ≤ Fo88, where Ni contents are even higher than at Deccan (Fig. 6A). This might be a signal of Ni-enriched magmas, but the crystal compositions can also be derived from fractionated, FeO-enriched magmas instead (at MgO ≤8 wt. % MgO; Fig. 1A), as shown by the orange curves in Figs. 7A, B. These orange curves connect these high Ni-in-Ol crystals (at ≤Fo88) to a corresponding whole rock MgO-liq-Ni-liq composition that can serve as a viable equilibrated liquid, at least in the case of Fe-Mg exchange equilibrium. The solutions are not unique, and depend upon the Fe/Mg ratio of the liquid. For this model we use observed Fo in Ol and FeO-liq to determine an equilibrium MgO-liq (see caption to Fig. 7). And then from the whole rock MgO-liq-Ni-liq trend (Fig. 7B) we obtain a putative Ni-liq value, which we assume is the equilibrium value for Ni^{Ol} ←→ Ni^{liq} equilibrium. (Fig. 7A) (see caption for equations and details). These results allow us to calculate a putative $D_{Ni^{ol-liq}}$ for each Ol (Fig. 7A), and to calculate $T$ using Eqn. (2). The temperatures from Eqn. (2) are remarkably close to those obtained from MgO-liq using Helz and Thornber (1987) (Fig 7A). An exception involves the lowest Fo Ol in this test (Fo73), where the $D_{Ni}$ value yields a $T$ from Eqn. (2) that is nearly 300°C lower than that obtained from MgO-liq. However, the two $T$ estimates are within 20°C if FeOt^{liq} = 18% (Fig. 7B; black connecting line). This is much higher than the FeOt of the host rocks we investigated, but such high values are exhibited by some low-MgO lavas at Hawaii, which may have mixed with our more primitive samples. A test would be to examine high FeOt samples, looking for high Ni Ol grains. In any case, all but the lowest Fo, high Ni-in-Ol crystals have quite little to do with high Ni^{liq}: in diagrams like Figs. 6A or 7A, we can see that it’s
not so much that Ni is enriched at a given Fo content, but rather that for a given Ni content, Fo is low.

Peridotite as Plausible Source

Finally, Fig. 7B shows that it is possible to obtain the requisite magmas that can be parental to these high Ni-in-Ol grains by partially melting a peridotite, having 1900 ppm Ni (and 65% Ol, 20% Opx and 15% Cpx), as shown by black and gray curves. These curves show the case for $F = 0.15$, assuming a $T$ of 50°C above the Hirschmann et al. (2002) solidus. To link $T$ and $F$, we use experimental results from Takahashi et al. (1993), Kushiro (1996) and Pickering-Witter and Johnston (2000), from which we obtain $\approx 0.18$ to 0.31% melt/°C at $F < 30\%$. At $F > 30\%$, the results diverge greatly, either maintaining a fertile rate of melt production, or reducing to 0.1% melt/°C; we assume a fertile source (0.3% melt/°C), for reasons discussed below. The Hirschmann et al. (2000) solidus yields array of $P-T$ partial melting conditions, which are then used in Eqn. (1d) to evaluate $D_{\text{Ni}} = f(T)$. From partial melting experiments, we also calibrate MgO$_{\text{liq}}$ just above the solidus as MgO$_{\text{liq}} = -55.96 + 0.0532[T(°C)] - 2.16[P(\text{GPa})]$, and then also $D_{\text{Ni}} = f(\text{MgO}_{\text{liq}}) = \exp(13.83/\text{MgO}_{\text{liq}} - 0.0147)$. These equations simultaneously yield a Hawaiian primitive magma (MgO$_{\text{liq}} = 18.8$ Wt. %; Ni$_{\text{liq}} = 815$ ppm; Fig. 7B), at $P = 3.4$ GPa, $T = 1521$°C. The value of $F$ provides the most important source of error, but at $F = 0.2$, at 66°C above the solidus we still obtain a magma that falls on the observed whole rock trend (MgO$_{\text{liq}} = 19.3$ Wt. %; Ni$_{\text{liq}} = 850$ ppm; $P = 3.5$ GPa, $T = 1526$°C). The results are by no means unique, but they illustrate that peridotites are a plausible mineralogy for plume-source lavas from the localities examined here.
Melting Conditions Assuming a Peridotite Source

As in Putirka (2011), we compare natural whole rock compositions at Hawaii and the EPR to the partial melts generated in experimental studies. Our model parent magmas are combinations of experimentally-derived liquids (see Fig. 1, caption) that, as precisely as possible, fall on a whole rock compositional trend for all of the major oxides, as in Fig. 1. This approach yields conditions of melt extraction of 10 kbar, 1325°C for MORB and 37.5 kbar and 1540°C at Hawaii. The experiments being averaged to achieve a match to observed whole rocks exhibit a 80 to 160°C temperature range for MORB and plumes respectively, and a pressure range of 10-15 kbar for Hawaii; the experimental starting compositions vary as well. We resort to such combinations as no single experiment describes MORB or Plume magmas precisely for every major oxide, while our hypothetical mixtures, provide a very close match. But how then to interpret the $P-T$ range? Besides experimental error (e.g., reproducibility, which translated to P-T conditions is about ±30°C and ±1-2 kbar), this almost certainly represents the challenge of searching $P-T$-composition space to find the “just so” conditions to explain natural magmas. But crucially, melting is not an isothermal, isobaric process. Our P-T estimates represent a mean set of conditions over which melt was equilibrated within the mantle, and the starting compositions of the experiments we employ represent an average composition of what we know to be a heterogeneous source. For our Plume 1 model then, the $P-T$ ranges exhibited by our averaged experiments (45-30 kbar; 1620–1460°C) might represent very real variations in what is assuredly a polybaric, polythermal partial melting process.
While Emieshan and Deccan have major oxides that are quite similar to Hawaii, Baffin Island is clearly a special case, since except for FeOt and SiO₂, its lavas are otherwise quite similar to our MORB samples—for example Baffin lavas have elevated Al₂O₃ compared to other plumes (Fig. 8C). The Baffin Al₂O₃ contents might seem to contradict our high \( T_p \), since this should also require elevated pressures, and at high-\( P \) garnet may be present in the solid residue. But high-\( P \) partial melting experiments exhibit more than sufficient scatter to accommodate Baffin lavas. For example, the 30 kbar model partial melts of Longhi (2002) match Al₂O₃ and other oxides at Baffin quite nicely, as do yet higher \( P \) experiments by Takahashi et al. (1993; 46 kbar, 1800°C) and Walter (1998; 45 kbar, 1650°C), which both fall on the high-MgO end of the Baffin compositional spectrum. A problem with Al₂O₃, then is that it decreases with increasing MgO. So while experimental data do indeed show decreasing Al₂O₃ in equilibrated melts as \( P \) increases, there is enough scatter in these to cover both the Baffin and Hawaiian lavas at high MgO. So the key question is whether we must match Al₂O₃ at the high or low MgO end of an observed whole rock trend? The answer is found with FeOt. High pressures are required to explain Baffin’s high FeOt compared to MORB (10-11 wt. % at Baffin, compared to 8% for MORB, when MgO>10%). So we find that, like Hawaii, high \( T_p \) and melting pressures in the 30-45 kbar range are most consistent with observed Oi and lava compositions.

