



## The debate over core–mantle interaction

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### Abstract

Some hotspot volcanism is likely the surface manifestation of hot upwelling mantle plumes that rise from the core–mantle boundary (CMB) or from compositional boundaries within the mantle. Plumes that rise from the CMB may generate magmas that carry compositional information about the diversity of materials present in the lowermost mantle. Some plume-derived materials have coupled enrichments in  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  relative to upper mantle materials. The coupled enrichments are consistent with Os isotopic compositions predicted for the liquid outer core that might result from elevated Pt/Os and Re/Os generated via progressive crystallization of a solid inner core over Earth history. If these enrichments are a reflection of core–mantle interaction, then the mechanisms of material transport between the core and the mantle, rates of whole mantle convection at present and over time, and cooling histories for the core and the mantle can potentially be constrained. However, fractionation may also occur between Pt/Re/Os via mantle and crustal processes and in particular, Pt and Pt/Re may be elevated in some portions of ancient recycled slabs thought to be present in certain plume sources. This possibility brings into question whether the coupled Os isotope enrichments are a product of core–mantle exchange. Hence, a lively debate over the causes of Os isotopic heterogeneities in plume-derived materials has ensued. Resolution of this debate has been hampered by limited constraints on the behavior of these elements in the Earth's core, mantle and crust. A variety of analytical and experimental tasks will have to be pursued to test different aspects of both the core–mantle interaction and crustal recycling models, and to further constrain the behaviors of these elements. These future endeavors may help to unravel the compositional complexities of plume-derived materials and their mantle sources, and ultimately provide important insights to processes operating at the CMB.

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### 1. Introduction

The core–mantle boundary (CMB) may be the most chemically reactive region of the Earth's interior [1,2]. Beneath it the outer core is composed dominantly of Fe- and Ni-rich molten metal with 5 to 10

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wt.% of a light element or elements [3]. Above it the mantle consists of oxygen- and silica-rich minerals, and possibly small amounts of melt. At present, there is a large temperature drop across the CMB of  $\geq 1000$  K [4]. Crystallization of the solid inner core has led to the production of substantial latent heat in the core, most of which is transferred from the core to the lower mantle through the seismically distinct, potentially reactive layer, termed the D'' region [2]. The transport of this heat drives thermal convection in the liquid outer core, resulting in the geodynamo that produces Earth's magnetic field, and is also at least partially responsible for convection in the silicate mantle. Transport of this heat is also intimately related to the plate tectonic cycle and the chemical evolution of the Earth's interior over its history.

A likely consequence of the dramatic thermal and compositional changes across the CMB is material transport and chemical exchange between the core and the mantle. The extent to which elemental exchange and mass transfer occurs are difficult to predict because interactions between the outer core and lower mantle are highly dependent on the properties of the materials present, such as density, viscosity, conductivity and composition. The composition and physical state of materials present at the boundary is currently highly debated and could be quite diverse. Materials that could be present in the lowermost mantle include the residues of early Earth differentiation, subducted slabs and derivatives thereof, silicate melt, and metal from the outer core [5–9]. The nature of materials present in the outermost core could also be more complex than simple liquid metal. For example, it has been proposed that the ultra-low velocity zone (ULVZ) at the base of D'' underlying two hotspot-rich regions of the South-Central Pacific Ocean, and Africa and surrounding regions [10] may be explained by silicate 'sediments' infiltrated by outer core liquid metal, which have been produced as a result of oversaturation of light elements in liquid metal as the solid inner core grew [11]. Alternatively, the ULVZ may result from melting of silicates [7].

The presence of silicate melt in D'' could enhance the uptake of outer core metal into an upwelling plume [12]. Furthermore, the periodic variations (nutations) of the Earth's rotation requires enhanced electrical conductivity that cannot result from the presence of silicates but instead may require a thin

layer (~200 m) of liquid metal [13]. While this layer may be on either side of the CMB, recent assessments suggest that this highly conductive layer coincides with the ULVZ above the CMB [14]. Infiltration of liquid metal into the mantle might occur via capillary action, where it is drawn up into the base of D'' and is subsequently oxidized [15]. An aggregate of metal and silicate matrix may, therefore, be entrained in an upwelling plume with as much as 5 wt.% metal incorporated [15].

The emerging view of D'' is that while some of the probable compositional diversity can be attributed to silicate heterogeneity, outer core materials have likely infiltrated across the CMB and potentially interacted with the overlying mantle (Fig. 1). In such a case, should some plumes arise from D'', chemical/isotopic evidence for core–mantle exchange might be present in certain plume-derived magmas. A major challenge for geochemists is to predict the nature of a core signature, and, if present, ultimately to identify it in appropriate materials. For the past decade efforts have been directed at doing this [17–32]. The results of this work have spawned a lively debate on which chemical and isotopic signatures measured in plume-derived lavas might result from core–mantle interactions as compared with processes that could occur solely in the upper mantle or crust (e.g. [31,33–37]).

The stakes of this debate on Earth's evolution and dynamics are great. If a core signature can be unambiguously identified in some plume-derived materials, then the prevailing dynamic view of the Earth being driven by plume generation at the CMB, setting up whole mantle convection and all of the consequences thereof, is strengthened. Identification of an outer core signature in materials brought to the surface might also permit the tracing of mechanisms of core–mantle exchange, the composition and the dynamics of the CMB, and the thermal evolution of the Earth. Some types of signatures, if present, could even be used to examine the crystallization rate of the inner core [30]. Alternatively, if the signatures claimed to be from the outer core in fact have resulted from mantle or crustal processes, then additional scenarios to whole mantle convection in the past and present, such as layered convection, must continue to be considered (e.g. [38]).

For the past 5 yr, much of the debate has primarily focused on Os isotopes because, as a highly side-

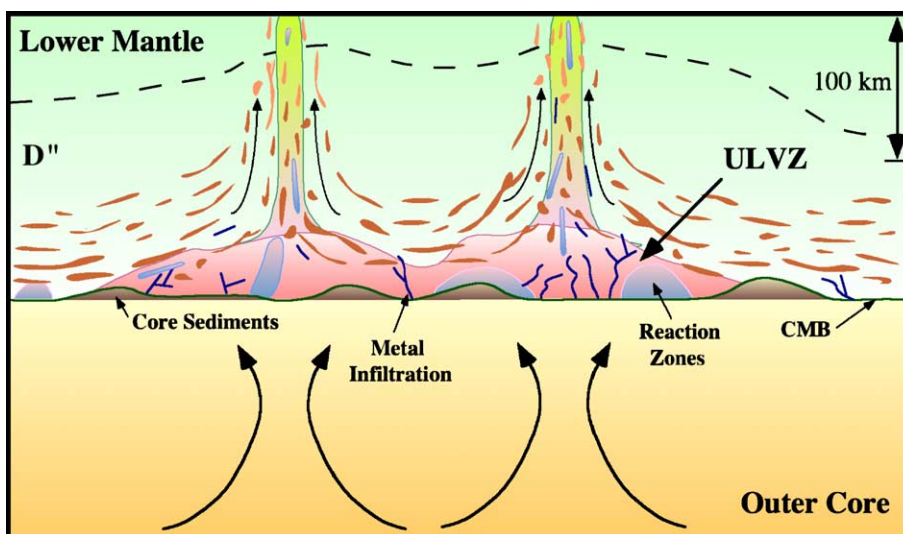


Fig. 1. Schematic cartoon showing one possible view of the core–mantle boundary underneath hotspots where the ultra-low velocity zone (ULVZ) is present (following [2,16]). Scale is approximate in vertical direction, no scale for horizontal. Arrows indicate flow orientation in both the lower mantle and the outer core. Core sediments may accumulate along the irregular core–mantle boundary (CMB) and may be distinct from the ULVZ as shown, or reside within the ULVZ altogether. Alternatively, the ULVZ may be zones of silicate partial melt. Compositional heterogeneities (brown and orange) comprised of ancient slab derivatives, melted zones, initial heterogeneities formed from early planetary differentiation, or all three, are drawn up into upwelling plumes initiated from the ULVZ. Liquid metal from the outer core may infiltrate across the CMB into the lower mantle and solidify, or may exchange with the surrounding mantle and then drain back into the outer core. Reaction zones may exist between the lower mantle and outer core. These processes may impart chemical signatures of the outer core into the lower mantle. These lower mantle materials with outer core signatures may then be drawn up into plumes.

rophile element, it is strongly enriched in the core relative to the mantle, and because the outer core may have developed a distinct isotopic composition that is probably unusual within the silicate Earth. Recently, W isotopes have been added to the fray. Mass balance arguments require that the core has a significantly different W isotopic composition compared to the silicate Earth. Tungsten is a moderately siderophile element, so to a lesser extent than Os, it too is enriched in the core relative to mantle. Here, the present state of the debate over Os and W isotopes for core–mantle interaction is reviewed. The implications for the mechanisms of core–mantle exchange based on chemical compositions of plume-derived materials are discussed. Several alternative mantle process scenarios have been proposed to explain existing data and are reviewed here. Finally, specific tests for how to further constrain the mechanisms that have created the Os isotopic variability and other possible chemical and isotopic fingerprints of core–mantle interaction in mantle-derived materials are presented.

