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Mantle plumes and geochemistry

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Abstract

There is considerable interest in the extent to which mantle plumes exist, how many there may be, and how best they can be recognized. It has proved unexpectedly difficult to image them consistently from seismology, and it has been suggested that they may be recognized from the geochemistry of rocks erupted at the Earth's surface. The difficulty is that plumes are physical features, and they can only be identified geochemically if they are either derived from, or entrain material that has a distinctive geochemical fingerprint. Too often plumes have been invoked because the erupted basalts have a within plate signature, irrespective of whether the volumes of magma or the rates of eruption can be estimated. U-series isotopes in basalts are sensitive to variations in the upwelling rates of their mantle source rocks, and those can be used to invoke upward movements that may be associated with mantle plumes. A contribution from the Earth's core might provide a possible geochemical tracer of deep-seated mantle plumes, although it is difficult to assess whether core material may be readily entrained in the mantle. Given the marked compositional differences between the core and the mantle, it should be possible to identify material that contains a contribution from the core and hence may be inferred to be from the core–mantle boundary. The core should have high Os and W abundances, and distinctive isotope ratios. Arguments for the recognition of core material using Os and W isotopes are therefore reviewed, as are those relying on rare gases to identify contributions from the lower mantle.

Keywords: Mantle plume; Geochemistry; Core contribution; Intraplate basalt

1. Introduction

Mantle plumes are broadly envisaged to be focused upward movement of material within the mantle (Morgan, 1971; Griffiths and Campbell, 1990). They transfer heat from within the earth, they are hotter than the mantle at shallower levels, and they have been widely invoked as the causes of intraplate magmatism. They have been proved difficult to image using seismology (e.g. Ritsema and Allen, 2003), they should be associated with domal uplift of up to about a kilometre, and they have been frequently invoked on the basis of the chemistry of the erupted basalts. But how robust are arguments that invoke plumes on the basis of geochemistry? Mantle plumes are a physical manifestation, and so they will only have a distinctive chemical signal if they happen to have originated in a segment of mantle that can be characterized geochemically. There is therefore an opportunity for some circularity of argument. Here we review how contributions from mantle plumes may be assessed in different intraplate settings.

Fluid dynamic models for the development of plumes indicate that they originate from boundary layers (Griffiths and Campbell, 1990), and in the Earth these

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are most strikingly the lithosphere and the core–mantle boundary (Morgan, 1971). Recently, however, plume-like structures have been identified that originate within layers, the splash plumes of Davies and Bunge (2006). In principle, a mantle plume that emanates from a boundary layer may record a distinctive geochemical signature if the boundary layer is also a chemical boundary. The core–mantle boundary may include material from the core, which should be readily identified, and the D″ layer at the base of the mantle is also thought to have distinctive compositions (e.g. Tolstikhin and Hofmann, 2005) In contrast, chemical changes across possible boundary layers within the mantle are both less obvious and more controversial.

The 670 km discontinuity is recognized as a phase change from the spinel to the perovskite structure with increasing depth. In layered convection models it was often taken as the boundary between a depleted upper mantle that is isolated from a less depleted lower mantle (Richter and McKenzie, 1978), whereas in whole mantle convection models it is simply a phase change with no accompanying change in composition (Albarède and Hilst, 1999). There is increasing evidence in support of transport of material across the 670 km discontinuity. Seismic evidence supports deep subduction through to the lower mantle (Creager and Jordan, 1984; Widiyantoro and van der Hilst, 1996; Albarède and Hilst, 1999; Kellogg et al., 1999; van der Hilst, 2004), and any down going flux must be matched by a rising counter flux. The latter might be diffuse and/or be focused through rising mantle plumes, and either would in turn influence the distribution of geochemical signatures in the upper mantle (Morgan and Morgan, 1999; McKenzie et al., 2004; Meibom and Anderson, 2004). A depleted end-member is likely to be more refractory in terms of major elements as it has already experienced a melting event, while a more fertile component will melt more readily.

The geochemistry of intraplate basalts is for the most part different from those generated in other tectonic settings. Current paradigms envisage that the source of mid-ocean ridge basalts is shallower than those of intraplate basalts, although some of the latter may have been very largely derived from shallow sources within or just below the mantle lithosphere. Nonetheless, such paradigms imply that intraplate basalts are mostly derived from mantle that originated at depths greater than the depleted upper mantle. That in turn implies the need to bring material up from such depths and this has been widely attributed to the presence of mantle plumes (Courtillot et al., 2003). One consequence is a tendency to attribute any basalt with a within plate geochemical signal to the presence of a mantle plume. However, basalts in intraplate settings may be generated in other ways, and it is difficult to invoke the presence of a mantle plume without evidence that there is some form of physical anomaly that might be reflected in regional uplift, relatively high rates of partial melting and large outpourings of basalt.