These \( P-T \) conditions, though, leave unexplained the fact that Baffin and MORB share similar, elevated Al₂O₃ contents relative to Hawaii and other plumes (Fig. 8), as well as lower TiO₂, and slightly elevated CaO, the latter being perhaps also in common with
Deccan. We hypothesize that these contrasts reflect differences in source regions, as indicated by other elements as well (see following discussion of Fig. 9).

Tests of a Pyroxenite Source: Ca, Al and Sc

We might expect that pyroxenite-influenced melts and crystals would be enriched in Ca and Al (or perhaps depleted if a high mode of Cpx during melting overrides the higher bulk concentrations): pyroxenite source materials have 7-22 wt. % Al₂O₃ and 2-14% CaO (Kogiso et al. 1998; Kogiso and Hirschmann 2001; Petermann et al. 2004; Lambart et al. 2009; Tsuno and Dasgupta 2011), while peridotites have lower Al₂O₃ and CaO (3.6-4.3 wt. % and 3.2-3.5 wt. % respectively; Walter 1998). However, peridotite partial melts alone yield a wide range of CaO<sub>liq</sub> and Al₂O₃<sub>liq</sub>. Ocean Island Basalts have lower CaO<sub>liq</sub> and Al₂O₃<sub>liq</sub> than MORB, and the contrasts are expected given current experimental studies, if the contrasting pressures required by Fe and Mn apply (Fig. 1; see also Putirka et a. 2011), i.e., \( P = 30-50 \text{ kbar} \) for Hawaii and 10 kbar for MORB. Our low-\( P \) MORB model (Fig. 1) yields 11.6 wt. % CaO<sub>liq</sub> and 14% Al₂O₃<sub>liq</sub> at 13.1 wt. % MgO<sub>liq</sub> (and 8% FeO<sub>liq</sub>), while our “Plume Model 2” (Fig. 1) has 8% CaO<sub>liq</sub> and 9% Al₂O₃<sub>liq</sub> at 20.6% MgO<sub>liq</sub> (and 11.5% FeO<sub>liq</sub>). It seems clear that Ca and Al are lower in high Fo Hawaiian Ol compared to MORB (Figs. 8B, D) as each reflects their contrasting parent liquids (Fig. 8A).

At Baffin, despite having a much greater mantle potential \( T_p \) than MORB (Table 2), these lavas exhibit similar Ca and Al contents to MORB for both whole rocks and olivine. Since the whole rock CaO and Al₂O₃ contents of both MORB and Baffin are explained by peridotite partial melting, at low and high \( P-T \) conditions respectively, we
cannot exclude a pyroxenite source, but have no reason to propose one. At Emeishan, however, olivine compositions range to distinctly high Ca despite their whole rocks having no more CaO than other lavas. Might the elevated Ca-in-Ol at Emeishan indicate the kind of garnet-pyroxenite source that Sobolev et al. (2007) suggested for Hawaii? This may be the case, as Emeishan lavas also have greater Sc-in-Ol and greater Sc in their whole rocks compared to Hawaii (Figs. 3C, D). Perhaps partial melting of a Ca- and Sc-rich source, e.g., pyroxene-rich, might be the cause. But there are problems with this model. Emeishan parent liquids are not the most Sc-enriched (Fig. 3C), ranging to 30 ppm Sc at 20% MgO, compared to 35 ppm Sc at Baffin (Fig. 3C), even though Emeishan Ol grains have the highest Sc-in-Ol values (22 ppm on average; Fig. 3D). No experimentally determined values for $D_{\text{Sc}}^{\text{ol-liq}}$ can explain these contrasts. For example, $D_{\text{Sc}}^{\text{ol-liq}}$ ranges to about 0.25 (Davis et al. 2013; Laubier et al. 2014), and for a liquid with 30 ppm Sc, a $D_{\text{Sc}}^{\text{ol-liq}}$ of 0.73 is required to obtain Sc-in-Ol of 22 ppm—nearly three times the highest experimental value (and Laubier et al. see no dependency of $D_{\text{Sc}}^{\text{ol-liq}}$ on $T$ or $f_{\text{O}_2}$, so we cannot at the present call on changes in such to increase $D_{\text{Sc}}^{\text{ol-liq}}$). Likewise, applying $D_{\text{Sc}}^{\text{ol-liq}} = 0.25$ requires a liquid with 89 ppm Sc (more than double observed Emeishan whole rock values; Fig. 3C) to precipitate Ol with 22 ppm Sc. So it would be a tenuous conclusion at best to link Emeishan Sc-in-Ol contents to enriched liquids, let alone enriched source materials. Finally, Lambart et al. (2009) report very low Al-in-Ol for their pyroxenite-equilibrated Ol, well below anything we observe at Emeishan, Deccan, Siqueiros or Hawaii (Fig. 8D). Given these problems for a pyroxenite source, we posit that high Ca-in-Ol at Emeishan might instead reflect lower $P$-$T$ conditions of crystallization (e.g., Stormer 1973; Koehler and Brey 1988), consistent with higher Mn-
in-Ol at Emeishan (Fig. 4B). But thermobarometry (Tao et al. 2015) at Emeishan indicates high P-T equilibration conditions for picrites, so Sc and Ca in Ol might instead reflect non-equilibrium processes (e.g. Shea et al. 2015a, b).