## 2. Isotopic evidence and mechanisms for core–mantle interaction

### 2.1. Osmium isotope evidence for core–mantle interaction

Recent work has discussed the potential value of combining the  $^{187}\text{Re}$ – $^{187}\text{Os}$  and  $^{190}\text{Pt}$ – $^{186}\text{Os}$  isotopic systems to sensitively detect core-derived Os in the sources of some purported plumes that may have risen from the CMB [17–21,23,30]. The isotope  $^{187}\text{Os}$  is produced from  $^{187}\text{Re}$  decay by  $\beta^-$  emission, with a half-life of  $\sim 42$  Ga ( $\lambda = 1.666 \times 10^{-11} \text{ yr}^{-1}$ ). The isotope  $^{186}\text{Os}$  is produced from  $^{190}\text{Pt}$  by  $\alpha$  decay, with a half-life of  $\sim 489$  Ga ( $\lambda = 1.417 \times 10^{-12} \text{ yr}^{-1}$ , recalculated based on  $^{190}\text{Pt} = 0.01296 \text{ at.}\%$  [19,39]). Because  $^{190}\text{Pt}$  is a minor isotope of Pt, in combination with the small decay constant, this system is very insensitive to perturbations by most geochemical processes. Long-term and relatively large fractionations of Pt from Os are required to produce measurable differences in  $^{186}\text{Os}/^{188}\text{Os}$  ratios. The

outer core likely developed higher Pt/Os and Re/Os relative to chondrites and the Earth's mantle, owing to the crystallization of the inner core [17,40]. This conclusion is based on the assumption that these elements partition between solid metal and liquid metal in the Earth's core in a similar manner to their partitioning behavior in asteroidal cores where  $D_{\text{Os}} > D_{\text{Re}} > D_{\text{Pt}}$  ( $D$ =solid metal/liquid metal bulk distribution coefficient)(e.g. [39]). Recent low and high pressure experiments examining solid metal–liquid metal partitioning of Re, Os and Pt supports the notion that the Earth's outer core may have developed Re/Os and Pt/Os ratios that are elevated relative to the chondritic silicate Earth, comparable to the fractionations observed resulting from similar extents of crystallization in asteroidal cores [41–44]. Although the development of coupled  $^{186}\text{Os}$ – $^{187}\text{Os}$  enrichments in the outer core now seems to be firmly established, based on empirical and experimental results, it must be noted that the magnitude of  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  enrichments in the present outer core are less well constrained because of uncertainties in the magnitude of Pt/Os and Re/Os fractionations, the timing of the initiation of crystallization, and growth rate of the inner core.

Although the level of mass transfer from the outer core to the lower mantle is presumed to be limited and probably no more than 0.5 wt.% metal is added to any portion of the overlying mantle, an Os isotopic fingerprint of the outer core might be detectable in derivative lavas generated from plumes rising from the CMB because the outer core has 100–300 times higher abundance of Os than the mantle (approximately 300 ppb to 1 ppm versus 3 ppb, respectively [30]). Coupled  $^{186}\text{Os}$ – $^{187}\text{Os}$  enrichments comparable to those predicted for outer core–lower mantle mixing [17] have been found via high precision isotope analyses of Hawaiian picrites [20,23], one Noril'sk ore representative of the 251 Ma Siberian Flood Basalt Province [19], and the 89 Ma Gorgona komatiites [30] (Fig. 2). The Os isotope systematics of these presumed major plume-derived systems are distinct from those of typical upper mantle materials. The Hawaii and Gorgona samples, with the exception of two Hawaiian Koolau flows that show strong evidence for ancient recycled crust components in their source [45,46], plot as linear arrays that converge to a common Os isotopic component (COs). These

arrays have been interpreted to reflect mixing of material similar to the upper mantle and a single uniform source with coupled  $^{187}\text{Os}$  and  $^{186}\text{Os}$  enrichment. If this interpretation is correct, the homogenous source of enriched  $^{186}\text{Os}$  and  $^{187}\text{Os}$  must extend over a wide region of the Earth's interior that encompasses the sources of at least these three plumes. These arguments, combined with evidence for the partitioning behavior between Pt, Re and Os, have led to the hypothesis that the present outer core has an Os isotopic composition consistent with that of the COs (Fig. 2). If so, this has implications for the timescales of inner core crystallization and cooling models for the Earth [30].

## 2.2. Tungsten isotopes as a potential tracer of core–mantle interaction

In addition to Os isotopes, the isotopic composition of W can potentially be used to detect the presence of core material in plume-derived materials [31]. The isotope  $^{182}\text{W}$  is produced by decay of  $^{182}\text{Hf}$ , which has a half-life of only  $\sim 9$  Ma [47]. Because of the short-lived nature of this system, existing W isotopic heterogeneities within the Earth were created during the first  $\sim 50$  Ma of solar system history. Tungsten behaves as a siderophile element under reducing conditions present during accretion and metal–silicate segregation [48]. Hafnium is strongly lithophile and is essentially absent from metallic cores. Consequently, metallic cores have Hf/W ratios of 0 and retain the isotopic composition of W at the time of their formation. Depletion of  $^{182}\text{W}$  in iron meteorites [averaging  $\epsilon_{\text{W}} = -3.5$ ; where  $\epsilon_{\text{W}}$  is the enrichment (+) or depletion (–) of  $^{182}\text{W}$  relative to a terrestrial standard in parts per 10,000] relative to chondrites ( $\epsilon_{\text{W}} = -2$ ) demonstrates that  $^{182}\text{Hf}$  was extant in the early solar system, and that for asteroids, metal–silicate segregation occurred quite early [49,50]. The Earth's mantle has a W isotopic composition that is approximately 2 parts per 10,000 enriched in  $^{182}\text{W}$  ( $\epsilon_{\text{W}} = 0$ ) relative to chondrites, and by inference, the bulk Earth [51–53]. Based on core formation models for the Earth and mass balance, the  $\epsilon_{\text{W}}$  of the core is estimated to be  $-2.1$  to  $-2.2$  [31,54]. Because the concentration of W is likely significantly greater in the core compared to the mantle (400–500 ppb vs. 5–50 of ppb in the mantle) [3,55,56], then small depletions in  $^{182}\text{W}$  in plume-derived magmas, relative to the

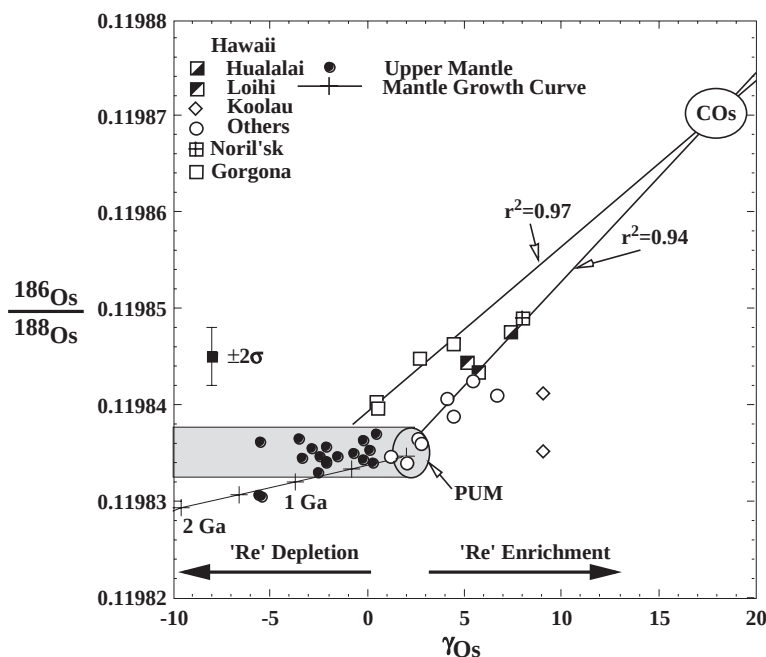


Fig. 2. The  $^{186}\text{Os}/^{188}\text{Os}$ — $\gamma_{\text{Os}}$  systematics for mantle-derived materials.  $\gamma_{\text{Os}}$  is the percent difference in  $^{187}\text{Os}/^{188}\text{Os}$  relative to average chondrites (Jargon Box) [87]. Only samples measured at the University of Maryland and Johnson Space Center are shown owing to interlaboratory calibration issues. All data have uncertainties of  $\leq$  to the  $\pm 2\sigma$  error bar shown. The upper mantle samples include chromites, Os-rich alloys and abyssal peridotites [19,20,24]. Regression lines for the Gorgona komatiites and all Hawaiian picrites, except for the two Koolau samples, are shown with calculated  $r^2$ 's [23,30]. Where the two regression lines converge, at  $^{186}\text{Os}/^{188}\text{Os}=0.11987$  and  $\gamma_{\text{Os}}=+17.5$ , is considered to be a common Os (COs) end-member for the different sample suites [30]. The mantle growth curve assumes a present-day mantle with PUM (primitive upper mantle) characteristics for  $^{186}\text{Os}/^{188}\text{Os}$  (0.119835) and  $\gamma_{\text{Os}}$  (+2.03), with  $^{190}\text{Pt}/^{188}\text{Os}=0.00174$ , and  $^{187}\text{Re}/^{188}\text{Os}=0.4346$  [30,88], and 'plus' symbols are for 500 Ma increments on the evolution curve. Trends for Re depletion and Re enrichment correspond to Re removal resulting from partial melting which will reduce  $\gamma_{\text{Os}}$  relative to PUM over time, and materials having long-term Re enrichment relative to PUM such as those expected in ancient recycled slabs with consequent increase in  $\gamma_{\text{Os}}$  over time, respectively.

mantle, may be an expected outcome of core–mantle interactions.