Partial melting may result from decompression of hotter material to shallower depths in the mantle, from the subduction of lower melting temperature material, such as eclogite, or to the introduction of volatiles, as at subduction zones. Decompression in turn may be linked to extension of the lithosphere (McKenzie and Bickle, 1988; White and McKenzie, 1989), to upwellings in response to edge-driven convection (King and Anderson, 1998) or delamination of portions of the mantle lithosphere (Elkins-Tanton and Hager, 2000; Elkins-Tanton, 2005), or to the emplacement of a mantle plume (Morgan, 1971; Courtillot et al., 2003). During lithospheric extension the degrees of partial melting, and the volumes of melt generated, are linked to the amounts of extension, whereas in mantle plumes they are linked to the excess temperature in the mantle plume. Mantle may melt more readily because it contains more volatiles than the surrounding mantle, and/or because it contains more of a low melting temperature basaltic component.

2. Recognition of intraplate basalts

Geochemical schemes are widely used to infer the tectonic setting in which basaltic magmas are generated. One of the first was the triangular plot of Ti–Y–Zr of Pearce and Cann (1973) which utilizes the observation that intraplate rocks have higher incompatible element contents, and hence high Zr and Ti relative to Y contents, and the mid-ocean ridge whereas island arc rocks are from more depleted sources with lower Zr and Ti relative to Y (Fig. 2). Such schemes are based on statistical analysis of the minor and trace element compositions of basalts generated in known tectonic settings, and then typically applied to older rocks where other evidence for how they were generated has been obliterated. In practice the intraplate basalts used to develop these schemes are ocean island basalts, and so they are basalts that for the most part contain no contribution from the crustal or mantle portions of the overlying lithosphere. Although recycled lithosphere has been invoked in the source of some oceanic basalts (e.g. Hawkesworth et al., 1986; Eiler et al., 1996; Class and Goldstein, 1997) it is rare for this contribution to displace the basalts from the intraplate fields on geochemical discriminant diagrams. Thus such schemes are in effect used to recognize basalts from sub-lithospheric mantle sources, rather than necessarily all those generated in intraplate settings (see Fig. 4), and sub-lithospheric intraplate sources have too often been linked to mantle plumes. These intraplate rocks have relatively smooth mantle normalized trace element patterns (e.g. Hofmann, 1997), they have higher incompatible element abundances than MORB, and are without the negative anomalies at Nb, Ta, and Ti, and positive anomalies at Pb, for example, that characterize subduction related magmas (Fig. 1). In summary, it remains useful to be able to recognize basalts generated in intraplate settings, but whereas such geochemical classification schemes indicate that similar source regions were involved they shed little light on how such magmas were generated. In other words, geochemistry can be used to identify the geochemical characteristics of the mantle source(s) but not the physical process that generates the magma.

3. Rates of partial melting

If mantle plumes represent a physical anomaly at the depths at which partial melting takes place, one approach is to contrast the implications of selected trace element ratios with the rates of partial melting, or at least average eruption rates. The latter can be estimated from the volcanic record, and rates of melting can also be constrained from short-lived U-series isotopes.

The Auckland volcanic field in New Zealand has been active for 150,000 year, an estimated 4.1 km^3 of magma has been erupted, implying an average eruption rate of 3×10^{-5} km^3/year. In contrast the Cape Verdes islands sit above a stationary hot spot in the Atlantic Ocean and have an estimated eruption rate of $\sim 10^{-4}$ km^3/year. Hawaii is the most productive ocean island system, it sits

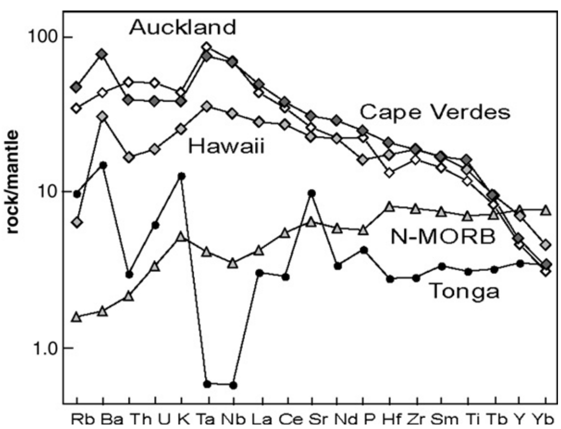

Fig. 1. A mantle normalized minor and trace element diagram illustrating the differences between an average mid-ocean ridge basalts, basalts from Hawaii, Cape Verdes (filled diamonds) and Auckland (open diamonds), and an island arc tholeiite from Tonga.