Mantle Source Compositions from Parental Liquids (and maximum Fo in Ol)

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Although Ol trace element compositions do not easily translate to a mantle composition, their Fo contents delimit parent liquid compositions, which provide a more direct inference of mantle source. Applying Putirka et al.’s (2011) melting models with Putirka (2016) for melt fraction estimates, we obtain mantle compositions as in Figures 9-10, where elements are arranged in order of decreasing enrichment at Hawaii relative to our calculated Siqueiros-MORB mantle, moving from left to right. To model the MORB source we rely on the very primitive lavas from the East Pacific Rise (Siqueiros Transform; Perfit et al., 1996; Hays, 2004) as they are closer to putative primary magmas, and so minimize error in reconstructing a MORB mantle source.

We find that the mantle source regions of Hawaii, Deccan and Emeishan share similar patterns and magnitudes of enrichments in incompatible elements relative to the MORB source mantle (DMM) (except for lower Cr; Fig. 9). This is not to say that our inferred plume sources are identical; they are not (e.g., Willbold and Stracke 2006), but we affirm prior work that indicates broadly shared enrichments among plumes sources (e.g., Willbold and Stracke, 2006; Arevalo et al. 2013). Our Hawaiian source is also enriched relative to the pyrolite models of McDonough and Sun (1995) and Lyubetskaya and Korenaga (2003) (Fig. 9B). Baffin, despite having plume-like $T_p$ (Table 1), interestingly has a mantle source with trace element contents that are quite similar to that for MORB,
except for being slightly enriched relative to our estimate of Cr (Fig. 9A); however, within uncertainties (see error bars in figures) the Baffin Island plume source overlaps with the sources for the other three plumes examined here. Interestingly, Jackson and Jellinek (2013) find that the Baffin source is slightly less depleted in Large Ion Lithophile Elements (LILE) than DMM than in the model used here. However, they infer lower degrees of partial melting: 14%, instead of 24% in this study (Table 1). Nonetheless, the Baffin Island plume composition considered here is within error of the composition calculated in Jackson and Jellinek (2013) and requires no addition of enriched sources to explain trace element concentrations. We should perhaps emphasize that, due to its very high $^{3}\text{He}/^{4}\text{He}$, Baffin is not the same as MORB; but the trace element similarities of the Baffin source and DM provides an apparent striking affinity.

In contrast, trace elements are enriched relative to DM (and the Baffin source) at Hawaii, Deccan and Emeishan, and by applying methods of Putirka et al. (2011) we invert our calculated melt compositions to estimate source compositions. We find that Hawaiian, Deccan and Emeishan enrichments can be explained by adding 18-24% average ocean crust (MORB) to DMM of Workman and Hart (2004). Our estimate of the amount of crust added back to the non-Baffin plume-source mantle is greater than in Putirka et al. (2011), as that earlier work assumed smaller degrees of partial melting (10%) for the Hawaiian source. Melt fraction estimates are quite uncertain, and so the actual amounts, if the general approach is correct, probably lie somewhere between those earlier values and our current estimates (see electronic appendix 3). What is especially compelling, though, is that nearly identical proportions of MORB and DMM simultaneously explain elements that are chemically quite different. The errors in such
mantle estimates are non-trivial (20-140% for compatible to incompatible elements), but
within such error our Hawaiian source estimates match our MORB + DMM pyrolite
model for all elements. Moreover, calculated MORB:DMM ratios are similar using
differently-derived estimates of both MORB and DMM (Fig. 10A).

So why then does Baffin lavas range to higher $^{3}\text{He}/^{4}\text{He}$ than, say, Hawaii? It has long
been recognized that high $^{3}\text{He}/^{4}\text{He}$ at Hawaii is inversely correlated with $^{87}\text{Sr}/^{86}\text{Sr}$ (Hauri
and Kurz 2002), and other studies, e.g., Jackson et al. (2008) and Grapic et al. (2015),
propose that the Baffin source is the receiver of subducted materials and the source of
high $^{3}\text{He}/^{4}\text{He}$ in plumes and that subducted oceanic crust provides the enriched TITAN
character as proposed by Jackson et al. (2008).

Because so many different elements (lithophile, chalcophile and moderately
siderophile) at Hawaii, Emeishan and Deccan are explained by a pyrolite-like source, this
would seem to argue against a peculiar mineralogy (e.g., pyroxenite) or intra-mantle
fractionation (e.g., bridgmanite) to explain plume compositions inferred from the lavas in
this study. Zhang et al. (2016) nonetheless intimate that wadsleyite may preferentially
partition Ti, V and Cr, while Bindi et al. (2017) report on a Ti-rich form of bridgmanite.
To be fair, neither of these studies attempt to explain plume compositions. Perhaps even
more interesting is the possibility of an Fe-enriched lower mantle (Kaminsky and Lin,
2017). But Fe-enrichments in OIB appear to be not so great as to be produced from a
mantle with a major element composition similar to MORB, and we find no pronounced
coupled enrichments in Ti and V that accompany Cr. Nor is it clear that the accumulation
of Ti-bridgmanite might yield the complete array of enrichments of Fig. 9A. This is not
to say that intra-mantle fractionation might not influence plume composition, but it would
be an odd coincidence that such a process was global in nature and would precisely
mimic the addition of oceanic crust to a DM source.