In order to test whether a W isotopic signature of core–mantle interaction is present in some plume-derived materials, Schersten et al. [31] measured the W isotopic composition of two of the Loihi and one of the Hualalai Hawaiian picrites that showed the largest coupled enrichments of  $^{186}\text{Os}$  and  $^{187}\text{Os}$ . They found that within the uncertainties of the measurements, the  $\varepsilon_{\text{W}}$  of these picrites did not deviate from that of the bulk-silicate Earth (BSE, Fig. 3). Their models considered mixing of two different mantle end-members with model outer core. The concentration of W in the two mantle end-members (with  $\varepsilon_{\text{W}}=0$ ) were 8 ppb ('preferred' model), and 19 ppb ('forced' model) that were calculated on the basis of whether W extraction to the continental crust

occurred from the whole mantle or only the upper mantle, respectively. Their 'forced' model was based on calculations derived in an attempt to fit the combined Os–W isotopic data to a core–mantle interaction mechanism. For this model, they argued that the parameters for the mixing systematics for both Os and W require rapid inner core crystallization that is not consistent with cooling models for Earth requiring slower inner core formation. Instead, the 'preferred' model, which they considered more realistic of conditions within the Earth, resulted in an  $\varepsilon_{\text{W}}$  of  $-0.55$  for the amount of core expected (0.5 wt.%) for the Hualalai sample, based on its  $^{186}\text{Os}/^{188}\text{Os}$  isotopic composition [20,23]. This value is much lower than the actual  $\varepsilon_{\text{W}}$  measured (Fig. 3). Hence, they concluded that there is no core component in the Hawaiian picrites.



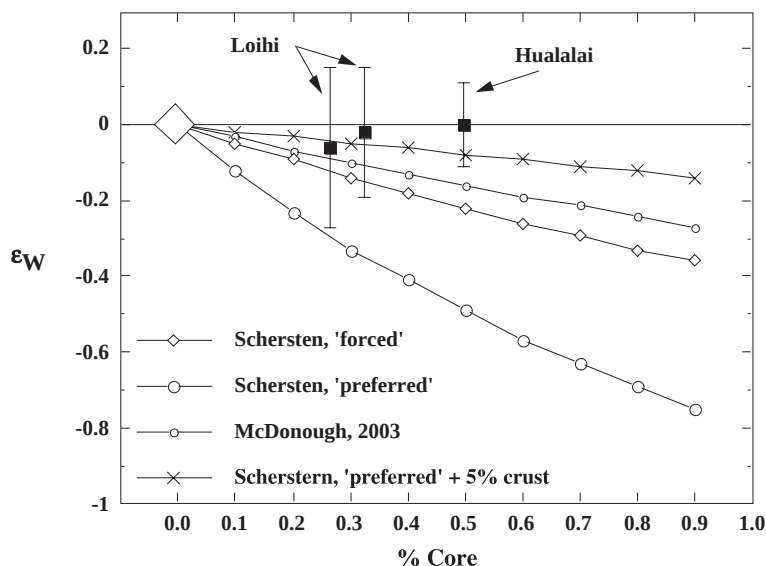


Fig. 3. The  $\epsilon_W$ –% Core (in wt.%) relationships for mixing between different mantle components (open diamond, representing bulk-silicate Earth) and the outer core. The wt.% core calculated for the Loihi and Hualalai picrite data [31] assumes mixing between PUM (3.0 ppb OS and  $^{186}\text{Os}/^{188}\text{Os}=0.119835$ ) and evolved outer core Model 4 of Brandon et al. [30] (332 ppb OS and  $^{186}\text{Os}/^{188}\text{Os}=0.119870$ ), where inner core crystallization begins at 3.5 Ga ([30], following the thermal cooling model of Stevenson et al. [89]). For the W mixing between core ( $\epsilon_W=-2.1$ ) and bulk-silicate Earth ( $\epsilon_W=0$ ), the following abundances were used: Schersten ‘forced’, core=440 ppb, mantle=19 ppb; Schersten ‘preferred’, core=490 ppb, mantle=8 ppb; McDonough [3], core=470 ppb, mantle=29 ppb; and for Schersten ‘preferred’ +5 wt.% crust, the hybrid crust (1100 ppb) plus mantle mixture is 62.6 ppb. The effect of adding ancient recycled crust into the source of plumes is to raise the W abundance of the mixture and mask the effect of adding low  $\epsilon_W$  outer core material.

Two issues relating to the abundance and origin of W in mantle plumes may complicate the interpretations of Schersten et al. [31]. First, the mantle sources of the Hawaiian picrites may have higher W abundances than estimated in their preferred model. McDonough [3] estimated a BSE concentration for W of 29 ppb. Such a high concentration of W might be present in a plume source if it originated in a portion of the mantle that was not significantly melt depleted. Mixing between outer core and BSE would result in a perturbation of the W isotopic value of only about  $-0.16 \epsilon_W$  units for the amount of core expected (0.5 wt.%) for the Hualalai sample (Fig. 3). This level of difference is just at the resolution limit of current analytical methods.

Second, a more significant problem with the use of W as a tracer of core–mantle interaction, at least in the case of plume-derived materials, is modest crustal contamination of the mantle source. With the exception of Mn crusts, which are considered below, the Schersten et al. [31] models do not take into consideration the possible effects of adding recycled

crust into the source of the Hawaiian plume. As much as 50 wt.% of recycled crust, consisting of typical oceanic basalts or sediments could be added to a peridotitic source and have little effect on the  $^{186}\text{Os}/^{188}\text{Os}$  ratio of the mantle–crust mixture [20,23]. Addition of such materials would, however, have detectable effects on the  $^{187}\text{Os}/^{188}\text{Os}$  and lithophile isotopes of magmas derived from the resulting hybrid source [57]. For example, in the case of Hawaiian lavas, 4–6 wt.% of pelagic sediments added to mantle peridotite may explain the observed positive correlations between  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{187}\text{Os}/^{188}\text{Os}$ , and negative correlations of Sr and Os isotopes with  $^{206}\text{Pb}/^{204}\text{Pb}$  [45,58]. Tungsten behaves as an incompatible lithophile element during partial melting of the mantle with similar partitioning behavior to U, such that oceanic and continental crust is greatly enriched in W (~1100 ppb) relative to the mantle [55]. Adding recycled crust into the source of plumes may significantly increase the W concentration of the hybrid silicate mantle source, while keeping the source at  $\epsilon_W=0$ . Pelagic sediments have W concen-

trations that are even higher than those for average continental crust, averaging from 1500 to 2700 ppb [59,60]. Addition of only ~5 wt.% crust having 1100 ppb of W with  $\varepsilon_w=0$  to the mantle end-member defined by the Schersten et al. [31] ‘preferred’ model, followed by mixing with as much as 0.7 wt.% core metal, results in minor changes of  $<0.1 \varepsilon_w$  units (Fig. 3). The concentration of W in average continental crust was chosen for this calculation in order to conservatively limit the effectiveness of sediment added to a plume source in masking a core component. Choosing a higher concentration, as is common for most oceanic sediments, would further reduce the amount of sediment necessary to mask the addition of a core component. If the McDonough [3] BSE is chosen for the mantle end-member in the mixture, adding only 2 wt.% of average continental crust into the plume source will produce a mixing curve nearly identical to the Schersten et al. [31] ‘preferred’ plus sediment curve (Fig. 3), and thereby mask the effects of core–mantle interaction to the W isotopic composition of the hybrid mixtures. Such low quantities of sediment additions to the Hawaiian plume source are consistent with the amounts of sediment necessary to explain the Sr and Pb isotopic compositions of Hawaiian lavas [45,58].

In summary, because of the differences in the W isotopic compositions and concentrations of the core and the silicate Earth, differences of  $\varepsilon_w$  in plume-derived materials could result from core–mantle interaction. However, the present level of analytical resolution may not yet be sufficient to unambiguously identify the presence of a core component, or rule out such a component.

### 2.3. The mechanism(s) of core–mantle interaction

Chemical exchange between the core and the mantle must by its nature be a complex process leading to a variety of consequences. In general, two types of models have been proposed, including straight addition (mixing) of core metal into plume sources, and equilibrium exchange in reaction zones between core metal and the mantle above the CMB (Fig. 1). Each scenario will result in different chemical effects and both may operate.

Perhaps the most straightforward process would be to directly mix bulk core metal into the mantle above

the CMB. Not only would the effects be imparted to the isotope systematics of elements such as Os and W, but elemental abundances and ratios would be shifted towards those that are strongly enriched in the core. Bulk addition of evolved outer core material should result in variably elevated Pt/Os and Re/Os in the hybrid metal–silicate mix, which presumably would correlate with  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$ . All four parameters would increase with greater amounts of core material added. For example, although limited to only three samples, Pt/Os for the Gorgona komatiites do correlate with  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  and indicate that the Gorgona source mantle was variably elevated in Pt/Os relative to the upper mantle (Fig. 4). The correlations in the komatiites can be used to back-calculate the Pt/Os of the source of each sample (Fig. 4). The elevated Pt/Os of the source of these komatiites could be explained by addition of core material ( $\leq 0.3$  wt.%), where any one of three slow inner core growth models are applied [30].

There are also some geochemical arguments against bulk mixing of outer core metal into silicate mantle to generate coupled Os isotopic systematics. For example, bulk mixing between core and mantle should result in concentrations of elements such as Os, Pt and Re that are higher than are calculated for the Hawaiian plume source [61]. However, it is difficult to estimate platinum group elements (PGE) abundances in mantle sources calculated from measured abundances in basalts and picrites. It is also possible the source retained some of the PGE in residual sulfides, thus masking the effects of excess PGE [61].

The same Hawaiian picrites have elevated Fe/Mn relative to MORB and Iceland picrites [32]. Humayun et al. [32] argued that the elevated Fe/Mn was not a result of fractionation during melting or fractional crystallization, but instead is a source characteristic of the Hawaiian plume and reflects an approximately 1 wt.% excess of Fe relative to normal convecting upper mantle. This could be a manifestation of reaction between the mantle at the CMB and outer core metal (Fig. 1). Such an interpretation does not easily connect with the Os isotope results, as the putative excess Fe does not correlate with the coupled  $^{186}\text{Os}$ – $^{187}\text{Os}$  enrichments. If the Os isotopes and Fe enrichment does reflect reaction between outer core metal and silicate mantle, such decoupling might reflect parti-

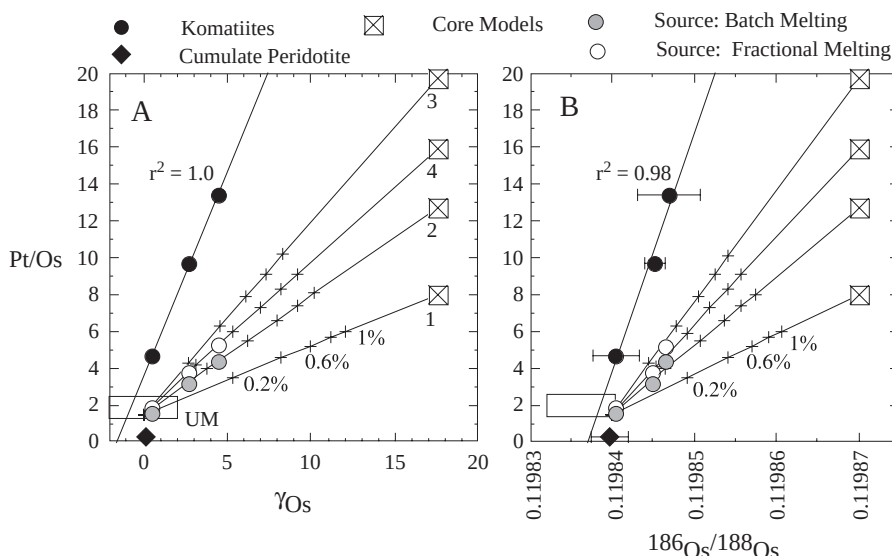


Fig. 4. The Pt/Os– $\gamma_{\text{Os}}$  (A) and  $^{186}\text{Os}/^{188}\text{Os}$  (B) relationships of Gorgona komatiites and a cumulate peridotite [30]. The komatiite data display positive correlations in these plots. The range for upper mantle materials (UM) is shown. The present values of Pt/Os and Os isotopic compositions calculated from four different core evolution models of Brandon et al. [30] are shown. Three of these begin with inner core growth at 4.4 Ga and have different crystallization rates: 1—near instantaneous, 2—rapid growth in the Archean with constant growth from 2.5 Ga to present, and 3—constant inner core growth from 4.4 Ga to present. Model 4 is similar to Model 2 but delays the onset of inner core growth to 3.5 Ga. The data are used to calculate the Gorgona komatiite source characteristics assuming batch and fractional melting where the degree of melting is 30 wt.% based on major element composition of Gorgona komatiites [90]. The  $D$ 's for silicate melt/mantle residue used,  $D_{\text{Os}}=2.12$  and  $D_{\text{Pt}}=0.41$ , are based on batch melting models to produce komatiite (Table 5 in [26]), and  $D_{\text{Re}}=0.1$ , based on Re abundances of Gorgona komatiites compared to the upper mantle [21]. Mixing lines between the model outer core compositions (Table 2 in [30]) and the Gorgona mantle with Os=3 ppb, Pt/Os=1.5,  $\gamma_{\text{Os}}=0$ , and  $^{186}\text{Os}/^{188}\text{Os}=0.11984$  are shown with 'plus' symbols representing 0.2 wt.% increments of outer core added to the Gorgona mantle. The following parameters were used for each model outer core composition (Table 2 in [30]) with  $\gamma_{\text{Os}}=17.5$ , and  $^{186}\text{Os}/^{188}\text{Os}=0.11987$ : Model 1—Os=611 ppb, Pt/Os=7.95; Model 2—Os=415 ppb, Pt/Os=12.66; Model 3—Os=267 ppb, Pt/Os=19.68; and Model 4—Os=332 ppb, Pt/Os=15.83. The enriched Pt/Os,  $\gamma_{\text{Os}}$  and  $^{186}\text{Os}/^{188}\text{Os}$  of these Gorgona komatiites are most consistent with mixing between the calculated source mantle and -0.3 wt.% outer core composition that is best matched to Model 4 where inner core growth begins at 3.5 Ga, although the other two slow growth models for the inner core are also reasonable solutions that match the expected Pt/Os and Os isotope systematics of the calculated sources of each komatiite.

tioning of Os and Fe into different phases in the mantle during infiltration of core metal across the CMB [32]. For instance, the mass transfer of iron and oxygen contained in core metal could result in a transfer of FeO into ferropericlasite, whereas the PGE transfer could be governed by the presence of immiscible FeS. Tungsten is more easily oxidized than Os, so it would not be expected to partition as strongly into FeS vein material. These different chemical signatures of core–mantle interaction could, therefore, be decoupled from each other in a complex distribution of heterogeneous material formed above the CMB.

One final note, if liquid metal infiltrates the lower mantle and ultimately drains back into the core, it is

possible that isotopic exchange between the core and mantle could take place without substantial mass transfer. If this occurs then the isotopic signal of the outer core could be inherited by the spatially associated mantle without collateral effects of mass transfer of bulk metal [26]. Little information is currently available regarding the rates of isotopic exchange of Os and W, especially with regard to metal–silicate equilibration.

Clearly, if bulk transfer or isotopic exchange occurs at the CMB, then correlations between different signatures indicative of core–mantle interaction are not necessarily a prerequisite of the mixing process. In the case for Gorgona, the correlation between Pt/Os and Os isotopes may be consistent with



a bulk transfer of platinum group elements across the CMB. The Hawaiian data, however, show that the interpretation is not straightforward and that the process of core–mantle interaction and later partial melting of the source might result in decoupling of different signatures during equilibrium exchange between core metal and the mantle. The possible lack of corroboration between isotopic systems or elemental abundances could make core–mantle interaction quite difficult to unambiguously identify.

### 3. Alternatives to a core–mantle interaction model

Alternate models have also been proposed to account for the observed, coupled Os isotope trends in Fig. 2. For example, it has been noted that some crustal rocks may have sufficiently high Pt/Os and Re/Os ratios, and corresponding Pt and Re concentrations, such that their recycling into the mantle via subduction, together with the long-term decay of  $^{190}\text{Pt}$  and  $^{187}\text{Re}$  could result in the formation of small domains within the mantle with appropriately coupled enrichments in  $^{186}\text{Os}$ – $^{187}\text{Os}$ . There is no question that recycled crust is an important contributor to the chemical signatures, including  $^{187}\text{Os}$  enrichments, of some ocean island basalts [62]. Given the high Re content of certain recycled materials, such as basalts, the radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratios for some OIB can be attributed to derivation from sources containing ancient recycled oceanic crust and/or sediments [45,46,63–67]. Not all  $^{187}\text{Os}$ -enriched magmas, however, can be explained via derivation from mantle containing recycled crust, let alone corresponding enrichments in  $^{186}\text{Os}$ . Indeed, failure of crustal recycling models to account for enrichments present in the Siberian plume led Walker et al. [17,68] to initially propose an outer core origin for the  $^{187}\text{Os}$  enrichment present in some systems.