Implications

Our Baffin Island results are perhaps the most interesting. The Baffin source is quite
hot, and we infer that it is rooted in as deep a part of the mantle as any other mantle
plume. But the Baffin source is also depleted, as reflected in both its major oxides and
trace elements, in a way that remarkably mimics the MORB source. Plumes other than
Baffin, by contrast, require at least 20-25% subducted MORB-crust to be mixed back into
a depleted MORB mantle source, to explain their bulk compositions. We appreciate that
the Baffin and MORB sources cannot be equivalent: MORBs have low $^3\text{He}/^4\text{He}$ (~8 Ra)
compared to the Baffin mantle (up to 50 Ra). Additionally, if we accept W isotope results
(Rizo et al. 2016), that indicate that the Baffin source has been isolated from the rest of
the mantle for 4.5 Ga, then the Baffin source was depleted at that early date. The
depletion of the MORB source, by contrast, occurred much later, as it is a residue
remaining after a presumably much later and prolonged continental crust extraction
event. There are several options to explain the MORB-Baffin contrast: The Baffin source
could be 1) perfectly unique—an ancient depleted source at the base of the mantle, with
an as yet unknown enriched counterpart, that otherwise matches MORB only by
coincidence, 2) a depleted matrix that pervades the lowermost mantle that elsewhere
receives subducted crust, but beneath Baffin, has been strangely resistant to such
accumulation, 3) related to the MORB source, where the materials that would eventually
form the crust were extracted into the upper part of the mantle at or before 4.5 Ga only to
be gradually tapped over the next 4.5 Ga from relatively shallow mantle only, leaving a shallow depleted MORB source, and a deeper Baffin source (again, resistant to subducted crust accumulation), 4) is not from a source that feeds other mantle plumes—representing something deeper still. None of these are terribly satisfying, or mutually exclusive. But Baffin is isotopically close to PREMA (Zindler and Hart 1986; having just slightly lower $^{206}\text{Pb}/^{204}\text{Pb}$) and FOZO (Hart et al. 1992)—and so if Baffin can be shown to be uniquely old among plumes (being presumably uniquely unaffected by admixtures of young subducted crust), Baffin may then represent a rare sampling of Earth’s most ancient mantle (Jackson et al., 2010).

Some of these results are not entirely new: Herzberg et al. (2007) infer that Baffin is hot, while Starkey et al. (2012) demonstrate that, despite having plume-like high $^3\text{He}/^4\text{He}$, Baffin is depleted compared to most plumes. Garnero et al. (2016) suggest that geochemical anomalies among ocean island basalts carry no information about source depth, and with one exception, we concur—that exception being high $^3\text{He}/^4\text{He}$, which along with high $T_p$ are the only viable indicators of deep-seated plumes, past or present (Putirka 2008). And we agree with Jackson et al. (2017) that to hide something like the Baffin source for an extended period of time, it must be quite dense, and quite deep. Given that $^{87}\text{Sr}/^{86}\text{Sr}$ is negatively correlated with $^3\text{He}/^4\text{He}$ at Hawaii, and trends toward a Baffin-like composition (see Fig. 1A of Hauri and Kurz 2002), we propose that a Baffin-like source, or perhaps the Baffin source itself, is the wellspring of high $^3\text{He}/^4\text{He}$ in plumes, and whose $^3\text{He}/^4\text{He}$ values are slightly diluted due to mixing of subducted crust. Despite the Baffin enigma, we appear to know the depleted MORB source with confidence. Estimates derived from very different mass balances of primitive melt and
peridotite samples (Salters and Stracke 2004; Workman and Hart 2005; Putirka et al. 2011) yield quite similar results. This should be expected, since residual peridotites and parental magmas are complementary derivatives of a common source and process. But the convergence also confirms that we have, at least roughly, correctly identified parental magmas and the processes and conditions under which they are created.

Finally, we confirm the current view of the deep mantle as a “graveyard” of subducted MORB crust (Wyession 1996; White 2015), but we reject the idea that this graveyard is necessarily resurrected with a pyroxenite mineralogy (e.g., Hofmann and White, 1982); we estimate that plumes entrain up to 25% subducted oceanic crust, rather than the nearly 100% indicated in the original model (Baffin providing a 0% end-member case). This material seems to be thoroughly admixed, with no clear evidence of a mineralogically distinct signal. Kogiso et al (2004) suggest otherwise, but as we show in an electronic supplement (ES1), their pyroxenite end-member is arbitrary and trace element ratios do not indicate a mineralogically distinct source for elevated $^{187}$Os/$^{188}$Os.

The deep mantle plume source is, however, significantly enriched compared to earlier “pyrolite” models (McDonough and Sun 1995; Lyubetskaya and Korenaga 2010) and may well be what is perceived in seismic studies (e.g., Zhao et al. 2015). Our estimates, perhaps not coincidentally, are also quite close to Ringwood’s (1962) basalt:dunite ratio of 1:4. Such high amounts of added crust may create an untenably “hyperfertile” source, with too much garnet to explain certain trace element ratios (Norman and Garcia 1999; Putirka et al. 2011). But our higher MORB:DMM ratios emanate from higher estimates of melt fraction (using Putirka 2016 instead of Putirka et al. 2007), which may allow sufficiently high dissolution of garnet to allay the key objection: Walter’s (1998)
experiments yield just 10% garnet (of all phases, including liquid) at 20% melting at 6
GPa, and no garnet at all at the same degrees of melting at 3 GPa. In any case, Baffin
Island shows that this slab graveyard is not ubiquitous (i.e., recycled slabs do not
permeate all deep mantle reservoirs), either because subducted slabs are unevenly
interred, or they can be efficiently excavated in later plume upwelling events, or perhaps
because the Baffin source lies below this graveyard, as a dense under-layer (e.g., Jackson
et al. 2017) that for some reason is not tapped at yet hotter flood basalt provinces.

Acknowledgements

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conclusions. We also thank NSF for support to K. Putirka that indirectly helped support
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acknowledges support from NSF-EAR 1624840. Yan Tao would like to thank NSF of
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Figure 1. Weight % MgO for MORB (East Pacific Rise, Siqueiros) and Hawaiian (HSDP2; Rhodes and Vollinger 2004) whole rocks are compared to (A) FeO, (B) MnO, (C) FeO/MnO and (D) TiO₂. Whole rock compositions are also compared to liquids from peridotite partial melting experiments, sorted by pressure and using depleted and pyrolite mantle model peridotites from Takahashi and Kushiro (1983; KLB-1); Takahashi et al. (1993, KLB-1); Baker et al. (1995, MM3); Herzberg and Zhang (1996, KLB-1); Walter (1998, KR4003); Longhi (2002, Model Depleted and Primitive Upper Mantle, DPUM and PUM). Highlighted with a beige fill are 20-30 kbar partial melts of a high FeO peridotite from Kushiro (1996, PHN1611), noted as “fertile” but lower in Al₂O₃ and CaO than the other peridotites noted. Plume model 1 is a 50-50 mixture of Walter (1998; 45 kbar, 1620°C) and Kushiro (1996; 30 bar, 1460°C). Plume model 2 is a 40-60 mixture of peridotite partial melts from Takahashi and Kushiro (1983; 35 kbar, 1600°C), and Walter (1998; 45 kbar, 1620°C). The MORB model is a 56-44 mixture of Kushiro (1996; 10 kbar, 1360°C), and Baker et al. (1995; 10 kbar, 1280°C).