Can crustal recycling account for any coupled enrichments in  $^{186}\text{Os}$ – $^{187}\text{Os}$ ? The Pt/Re of crustal materials that may make up ancient recycled slabs typically range from <0.1 to 33 [23]. Platinum/Re ratios of 88–100, however, are required for ancient recycled crust to generate the observed coupled  $^{186}\text{Os}$ – $^{188}\text{Os}$  enrichments [23,30]. Such high Pt/Re ratios are not typical of the volumetrically dominant materials that are subducted into the mantle. The main

problem is that Pt is insufficiently enriched in most types of oceanic crust and sediments to account for the magnitude of  $^{186}\text{Os}$  enrichment present in the Hawaiian suite. Calculations made using data for materials typical of average recycled crust suggest that  $\geq 70$  wt.% of a 2 Ga recycled component would need to be mixed with peridotite to generate the most  $^{186}\text{Os}$ -rich Hawaiian lavas (Fig. 2, [20,23]), yet this would lead to a dramatically greater enrichment in  $^{187}\text{Os}$  than is observed. Melting of mantle sources that incorporate such large proportions of mafic crust could not likely not generate the picritic or komatiitic lavas with high Os contents that delineate the coupled trends [69]. In general the bulk of recycled oceanic crustal materials should result in a ‘Re-enrichment’ trend that shift data along a nearly horizontal vector to the right in Fig. 2, rather than result in a coupled enrichment of  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$ .

Despite the apparent inadequacy of recycled mafic crust to account for couple Os isotopic enrichments, there are several types of additional materials that may have sufficiently high Pt/Re to account for the coupled trends. In the past several years, different types of materials that may be present in the sources of deep mantle plumes have been proposed to explain the coupled enrichments of  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$ . These include Mn-rich materials, including umbers [34], and Fe–Mn crusts and nodules [37] that may be present in slabs. These materials have strong enrichments in Pt of as much as 100 times average upper mantle concentrations, and also have Pt/Re ratios that are sufficiently elevated to generate coupled enrichments with time (e.g. [70]). When aged for several billion years and mixed with peridotites, relatively modest amounts of these materials (2 to 10 wt.%) could potentially create the observed enrichments in  $^{186}\text{Os}/^{188}\text{Os}$  for some plume-derived materials. While the Pt/Os, Re/Os, and  $^{187}\text{Os}/^{188}\text{Os}$  ratios for such materials are highly variable, under some circumstances, mixing lines similar to those displayed by the Hawaiian–Siberian, and Gorgonian data could be generated [31,37].

Brandon et al. [30] discounted Mn-rich umbers as the source for the coupled enrichments of  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  based on three arguments. First, because of the large variations in predicted compositions of aged umbers, mixing such material from different locations into deep plumes should result in

large scatter of data from lavas produced from hybrid umber–peridotite sources. These relationships are not consistent with the smooth mixing lines observed between mantle and COs compositional end-members. Second, mixing of only a few wt.% umber into a plume source would have a dramatic effect on the Mn content of the source and magmas derived from such a source (Fig. 5). These relationships also hold for Fe–Mn crusts and Mn nodules. Addition of only 1 to 2 wt.% of these materials [31,37] to a peridotitic source would result in anomalously high Mn contents in derivative lavas. Such high Mn contents and corre-

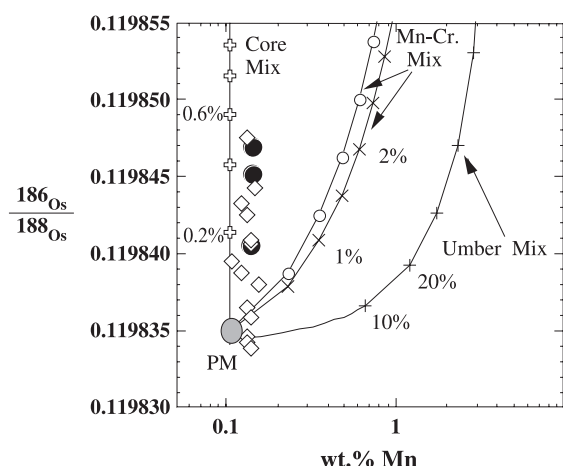


Fig. 5. The  $^{186}\text{Os}/^{188}\text{Os}$ –wt.% Mn relationships for the Hawaii and Gorgona samples. Mixtures between evolved outer core, and the primitive mantle (PM) are nearly vertical. The ‘plus’ symbols are for 0.2 wt.% increments of added outer core. Mixtures between the mantle and Mn crust (Cr.) with symbols for 0.5 wt.% increments of added Mn material, and Umlers with symbols for 10 wt.% increments between end-members, plot as curves away from the vertical trend of Gorgonian and Hawaiian data. The mixing lines with open circles is for mixing between mantle and average Mn crust of Schersten et al. [31] that takes their maximum Pt/Os and Os values to minimize the amount of Mn crust necessary to <2 wt.% to create the observed  $^{186}\text{Os}/^{188}\text{Os}$ . The mixing line with crosses is for mixing between mantle and average Mn crust of Baker and Jensen [37]. Mixing parameters are as follows: outer core:  $^{186}\text{Os}/^{188}\text{Os}$  and Os concentration as in Fig. 3, Mn=0.03 wt.%, [3]; primitive mantle (PM),  $^{186}\text{Os}/^{188}\text{Os}$  and Os concentration as in Fig. 3, Mn=0.1045 wt.% [3]; Umler is aged for 2 Ga, Pt/Os=127.43 resulting in  $^{186}\text{Os}/^{188}\text{Os}$ =0.12024 Os=0.175 ppb, and Mn=5.62 wt.% [30,34]; Schersten et al. [31] Mn crust is aged for 2 Ga using a Pt=662 ppb, and Os=2 ppb, resulting in  $^{186}\text{Os}/^{188}\text{Os}$ =0.12082 after 2 Ga, Mn=25 wt.% [31], the Baker and Jensen [37] Mn crust differs in Os characteristics only with Pt=675 ppb, Os=2.7 ppb,  $^{186}\text{Os}/^{188}\text{Os}$ =0.12062 after being aged for 2.2 Ga, but mixed with their mantle having 2.7 ppb Os.

sponding low Fe/Mn ratios are not observed in the Hawaiian or Gorgonian systems examined to date for Os isotopes (Fig. 5, [32]). Third, all of these materials represent volumetrically insignificant fractions of oceanic crust. Manganese nodules and crusts make up about 70 kg/m<sup>2</sup> of area of the seafloor, yet represent less than 3 wt.% of the mass of the uppermost 1 m<sup>3</sup> of oceanic crust [37]. If oceanic crust is considered as a package several kilometers thick, then on a large scale, the addition of Mn crusts to the seafloor (as with cosmic dust additions) has essentially no effect on the concentrations of recycled platinum group elements. Thus, the Pt-rich material would have to be isolated and accumulated into a volume sufficiently significant to cause a perturbation in a system as large as the Hawaiian or Siberian plumes. Unless some type of focusing mechanism can be conceived that can transfer an Os isotopic signature to a source of plume lavas without collateral effects from the Mn-rich materials, it is difficult to advocate these materials for creating the observed enrichments of  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  in some plume-derived lavas.

A second material that has been proposed to generate the observed enrichments of  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  is pyroxenite [33,35,36]. Pyroxenite is very common in the subcontinental mantle lithosphere and peridotite sections in ophiolites [71,72], and does not suffer from the volume problems that Mn-rich materials have. These rocks may constitute as much as 5 wt.% of the upper mantle [73]. At present there is a paucity of high-quality platinum-group element concentration data for pyroxenites and it is unclear whether they have sufficient Pt combined with the high Pt/Re necessary to make these rocks favorable candidates to produce the coupled Os isotope enrichments when mixed with normal mantle peridotite. Smith [33] noted that one pyroxenite associated with the Bay of Islands ophiolite [74] actually did have appropriate Pt/Re/Os ratios and concentrations to generate an appropriate mixing trend. Whether or not such materials are common in the upper mantle is unknown at present, although Pt, Re and Os partitioning data between silicate melt and pyroxene suggest that this is unlikely. Platinum is only slightly compatible in pyroxene with  $D_{\text{mineral/melt}}$  of around 1.5, and Re is slightly incompatible [75]. Such systematics should result in Pt abundances and Pt/Re

ratios in most pyroxenites that are only slightly enriched in Pt relative to the mantle. Nevertheless, pyroxenites that crystallize from sulfur-saturated melts may contain high concentrations of Os (up to 4 ppb) combined with substantially higher concentrations of Pt (up to 520 ppb) [36] because of extraction of these elements into stabilized sulfides in the pyroxenite cumulates. Hence a systematic investigation is necessary to constrain the role of pyroxenite as a source of Os isotope variation in the mantle. If the arguments presented by Smith [33] and Meibom et al. [36] are correct, then such rocks may be the most favorable candidate as an alternative to core–mantle interaction in these debates.

One final note, it may be possible that the fractionations between Re, Pt and Os in subducting slabs during dehydration and partial melting under subduction zones are such that the residual slabs have elevated Pt/Re. This could lead to Os isotopic systematics when aged over several Ga, which could mimic the trends for Hawaii, Gorgona and Siberia in Fig. 2. Evidence from melt inclusions in arc lavas, bulk arc mantle peridotites and pyroxenites are consistent with dehydration and partial melting resulting in loss of Re, Os and Pt [71,76–80]. In such a case, and even if all of the Pt is conserved in residual slabs, the mixing relationships between ancient residual crust and mantle would require the same unrealistic amounts of the crustal material discussed above, and render such a model petrologically difficult to reconcile. However, until dehydration and partial melting processes are better understood, this issue cannot be tested further.

#### 4. Future challenges

At present, coupled enrichments of  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  of some plume-derived materials may best be explained by core–mantle interactions, but the inherent assumptions can be questioned on a variety of fronts. While there is a general consensus that recycled oceanic crust is present in many plumes, materials considered to be the major constituents of recycled crust cannot result in the production of coupled Os isotope enrichments consistent with those observed in Gorgonian, Hawaiian and Siberian rocks. However, specific scenarios for the latter cannot be

completely ruled out and may actually have favorable qualities. The challenge for future studies is to test specific questions that remain with a comprehensive analytical and experimental program.

Materials from additional hotspots should be measured for high precision Os isotopes, to test if the interpreted convergence of  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  data observed for the three plume systems prevails, or if greater scatter results, as would be predicted by some of the alternate models discussed above. Additional mantle-derived materials unrelated to the plume environment, including peridotites, primitive lavas, and Os-rich alloy minerals, must be measured for high precision Os isotopes to determine if the coupled enrichments found in some plume-derived materials are unique to plumes that may rise from the CMB (e.g. [22,29,36,81]).

Samples from putative ancient plume systems also need to be analyzed for high precision Os isotopes. These materials could track the evolution of different mantle reservoirs over time, and could provide a test of whether  $^{186}\text{Os}/^{188}\text{Os}$ -enriched reservoirs existed in the Proterozoic and Archean, with ramifications to core–mantle interaction and crustal recycling models. Studies of Precambrian komatiites have recently begun (e.g. [82]).

A comprehensive analytical program to obtain Pt, Re and Os concentrations of upper mantle materials, using the most recent chemical extraction and mass spectrometric techniques (e.g. [83]), is necessary to assess the Pt/Re/Os variability of the mantle. This should include measurements of both pyroxenites and peridotites from diverse tectonic settings. It may be possible that under certain conditions crystallization of minerals from melts or metasomatism in the mantle can produce the necessary enrichments in Pt/Os and Pt/Re, which when allowed to age for several billion years, will result in mantle sources that may have the necessary coupled enrichments of  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  to produce the Hawaiian, Gorgonian and Siberian Os isotopic systematics (Fig. 2). Such data will aid in examining alternative models to core–mantle interaction for producing coupled enrichments of  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  as well as constraining the geochemical behavior of Pt, Re and Os under a variety of conditions in the mantle.

The behavior of Pt, Re and Os during metal crystallization is well understood and the Os isotope

enrichments observed are consistent with this known behavior, but no partitioning data exist for pressures and temperatures present in the Earth's core. Many factors need to be explored to determine if the behaviors of these elements are the same under these conditions. This includes partitioning between liquid metal and hexagonal close packed (hcp) Fe-rich alloys, the latter thought to be the Fe-rich solid phase in the inner core. Experimental partitioning data have generally been obtained at much lower pressures than the outer core–inner core boundary, and only face center cubic Fe-rich phases have been synthesized. Experiments synthesizing hcp Fe-rich alloys in equilibrium with molten metal for investigating the partitioning of Re, Pt and Os are underway and will provide important constraints on their behavior at the pressures of the Earth's core [Campbell 2004, personal communication]. The partitioning behavior of Pt, Re and Os may also depend to some degree on which light element alloys with Fe and Ni in the Earth's core as shown by experimental data produced using varying light elements in the Fe–Ni alloys [41–44,84]. The final solution to this debate will have implications for whether the coupled enrichments of  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  in plume-derived samples can be produced by long-term Pt/Os and Re/Os fractionation during crystallization of a solid inner core.

Other isotopic systems that may shed light on core–mantle interaction need to be further utilized. This would include more high precision tungsten isotope measurements. Also,  $^{107}\text{Pd}$  decays to  $^{107}\text{Ag}$  with a half-life of  $\sim 6.5$  Ma [85,86]. A limited number of preliminary  $^{107}\text{Ag}/^{108}\text{Ag}$  data for lavas from Hawaii have excess  $^{107}\text{Ag}$  relative to chondrites [85,86]. One possible reason for this difference is that the Earth's core formed while  $^{107}\text{Pd}$  was extant, and that the excess  $^{107}\text{Ag}$  reflects a contribution from the core as Pd is enriched relative to Ag during metal–silicate equilibrium [85,86]. Further work on the  $^{107}\text{Pd}$ – $^{107}\text{Ag}$  system may therefore provide additional insights to the debate over core–mantle interaction.

The process of core–mantle interaction needs to be further investigated experimentally. Constraining how core material may infiltrate into the mantle, what reactions take place, what phases may be produced, and whether models of bulk addition or equilibrium

exchange are more realistic, will be vital for interpreting chemical and isotopic compositions of plume-derived materials.

In summary, integration of experimental and compositional data with ongoing geophysical studies of the deep mantle will provide rigorous tests of the chemical consequences of core–mantle interaction. These studies will have a significant role in extending our comprehension of the origin of compositional variation of mantle plumes over Earth history, and the chemical evolution of the core and the mantle. These investigations will enhance our understanding of how processes operating at the CMB are linked to the rate of cooling and the scale of convection in the Earth over time.

### Jargon Box

$\gamma_{\text{Os}}$  notation:

$$\gamma_{\text{Os}} = \left\{ \left[ \left( ^{187}\text{Os}/^{188}\text{Os}_{\text{sample}(t)} \right) / \left( ^{187}\text{Os}/^{188}\text{Os}_{\text{chondrite}(t)} \right) \right] - 1 \right\} \times 100$$

where  $t$ =time, and:

$$\begin{aligned} & ^{187}\text{Os}/^{188}\text{Os}_{\text{chondrite}(t)} \\ &= ^{187}\text{Os}/^{188}\text{Os}_i + ^{187}\text{Re} \\ & \quad / ^{188}\text{Os}_{\text{chondrite}} (e^{\lambda(4.558\text{Ga})} - e^{\lambda t}) \end{aligned}$$

$\epsilon_{\text{w}}$  notation:

$$\epsilon_{\text{w}} = \left\{ \left[ (\epsilon_{\text{w sample}}) / (\epsilon_{\text{w reference value}}) \right] - 1 \right\} \times 10^4$$

where  $\epsilon_{\text{w reference value}} = 0 = \text{bulk-silicate Earth}$ .