Figure 2. Trace element concentrations in Fo89 olivine, from average or projected values, normalized to Fo89 olivine compositions from MORB (Siqueiros). From Ca to Mn, elements are listed in order of increasing OI/Liq partition coefficients (element [D]): Ca [0.01], Ti [0.01], Al [0.015], Na [0.015], Cu [0.1], Sc [0.2], Mn [0.9]. From Mn to P, elements are listed in order of increasing core/mantle partitioning using the mid-point of minimum and maximum values of Siebert et al. (2011; their Table 6) (element [D]): Mn [1], V [1.9], Cr [3], Zn [4], Co [24.5, Ni [26], P [35].

Figure 3. Comparison of the highly incompatible elements (in Ol), Ti (A) and (B) and Sc (C) and (D) for host liquids and olivine grains (data from GEOROC; http://georoc.mpch-mainz.gwdg.de/georoc/); Hawaii (Rhodes and Vollinger 2004); MORB (PetDB; http://www.earthchem.org/petdb). Black curves are high-T plume LLD and CLDs; gray
curves are low-T mid-ocean ridge LLD and CLDs (see text for discussion and calculation details). We find that an enriched mantle source and very low partition coefficients for Ti are required to simultaneously explain Ti in whole rocks and co-existing olivine; see text for discussion. Symbols as in Fig. 2; $D_{\text{Ti}} = \exp(-5.2 + 1979/[T^\circ C])$, initial TiO$_2$$_{\text{liq}}$ = 1.6 wt.

% or 9592 ppm Ti, at 20% MgO$_{\text{liq}}$; $T(\circ C) = 1014+20.1[MgO]_{\text{liq}}$.

Figure 4. Comparison of compatible elements (Ol-liq partition coefficients near 1.0), Mn (A) and (B), Zn (C) and (D) and Cr (E) and (F), for published whole rocks (putative liquids; see caption to Fig. 3) and our new data for olivine grains. When $D_{\text{ol-liq}}$ is close to 1, the trace element contents of Ol can be quite sensitive to T. For example, in Mn and Zn, liquid compositions don’t vary at MgO$_{\text{liq}}$>10%, and yet Zn-in-Ol and Mn-in-Ol increase greatly, as $D_{\text{ol-liq}}$ increases (from slightly <1 to slightly > 1) with decreasing $T$. On the other hand, Cr-in-Ol mostly decreases as MgO decreases, as other phases (most likely spinel) deplete coexisting liquids in Cr. Symbols as in Fig. 2. $D_{\text{Cr}} = \exp(-2.51 + 3003.7/[T^\circ C])$, initial Cr$_{\text{liq}}$ = 680 ppm at 20% MgO$_{\text{liq}}$; $D_{\text{Mn}} = \exp(-3.6 + 4500/[T^\circ C])$, initial MnO$_{\text{liq}}$ = 0.17 wt. % at 18% MgO$_{\text{liq}}$; see caption to Fig. 3 for similar calculations of LLD and CLD curves (black for plume, gray for MORs). Curves are not shown for Zn, as current partitioning experiments are too few and fail to reproduce Zn-in-Ol trends.

Figure 5. (A) Whole rock Ni (ppm) vs. MgO (wt. %) compositions from Emeishan, Baffin Island, Deccan and MORB (see caption to Fig. 3). (B) Whole rock Hawaii and MORB compositions are compared to olivine compositions from Putirka et al. (2011). (C) Histogram of Hawaiian Ol compositions; (D) Cation fractions of MgO and FeO in Hawaiian whole rocks (triangles), with isopleths that show the positions of liquids in equilibrium with a given Fo content, when $K_D$(Fe-Mg)$_{\text{ol-liq}}$ = 0.34; isotherms are from Putirka (2005); red circles indicate Hawaiian liquids needed to produce maximum, minimum and median Ol compositions in panel C; dashed line in D shows the position of Hawaiian glass compositions. Other symbols as in Fig. 2. In (A), it is clear that at a given MgO content, Ni contents for plumes are not enriched relative to MORB. In (B), whole rock Ni contents at MgO>21%, are controlled by mixing with Ol, which likely explains subtle contrasts between Ni contents at Baffin compared to Emeishan, Hawaii or Deccan in panel (A). Panel (D), with isotherms and Ol isopleths from Putirka (2005), similarly shows the range of liquids required to produce observed Hawaiian Ol compositions (gray area, Fo71.7-Fo90.5, as in panel C). Such liquids must have up to 20.8% MgO, with a continuum down to 6.3% MgO, to create the continuum of Ol compositions in panel C.

Figure 6. (A) New data for Olivine Ni v. Forsterite (Fo) contents. (B) and (C) Whole rock Ni v. MgO. (D) New Cr vs. Ni in Ol compositions. Symbols are as in Fig. 2; whole rock data are as in Fig. 3 caption; see electronic supplement for new Ol data. Panels (A) and (B) show models that explain high Ni-in-Ol at moderate to low Fo (≤Fo88). For (A) and (B) Crystal Lines of Descent (CLDs) and Liquid Lines of Descent (LLDs) are calculated by selecting as starting compositions, MgO$_{\text{liq}}$-Ni$_{\text{liq}}$ values that fall on the observed whole rock trends of (B), and then subtracting calculated Ol compositions in 2% increments using mass balance. Gray curves use Eqn. (1e), black and red curves Eqn. 1b, and the blue curve Eqn. (1c); in panel (A) we use Eqn. (3) to obtain Fo contents in Ol;
in panel (B) we use Eqn. (4) for FeOt\textsuperscript{liq} = 11.5 wt.% to obtain MgO\textsuperscript{liq}, and then calculate MgO\textsuperscript{liq} from mass balance. To evaluate all of Eqns. (1b,c), (3) and (4), T is re-calculated at each step using Helz and Thornber (1987) \[T(\degree C) = 20.1[MgO\textsuperscript{liq}] + 1014\] for both MORB and Hawaiian lavas, although a separate calibration for MORB, \(T(\degree C) = 17.5[MgO\textsuperscript{liq}] + 1054\) (calibrated from Bender et al. 1984; Grove and Juster 1989; Grove and Bryan 1983) yields similar results at high \(T\). Dashed curves are “failed” models: they explain some Ni vs. Fo trends in olivine, but not Ni vs. MgO in whole rocks (nominal liquids) or Liq + Ol mixtures (see Fig. 5B for Liq + Ol trajectories). Green dashed curve is a modified version of the Cpx-dominated CLD and LLD from Putirka et al. (2011), while red dashed curve uses Eqn. (1b) and assumes that high Ni in Fo88 olivine derives from a Ni-enriched liquid. Predicting observed Ni contents for olivines with <Fo88 yield coexisting liquids displaced even further from observed whole rock trends. In (C), we show the difficulty of explaining whole rock Ni contents if we assume Ni-enriched parent liquids: the red curve from (B) is reproduced as Ol LLD1 (with 1500 ppm Ni at 20% MgO), and is compared to Ol LLD2, which uses the same starting liquid, but uses Eqn. 1c and the thermometer of Putirka (2008), and Ol LLD3, which uses Eqn. 1a with the Helz and Thornber (1987) thermometer, and a liquid with 1200 ppm Ni at 20% MgO; each model successfully predicts Ni-in-Ol at Fo88, but fails to reproduce Ni contents of whole rocks. The models are derived assuming that Ol precipitates from melts derived by partial melting of pyroxenite (gray curves) or peridotite (green curves). Le Roux et al. (2011) suggest that \(D_{\text{Ni}}^{\text{Cpx-liq}} = 22\) in some circumstances, but we see little evidence for such high values in experimental data, and we find that \(D_{\text{Ni}}^{\text{Cpx-liq}} = 3\) fits observed Ni-in-Ol compositions much better (see discussion for details).

**Figure 7.** Magnified view of Hawaiian (and Siqueiros) samples as in Figure 5, to compare olivine Ni v Fo (A), and whole rock Ni vs. MgO (B), for olivines with moderate Fo contents but high Ni. Olivine grains at ≤ Fo88 cannot form from Ni-enriched MgO, and is compared to Ol LLD2, which uses the same starting liquid, but uses Eqn. 1c and the thermometer of Putirka (2008), and Ol LLD3, which uses Eqn. 1a with the Helz and Thornber (1987) thermometer, and a liquid with 1200 ppm Ni at 20% MgO; each model successfully predicts Ni-in-Ol at Fo88, but fails to reproduce Ni contents of whole rocks. The models are derived assuming that Ol precipitates from melts derived by partial melting of pyroxenite (gray curves) or peridotite (green curves). Le Roux et al. (2011) suggest that \(D_{\text{Ni}}^{\text{Cpx-liq}} = 22\) in some circumstances, but we see little evidence for such high values in experimental data, and we find that \(D_{\text{Ni}}^{\text{Cpx-liq}} = 3\) fits observed Ni-in-Ol compositions much better (see discussion for details).
(Hirschmann 2000), which approximates a melt fraction \( F \) of 10% (e.g., Baker et al. 1995). We calculate \( \text{MgO}_{\text{liq}} \) (wt. %) = \(-55.96 + 0.0532[T(\degree C)] - 2.16[P(\text{GPa})]\), using this “solidus + 25\degree C” curve as input; this expression for \( \text{MgO}_{\text{liq}} \) reproduces calibration data (Takahashi et al. 1993; Baker et al. 1995; Herzberg and Zhang 1996; Kushiro 1996; Robinson et al. 1998; Walter 1998; Pickering-Witter and Johnston 2000) to ±2 wt. %. For Ni-in-Liq we use \( F = 0.1 \), and \( D_{\text{Ni}}^{\text{bulk}} \) assumes: 20% Opx, 15% Cpx and 65% Ol, \( D_{\text{Ni}}^{\text{optx-liq}} = 3.2 \) and \( D_{\text{Ni}}^{\text{optx-liq}} = 3.7 \) (from Le Roux et al. 2015). For \( D_{\text{Ni}}^{\text{ol-liq}} \), the gray curve uses Eqn. (1a) and the black curve uses (1b).

**Figure 8.** A comparison of CaO (A and B) and Al or Al\(_2\)O\(_3\) (C and D) between whole rock MgO (see Fig. 3 caption) and Fo from new olivine compositions (see electronic supplements). In (E) and (F), Ni in Ol is compared to Ca and Al in Ol respectively from these same data sets. The experimentally-derived MORB and Plume model 2 peridotite partial melts are determined as in the caption to Fig 1. (A) and (C) show that MORB have higher CaO and Al\(_2\)O\(_3\) compared to plume derived lavas, and that in both cases, such contrasts likely result from contrasts in melting conditions of a peridotite source. Such partial melts with low Al\(_2\)O\(_3\) are mostly garnet saturated, indicating that deep-seated partial melting, within the garnet stability field, is much more important at Hawaii, Emeishan and Deccan, compared to Baffin or MORB. Olivine Ca and Al concentrations reflect these contrasts in liquid composition. Also plotted in (B) is the field of Ca for olivines precipitated from experimental pyroxenite partial melts, from Kogiso et al. (1998), Kogiso and Hirschmann (2001) and Lambart et al. (2009). Only the Ca contents of olivine from Emeishan and Deccan are consistent with a pyroxenite derivation. But all natural plume-derived olivine grains have vastly more Al than expected compared to pyroxenite-melt equilibrated Ol from Lambart et al. (2009) (D).