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## References

- [1] R. Jeanloz, The nature of the Earth's core, *Annu. Rev. Earth Planet. Sci.* 18 (1993) 357–386.
- [2] E.J. Gamero, Heterogeneity in the lowermost mantle, *Annu. Rev. Earth Planet. Sci.* 28 (2000) 509–537.
- [3] W.F. McDonough, Compositional model for the Earth's core, *Treat. Geochem.* 2 (2003) 547–568.
- [4] R. Boehler, A. Chopelas, A. Zerr, Temperature and chemistry of the core–mantle boundary, *Chem. Geol.* 120 (1995) 199–205.
- [5] A.E. Ringwood, *Composition and Petrology of the Earth's Mantle*, McGraw-Hill, USA, 1975, 618 pp.
- [6] A.W. Hofmann, W.M. White, Mantle plumes from ancient oceanic crust, *Earth Planet. Sci. Lett.* 57 (1982) 421–436.
- [7] Q. Williams, E.J. Garnero, Seismic evidence for partial melt at the base of the mantle, *Science* 273 (1996) 1528–1530.
- [8] E. Knittle, R. Jeanloz, Simulating the core–mantle boundary: an experimental study of high-pressure reactions between silicates and liquid iron, *Geophys. Res. Lett.* 16 (1989) 609–612.
- [9] E. Knittle, R. Jeanloz, The Earth's core–mantle boundary: results of experiments at high pressures and temperatures, *Science* 251 (1991) 1438–1453.
- [10] A.M. Jellinek, M. Manga, Links between long-lived hotspots, mantle plumes D' and plate tectonics, *Rev. Geophys.* 42 (2004), doi:10.1029/2003RG000144.
- [11] B.A. Buffett, E.J. Garnero, R. Jeanloz, Sediments at the top of the Earth's core, *Science* 290 (2000) 1338–1341.
- [12] V. Steinbach, D.A. Yuen, Viscous heating: a potential mechanism for the formation of the ultralow velocity zone, *Earth Planet. Sci. Lett.* 172 (1999) 213–220.
- [13] B.A. Buffett, P.M. Matthews, T.A. Herring, Modelling of nutation and precession: effects of electromagnetic coupling, *J. Geophys. Res.* 107 (2002), doi:10.1029/2000JB000056.
- [14] S.O. Costin, B.A. Buffett, Preferred reversal paths caused by a heterogeneous conducting layer at the base of the mantle, *J. Geophys. Res.* 109 (2004), doi:10.1029/2003JB002853.
- [15] L.H. Kellogg, S.D. King, Effect of mantle plumes on the growth of D' by reaction between the core and the mantle, *Geophys. Res. Lett.* 20 (1993) 379–382.
- [16] E.J. Garnero, A new paradigm for Earth's core–mantle boundary, *Science* 304 (2004) 834–836.
- [17] R.J. Walker, J.W. Morgan, M.F. Horan, <sup>187</sup>Os enrichment in some mantle plume sources: evidence for core–mantle interaction? *Science* 269 (1995) 819–822.
- [18] E. Widom, S.B. Shirey, Os isotope systematics in the Azores: implications for mantle plume sources, *Earth Planet. Sci. Lett.* 142 (1996) 451–465.
- [19] R.J. Walker, J.W. Morgan, E. Beary, M.I. Smoliar, G.K. Czamanske, M.F. Horan, Applications of the <sup>190</sup>Pt–<sup>186</sup>Os isotope system to geochemistry and cosmochemistry, *Geochim. Cosmochim. Acta* 61 (1997) 4799–4808.
- [20] A.D. Brandon, R.J. Walker, J.W. Morgan, M.D. Norman, H.M. Pritchard, Coupled <sup>186</sup>Os and <sup>187</sup>Os evidence for core–mantle interaction, *Science* 280 (1998) 1570–1573.
- [21] R.J. Walker, M. Storey, A.C. Kerr, J. Tarney, N.T. Arndt, Implications of <sup>187</sup>Os isotopic heterogeneities in a mantle plume: evidence from Gorgona Island and Curacao, *Geochim. Cosmochim. Acta* 63 (1999) 713–728.
- [22] J.M. Bird, A. Meibom, R. Frei, Th.F. Nägler, Osmium and lead isotopes of rare OsIrRu minerals: derivation from the core–mantle boundary region? *Earth Planet. Sci. Lett.* 170 (1999) 83–92.
- [23] A.D. Brandon, M.D. Norman, R.J. Walker, J.W. Morgan, <sup>186</sup>Os–<sup>187</sup>Os systematics of Hawaiian picrites, *Earth Planet. Sci. Lett.* 174 (1999) 25–42.
- [24] A.D. Brandon, J.E. Snow, R.J. Walker, J.W. Morgan, T.D. Mock, <sup>190</sup>Pt–<sup>186</sup>Os and <sup>187</sup>Re–<sup>187</sup>Os systematics of abyssal peridotites, *Earth Planet. Sci. Lett.* 177 (2000) 319–335.
- [25] C.G. Macpherson, D.R. Hilton, D.P. Matthey, J.M. Sinton, Evidence for an <sup>18</sup>O-depleted mantle plume from contrasting <sup>18</sup>O/<sup>16</sup>O ratios of back-arc lavas from the Manus Basin and Mariana Trough, *Earth Planet. Sci. Lett.* 176 (2000) 171–183.
- [26] I.S. Puchtel, M. Humayun, Platinum group elements in Kostomuksha komatiites and basalts: implications for oceanic crust recycling and core–mantle interaction, *Geochim. Cosmochim. Acta* 64 (2000) 4227–4242.
- [27] I.S. Puchtel, G.E. Brugmann, A.W. Hofmann, <sup>187</sup>Os-enriched domain in an Archean mantle plume, evidence from 2.8 Ga komatiites of the Kostomuksha greenstone belt, NW Baltic Shield, *Earth Planet. Sci. Lett.* 186 (2001) 513–526.
- [28] D. Porcelli, A.N. Halliday, The core as a possible source of mantle helium, *Earth Planet. Sci. Lett.* 192 (2001) 45–56.
- [29] A. Meibom, R. Frei, Evidence for an ancient osmium isotopic reservoir in earth, *Science* 296 (2002) 516–518.
- [30] A.D. Brandon, R.J. Walker, I.S. Puchtel, H. Becker, M. Humayun, S. Revillon, <sup>186</sup>Os–<sup>187</sup>Os systematics of Gorgona Island komatiites: implications for early growth of the inner core, *Earth Planet. Sci. Lett.* 206 (2003) 411–426.
- [31] A. Schersten, T. Elliott, C. Hawkesworth, M. Norman, Tungsten isotope evidence that mantle plumes contain no contribution from the Earth's core, *Nature* 427 (2004) 234–237.
- [32] M. Humayun, L. Qin, M. Norman, Geochemical evidence for excess iron in the Hawaiian mantle: implications for mantle dynamics, *Science* 306 (2004) 91–94.
- [33] A. Smith, Critical evaluation of Re–Os and Pt–Os isotopic evidence on the origin of intraplate volcanism, *J. Geodyn.* 36 (2003) 469–484.
- [34] G. Ravizza, J. Blusztajn, H.M. Pritchard, Re–Os systematics of platinum-group element distribution in metalliferous sediments from the Troodos ophiolite, *Earth Planet. Sci. Lett.* 188 (2001) 369–381.
- [35] F.E. Brenker, A. Meibom, R. Frei, On the formation of peridotite-derived Os-rich alloys, *Am. Mineral.* 88 (2003) 1731–1740.



- [36] A. Meibom, R. Frei, N. Sleep, Osmium isotopic compositions of Or-rich platinum group element alloys from the Klamath and Siskiyou Mountains, *J. Geophys. Res.* 109 (2004), doi:10.1029/2003JB002602.
- [37] J.A. Baker, K.K. Jensen, Coupled  $^{186}\text{Os}$ – $^{187}\text{Os}$  enrichments in the Earth's mantle–core–mantle interaction or recycling of ferromanganese crusts and nodules? *Earth Planet. Sci. Lett.* 220 (2004) 277–286.
- [38] D.L. Anderson, Thermal state of the upper mantle; no role for mantle plumes, *Geophys. Res. Lett.* 27 (2000) 3623–3626.
- [39] D.L. Cook, R.J. Walker, M.F. Horan, J.T. Wasson, J.W. Morgan, Pt–Re–Os systematics of group IIAB and IIIAB iron meteorites, *Geochim. Cosmochim. Acta* 68 (2004) 1413–1431.
- [40] J.W. Morgan, M.F. Horan, R.J. Walker, J.N. Grossman, Rhenium–osmium concentration and isotope systematics in group IIAB iron meteorites, *Geochim. Cosmochim. Acta* 59 (1995) 2331–2344.
- [41] H.V. Lauer, J.H. Jones, Partitioning of Pt and Os between solid and liquid metal in the iron–nickel–sulfur system, *Proc. Lunar Planet. Sci. Conf. XXIX* (1998) 1796.
- [42] M.E. Fleet, M. Liu, J.H. Crockett, Partitioning of trace amounts of highly siderophile elements in the Fe–Ni–S system and their fractionation in nature, *Geochim. Cosmochim. Acta* 63 (1999) 2611–2622.
- [43] D. Walker, Core participation in mantle geochemistry, *Geochim. Cosmochim. Acta* 64 (2000) 2897–2911.
- [44] N.L. Chabot, A.J. Campbell, J.H. Jones, M. Humayun, C.B. Agee, An experimental test of Henry's law in solid metal–liquid metal systems with implications to iron meteorites, *Meteorit. Planet. Sci.* 38 (2003) 181–196.
- [45] E.H. Hauri, J.C. Lassiter, D.J. DePaolo, J.M. Rhodes, Osmium isotope systematics of drilled lavas from Mauna Loa, Hawaii, *J. Geophys. Res.* 101 (1996) 11793–11806.
- [46] J.C. Lassiter, E.H. Hauri, Osmium isotope variation in Hawaiian lavas: evidence for recycled oceanic lithosphere in the Hawaiian plume, *Earth Planet. Sci. Lett.* 164 (1998) 483–496.
- [47] D.-C. Lee, A.N. Halliday, Hafnium–tungsten chronometry and the timing of terrestrial core formation, *Nature* 378 (1995) 771–774.
- [48] H.E. Newsom, Accretion and core formation in the earth: evidence from siderophile elements, in: H.E. Newsom, J.H. Jones (Eds.), *Origin of the Earth*, Oxford University Press, New York, 1990, pp. 273–288.
- [49] C.L. Harper, S.B. Jacobsen, Evidence for  $^{182}\text{Hf}$  in the early Solar System and constraints on the timescale of terrestrial accretion and core formation, *Geochim. Cosmochim. Acta* 60 (1996) 1131–1153.
- [50] M.F. Horan, M.I. Smoliar, R.J. Walker,  $^{182}\text{W}$  and  $^{187}\text{Re}$ – $^{187}\text{Os}$  systematics of iron meteorites: chronology for melting, differentiation, and crystallization of asteroids, *Geochim. Cosmochim. Acta* 62 (1998) 545–554.
- [51] T. Kleine, C. Munker, K. Meager, H. Pahne, Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf–W chronometry, *Nature* 418 (2002) 952–955.
- [52] R. Schonberg, B.S. Kamber, K.D. Collerson, O. Eugster, New W isotope evidence for rapid terrestrial accretion and very early core formation, *Geochim. Cosmochim. Acta* 66 (2002) 3151–3160.
- [53] Q. Yin, S.B. Jacobsen, K. Yamashita, J. Blicher-Toft, P. Telouk, F. Albarede, A short timescale for terrestrial planet formation from Hf–W chronometry of meteorites, *Nature* 418 (2002) 949–952.
- [54] A.N. Halliday, Mixing, volatile loss and compositional change during impact-driven accretion of the earth, *Nature* 427 (2004) 505–509.
- [55] H.E. Newsom, K.W.W. Sims, P.D. Noll, W.L. Jaeger, S.A. Maehr, T.B. Beserra, The depletion of tungsten in the bulk silicate earth: constraints on core formation, *Geochim. Cosmochim. Acta* 60 (1996) 1155–1169.
- [56] W.F. McDonough, S.-s. Sun, The composition of the earth, *Chem. Geol.* 120 (1995) 223–253.
- [57] R.J. Walker, L.M. Echeverria, S.B. Shirey, M.F. Horan, Re–Os isotopic constraints on the origin of volcanic rocks, Gorgona Island, Colombia: Os isotopic evidence for ancient heterogeneities in the mantle, *Contrib. Mineral. Petrol.* 107 (1991) 150–162.
- [58] V.C. Bennett, T.M. Esat, M.D. Norman, Two mantle–plume components in Hawaiian picrites inferred from correlated Os–Pb isotopes, *Nature* 381 (1996) 221–224.
- [59] S. Gao, T.-C. Luo, B.-R. Zhang, H.-F. Zhang, Y.-W. Han, Z.-D. Zhao, Y.-K. Hu, Chemical composition of the continental crust as revealed by studies in East China, *Geochim. Cosmochim. Acta* 62 (1998) 1959–1975.
- [60] S.V. Strekopytov, Molybdenum and tungsten in oceanic sediments and nodules, *Geochem. Int.* 36 (1998) 838–845.
- [61] V.C. Bennett, M.D. Norman, M.O. Garcia, Rhenium and platinum group element abundances correlated with mantle source components in Hawaiian picrites: sulphides in the plume, *Earth Planet. Sci. Lett.* 183 (2000) 513–526.
- [62] A.W. Hofmann, Mantle geochemistry, the message from oceanic volcanism, *Nature* 385 (1997) 219–229.
- [63] W.J. Pegram, C.J. Allegre, Osmium isotopic compositions from oceanic basalts, *Earth Planet. Sci. Lett.* 111 (1992) 59–68.
- [64] E.H. Hauri, S.R. Hart, Re–Os isotope systematics of EM11 and HIMU oceanic island basalts from the south Pacific Ocean, *Earth Planet. Sci. Lett.* 114 (1993) 353–371.
- [65] L.C. Reisberg, A. Zindler, F. Marcantonio, W.M. White, D. Wyman, B. Weaver, Os isotope systematics in ocean island basalts, *Earth Planet. Sci. Lett.* 120 (1993) 149–167.
- [66] M. Roy-Barman, C.J. Allegre,  $^{187}\text{Os}/^{186}\text{Os}$  in oceanic island basalts: tracing oceanic crust recycling in the mantle, *Earth Planet. Sci. Lett.* 129 (1995) 145–161.
- [67] F. Marcantonio, A. Zindler, T. Elliott, H. Staudigel, Os isotope systematics of La Pohna, Canary Islands: evidence for recycled crust in the mantle source of HIMU ocean islands, *Earth Planet. Sci. Lett.* 133 (1995) 397–410.
- [68] R.J. Walker, J.W. Morgan, M.F. Horan, G.K. Czamanske, E.J. Krogstad, V.A. Fedorenko, V.E. Kunilov, Re–Os isotopic evidence for an enriched-mantle source for the Noril'sk-type, ore-bearing intrusions, Siberia, *Geochim. Cosmochim. Acta* 58 (1994) 4179–4197.