**Figure 9.** The trace element concentrations in our selected plume sources are calculated from parental magma compositions (see appendix tables 2 and 3) as in Putirka et al. (2011), and normalized to (A) our MORB-source mantle (“MORB-Siqueiros”; calculated from Siqueiros parental magmas) and (B) various estimates of depleted and pyrolite mantle, where “Pyrolite(M&S)” is the pyrolite model of McDonough and Sun (20015); “Baffin” is our estimate of the Baffin Island source; “DMM (W&H)” is “depleted MORB mantle of Workman and Hart (2005); and “DM(S&S)” is the MORB Depleted mantle source of Salters and Stracke (2004). The pyrolite model of Lyubetskaya and Korenaga (2010) is not plotted, but is effectively identical to the curve for McDonough and Sun (1995). The “anticipated” errors are calculated as the maximum – minimum (range) normalized concentration ratios, calculated using maximum and minimum ranges of \( F \) at both MORB and Hawaii, and maximum and minimum partition coefficients for MORB and Hawaii, as in Putirka et al. (2011) (i.e., the highest normalized ratio for Th is that obtained by allowing \( F \) at Hawaii to be 0.25, so requiring more Th in the Hawaiian source, and using \( F = 0.08 \) for MORB, to minimize calculated Th in the MORB source). As noted in the text, our Cr estimate for DM (1,100 ppm) is much lower than Salters and Stracke (2004; 2,500 ppm). We assume 600 ppm in mantle-equilibrated MORB (Fig. 4E), and a bulk \( D_{\text{Cr}} \) during mantle melting of 1.92. We can obtain 2,500 ppm by increasing \( \text{Cr}_{\text{liq}} \) to
1400 ppm, which seems vastly too high compared to primitive MORB, or by increasing bulk $D_{Cr}$ to 4.5, which can only be reached or exceeded in garnet at high $T$ and would require very high residual garnet in the source (e.g., Putirka 1998).

Figure 10. (A) Our Hawaiian trace element source is compared to our model plume sources, obtained by mixing MORB crust with depleted MORB-source mantle (effectively the “pyrolite” of Ringwood (1962)). “HMS” = Hawaiian mantle source. “SMS” is our depleted Siqueiros mantle source (appendix Table 3); “DM1” is depleted mantle from Workman and Hart (2005); “DM2” is depleted mantle from Salters and Stracke (2004); “BMS” is our calculated Baffin mantle source. The models that make use of DM1 and BMS depleted mantles are mixed with ocean crust that is equal to the mean MORB estimate of Gale et al. 2013), while the DM and DM2 models are mixed with MORB from Putirka et al. (2011). (B) Our calculated depleted mantle source for Baffin Island (BMS) is compared directly to SMS, DM1, DM2 as in panel (A), and the pyrolite model of McDonough and Sun (1995).
Table 1. Estimates of mantle potential temperature and related parameters.

<table>
<thead>
<tr>
<th>Source</th>
<th>( T_p ) ('C) (1)</th>
<th>Source</th>
<th>Olivine Fo (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emeishan (Low Ti)</td>
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<td></td>
<td>92.5</td>
</tr>
<tr>
<td>Emeishan (High Ti)</td>
<td>1480(84)</td>
<td></td>
<td>89.5</td>
</tr>
<tr>
<td>Deccan (H&amp;G 2009)</td>
<td>1620(54)</td>
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<td>91.5</td>
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<tr>
<td>Hawaii (SR0061-0)</td>
<td>1630(77)</td>
<td></td>
<td>91.0</td>
</tr>
<tr>
<td>Baffin (Hole 2015)</td>
<td>1630(65)</td>
<td></td>
<td>92.0</td>
</tr>
<tr>
<td>MORB-Siqueiros</td>
<td>1420(40)</td>
<td></td>
<td>91.4</td>
</tr>
<tr>
<td>MORB Mean Mean Cottrell and Kelley (2011)</td>
<td>1320(39)</td>
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<td>89.3</td>
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**Other plume and MORB estimates**

<table>
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<tr>
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<tr>
<td>Siberian Traps</td>
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<tr>
<td>Ferropicrites</td>
<td>1780(155)</td>
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<td>Samoa</td>
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<td>91.7</td>
</tr>
<tr>
<td>MORB, 9°N; Cottrell &amp; Kelley (2011)</td>
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<td>90.5</td>
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<td>MORB (Herzberg )</td>
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<td>MORB Cottrell and Kelley</td>
<td>1390(45)</td>
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<td>90.7</td>
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Notes: (1) \( T_p \) = mantle potential temperature; \( T_p \) is calculated as in Putirka (2011).
(2) Olivine forsterite (Fo) contents are calculated from liquid compositions using the equation of Cottrell and Kelley (2011). Olivine and liquid compositions are not arbitrary. Liquid compositions are selected based on the best fit to the observed data.
<table>
<thead>
<tr>
<th>$P$ (GPa)</th>
<th>$\log[fO_2]$ at NNO</th>
<th>$K_{D(Fe-Mg)}^{ol-liq}$</th>
<th>$T^{ol-liq}$ (°C)</th>
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<td>1.50</td>
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16); see electronic appendix for input liquid compositions, and olivine + liquid temperature the calculated oxygen fugacity, and Fe3+/Fe2+ ratios as determined using equation cted so that the calculated Fo contents for olivine match observed maximum Fo conte
<table>
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<td>0.183(0.004)</td>
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<tr>
<td></td>
<td>0.032(0.029)</td>
<td>0.069(0.022)</td>
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The table above summarizes the melt fraction contents in Putirka (2016). The average values are derived from Eqns. 14a-c. The numbers represent the percentage of high Ca olivine phenocrysts.
Figure 1

A

B

C

D

FeO/MnO vs. MgO (wt. %)

FeO (wt. %)

MnO (wt. %)

TiO2 (wt. %)

MORB (EPR, Siqueiros)

Hawaii (HSDP2 low Si)

Hawaii (HSDP2 high Si)

Plume model 1

Plume model 2

MORB model

8-15 kbar

20-35 kbar

20-30 kbar; High Fe

40-50 kbar

60-70 kbar

85

80

75

70

65

60

55

50

45

40

35

30

25

20

15

10

5

0

80

70

60

50

40

30

20

10

0

20-35 kbar

20-30 kbar; High Fe

40-50 kbar

60-70 kbar

TiO2 (wt. %)

MgO (wt. %)

FeO (wt. %)