- [69] M.D. Norman, M.O. Garcia, Primitive magmas and source characteristics of the Hawaiian plume: petrology and geochemistry of shield picrites, *Earth Planet. Sci. Lett.* 168 (1999) 27–44.
- [70] D.K. McDaniel, R.J. Walker, S.R. Heming, M.F. Horan, H. Becker, R.L. Grauch, Source of osmium in the modern oceans: new evidence from the  $^{190}\text{Pt}$ – $^{186}\text{Os}$  system, *Geochim. Cosmochim. Acta* 68 (2004) 1243–1252.
- [71] H. Becker, S.B. Shirey, R.W. Carlson, Effects of melt percolation on the Re–Os systematics of peridotites from a Paleozoic convergent margin, *Earth Planet. Sci. Lett.* 188 (2001) 107–121.
- [72] R.C. Coleman, *Ophiolites*, Springer Verlag, New York, 1977, 229 pp.
- [73] M.M. Hirschmann, E.M. Stolper, A possible role for garnet pyroxenite in the origin of the “garnet signature” in MORB, *Contrib. Mineral. Petrol.* 124 (1996) 185–208.
- [74] S.J. Edwards, Harzburgites and refractory melts in the Lewis Hills Massif, Bay of island ophiolite complex: the base-metal and precious metal story, *Can. Mineral.* 28 (1990) 537–552.
- [75] K. Righter, A.J. Campbell, M. Humayun, R.L. Hervig, Partitioning of Ru, Rh, Pd, Re, Ir, and Au between Cr-bearing spinel, olivine, pyroxene and silicate melts, *Geochim. Cosmochim. Acta* 68 (2004) 867–880.
- [76] A.D. Brandon, R.A. Creaser, S.B. Shirey, R.W. Carlson, Osmium recycling in subduction zones, *Science* 272 (1996) 861–864.
- [77] A.D. Brandon, H. Becker, R.W. Carlson, S.B. Shirey, Isotopic constraints on time scales and mechanisms of slab material transport in the mantle wedge: evidence from the Simcoe mantle xenoliths, Washington, USA, *Chem. Geol.* 160 (1999) 387–407.
- [78] B.I.A. McInnes, J.S. McBride, N.J. Evans, D.D. Lambert, A.S. Andrew, Osmium isotope constraints on ore metal recycling in subduction zones, *Science* 286 (1999) 512–516.
- [79] W. Sun, V.C. Bennett, V.S. Kamenetsky, The mechanism of Re enrichment in arc magmas: evidence from Lau Basin basaltic glasses and primitive melt inclusions, *Earth Planet. Sci. Lett.* 222 (2004) 101–114.
- [80] H. Becker, R.W. Carlson, S.B. Shirey, Slab-derived osmium and isotopic disequilibrium in garnet pyroxenites from a Paleozoic convergent plate margin (lower Austria), *Chem. Geol.* 208 (2004) 141–156.
- [81] R.J. Walker, A.D. Brandon, J.M. Bird, P.M. Piccoli, W.F. McDonough, R.D. Ash,  $^{187}\text{Os}$ – $^{186}\text{Os}$  systematics of Os–Ir–Ru alloy grains from southwest Oregon, *Earth Planet. Sci. Lett.* 224 (2004), 399–413.
- [82] I.S. Puchtel, A.D. Brandon, M. Humayun, Precise Pt–Re–Os isotope systematics of the mantle from 2.7 Ga komatiites, *Earth Planet. Sci. Lett.* 224 (2004) 157–174.
- [83] H. Becker, M.F. Horan, R.J. Walker, S. Gao, J.-P. Lorand, R.L. Rudnick, New constraints on the origin of the highly siderophile elements in the Earth’s upper mantle, *Lunar Planet. Sci. XXXV* (2004) 1310.
- [84] J. Li, Y. Fei, Experimental constraints on core composition, *Treat. Geochem.* 2 (2003) 521–546.
- [85] E.H. Hauri, R.W. Carlson, J. Bauer, The timing of core formation and volatile depletion in solar system objects from high precision  $^{107}\text{Pd}$ – $^{107}\text{Ag}$  isotope systematics, *Lunar Planet. Sci.* 31 (2000) 1812.
- [86] R.W. Carlson, E.H. Hauri, Extending the  $^{107}\text{Pd}$ – $^{107}\text{Ag}$  chronometer to low Pd/Ag meteorites with multicollector plasma-ionization mass spectrometry, *Geochim. Cosmochim. Acta* 65 (2001) 1839–1848.
- [87] S.B. Shirey, R.J. Walker, the Re–Os isotope system in cosmochemistry and high-temperature geochemistry, *Annu. Rev. Earth Planet. Sci.* 26 (1998) 423–500.
- [88] T. Meisel, R.J. Walker, A.J. Irving, J.-P. Lorand, Osmium isotopic compositions of mantle xenoliths: a global perspective, *Geochim. Cosmochim. Acta* 65 (2001) 1311–1323.
- [89] D.J. Stevenson, T. Spohn, G. Schubert, Magnetism and thermal evolution of the terrestrial planets, *Icarus* 54 (1983) 466–489.
- [90] M.J. Walter, Melting of garnet peridotite and the origin of komatiite and depleted lithosphere, *J. Petrol.* 39 (1998) 29–60.



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