MgO (wt. %)
Figure 2

Compare Fo89 Olivine

- Deccan
- ELIP
- Baffin
- HSDP2 High Si
- HSDP2 Low Si
- KLB

Concentration relative to EPR

Increasing core/mantle partitioning

Increasing Ol/Liq partitioning
Figure 3

A B

Ti (ppm) in Olivine

C D

Sc (ppm) in Olivine

MgO (wt. %) in whole rock

TiO₂ (wt. %) in whole rock

Sc (ppm) in whole rock

Fo Content of Olivine

MgO (wt. %) in whole rock

Hawaii

Emeishan

Deccan

MORB

Baffin

KLB

Plume CLD & LLD

MOR CLD & LLD
Figure 4

- **Figure 4A**: MnO (wt. %) in whole rock
- **Figure 4B**: Zn (ppm) in Olivine with Cr (ppm) in whole rock
- **Figure 4C**: Zn (ppm) in Olivine
- **Figure 4D**: Cr (ppm) in whole rock
- **Figure 4E**: MgO (wt. %) in whole rock
- **Figure 4F**: Fo Content of Olivine
Figure 5

A

B

Ni (ppm) in Whole Rock vs. MgO (wt. %) in Whole Rock

Hawaii
Emeishan
Deccan
MORB
Baffin

Break in slope:
21.5% MgO

Ni (ppm) in Whole Rock vs. MgO (wt. %) in Whole Rock

Hawaii
MORB
Hawaiian Olivine

Liq fractionation + mixing
Mixing with Ol
Figure 6E

Mean = Fo86
Median = Fo86
Max = Fo90.5
Min = Fo71.7

MgO\textsuperscript{liq} = 20.8 wt. %
MgO\textsuperscript{liq} = 13.3 wt. %
MgO\textsuperscript{liq} = 6.3 wt. %
Figure 7

A

- \( D_{Ni} = 10.9 \)
- \( \gamma^{ol-liq} = 1175^\circ C \)
- \( \gamma^{Ni-liq} = 1019^\circ C \)
- FeOt = 13 wt. %
- MgO = 15.8 wt. %

B

- \( D_{Ni} = 59 \)
- \( \gamma^{ol-liq} = 1143^\circ C \)
- \( \gamma^{Ni-liq} = 845^\circ C \)
- FeOt = 13 wt. %
- MgO = 6.4 wt. %

- \( D_{Ni} = 9.1 \)
- \( \gamma^{ol-liq} = 1218^\circ C \)
- \( \gamma^{Ni-liq} = 1200^\circ C \)
- FeOt = 18 wt. %
- MgO = 10.2 wt. %

\( D_{Ni} = f(MgO) \)

\( D_{Ni} = f(T) \)

Mantle Partial Melts
Figure 8

A

B

C

D

E

F

CaO in whole rock (wt. %)

CaO in Ol (wt. %)

Al (ppm) in Olivine

Al₂O₃ in whole rock (wt. %)

MgO (wt. %) in whole rock

Fo Content of Olivine

Ni in Olivine (ppm)

Pyroxenite median (0.37)

Pyroxenite mean (0.44)

Pyroxenite range (32-42 ppm)

Pyroxenite range (0.25-0.71 wt. %)

MORB model

Plume Model 2

Pyroxenite median (0.37)

Pyroxenite mean (0.44)
Figure 9

A. Plume Mantle/Siqueiros (MORB) Mantle

B. Hawaiian Mantle/Depleted & Pyrolite Mantle

Anticipated error in incompatible elements

Anticipated error in compatible elements
HMS = Hawaiian Mantle Source
BMS = Baffin Mantle Source
DM1 = Depleted Mantle (W&H)
DM2 = Depleted Mantle (S&S)
G-MORB = MORB (Gale et al.)
P-MORB = MORB (Putirka et al.)
Figure ES1. $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ ratios for (A) Hawaiian shield stage and post-shield lavas, with shield stage Koolau lavas highlighted; also shown are fields for peridotites and lavas from Baffin Island, and (B) Arc lavas, Continental Flood Basalts, Pyroxenites, and Precambrian lavas. Orange curves show mixing between the Kogiso et al. (2004) components of peridotite ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7033$, [Sr] = 10 ppm, $^{187}\text{Os}/^{188}\text{Os} = 0.126$, and [Os] = 300 ppt), and a pyroxenite ($^{87}\text{Sr}/^{86}\text{Sr} = 0.706$, [Sr] = 100 ppm, $^{187}\text{Os}/^{188}\text{Os} = 2$, and [Os] = 10 ppt). The black curves show mixing between this same peridotite source, and a hypothetical source similar to the pyroxenite, but with $^{87}\text{Sr}/^{86}\text{Sr} = 0.702$ ([Sr] = 100 ppm, $^{187}\text{Os}/^{188}\text{Os} = 2$, and [Os] = 10 ppt). In (C), $^{187}\text{Os}/^{188}\text{Os}$ is compared to Sc/MgO, which should be either fractionated by pyroxene- or garnet-rich source materials. And in (D) we see that Al2O3 contents are not any higher, relative to degree of fractionation (MgO) for Hawaiian lavas with elevated $^{187}\text{Os}/^{188}\text{Os}$. These plots collectively show that a pyroxenite source, or any ancient source material, is an unlikely candidate for high $^{187}\text{Os}/^{188}\text{Os}$ ratios, as these would likely have much greater $^{87}\text{Sr}/^{86}\text{Sr}$ than supposed by Kogiso et al. (2004), and because there is no distinctive mineralogic signal with respect to major oxides or trace elements. An intriguing pattern is that CFBs and arcs are both enriched in $^{187}\text{Os}/^{188}\text{Os}$ with CFBs ranging to higher $^{87}\text{Sr}/^{86}\text{Sr}$, and with Hawaiian lavas sharing a muted arc-like $^{187}\text{Os}/^{186}\text{Os}$ enrichment. These patterns point to a shallow source for high $^{187}\text{Os}/^{188}\text{Os}$, one that may be driven by assimilation/mixing processes, with a crustal influence for CFBs (and so their elevated $^{87}\text{Sr}/^{86}\text{Sr}$), but not so (or much less so) for oceanic islands and arcs.