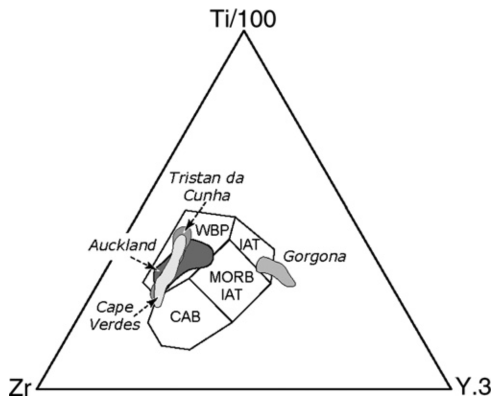

Fig. 2. A Y–Ti–Zr discriminant diagram, after Pearce and Cann (1973), illustrating that intraplate basalts plot in the within plate field irrespective of their estimated melt generation rates. Basalts from Hawaii were used for the initial definition of the within plate field, and the Gorgona rocks are inferred to be from source regions which had undergone a previous partial melting event. WPB — within plate basalts; IAT — island arc tholeiites; MORB — mid-ocean ridge basalts; CAB — calc alkali basalts.

at the end of a hot spot chain, and the eruption rates include values as high as 0.12 km^3/year for Kilauea with an overall average eruption rate of 0.04 km^3/year. Despite the differences of four orders of magnitude in their eruption rates, the magmas generated in these three areas plot in the within plate field of the Ti–Y–Zr discriminant diagram (Fig. 2), and they have fairly smooth mantle normalized trace element patterns (Fig. 1). The implication is that similar mantle source regions underwent partial melting under physical conditions that resulted in very different melt generation rates and volumes of melt. The Hawaiian Chain is widely attributed to the emplacement of a mantle plume, and detailed studies have invoked variations in melt generation rates across the plume from short-lived U-series isotopes (Sims et al., 1999). In contrast, the Auckland volcanic field may reflect lithospheric tensions associated with subduction along the Tonga–Kermadec-New Zealand plate margin. Yet both settings result in broadly similar magmas, although probably generated at different degrees of partial melting. To take one more example, the basalts and komatiites on the island of Gorgona are widely attributed to the presence of a mantle plume (Kerr, 2005) and yet they plot close to the MORB–IAT (island arc tholeiite) fields on the Ti–Y–Zr diagram (Fig. 2), and not in the field for intraplate rocks. In summary, geochemistry constrains the nature of the source regions of intraplate magmatism, but rarely the causes of particular magmatic events.

U-series isotopes are used to investigate the time scales of element fractionation processes within the last few hundred thousand years. But they can be linked to upwelling rates of the mantle source of erupted basalts, and so they bear on discussions of mantle dynamics at sites of mafic magmatism (Bourdon and Sims, 2003, and references therein). Many young igneous rocks have ^{238}U–^{230}Th–^{231}Pa–^{226}Ra isotope values that are out of isotope equilibrium, and these are widely interpreted using dynamic melting models in which the degree of isotope disequilibrium is closely linked to the upwelling velocity of the source peridotite. Such upward movement of mantle in intraplate settings may be in response to lithospheric extension and/or to the emplacement of mantle plumes, and overall there is a broad negative relationship between the degree of isotope disequilibrium and the buoyancy flux at different hot spots (Chabaux and Allègre, 1994; Fig. 3). The faster the upwelling rate the less time the upwelling mantle is in the melt zone, and so the smaller the degree of isotope disequilibrium that results. Hawaii has by far the largest buoyancy flux of the current hot spots, and so it tends to have small degrees of isotope disequilibrium (Fig. 3). In more detail it has been shown that the variation in U-series isotopes in rocks across the Hawaiian hot spot is consistent with variations in upwelling velocity of over two orders of magnitude from the centre to the margin of the hotspot (Sims et al., 1999; Bourdon and Sims, 2003). Thus the U-series isotope data are widely interpreted to require upwelling of the mantle in intraplate settings, even in sites where there is no lithospheric extension. The upward flow is focused in ways that many would interpret as a mantle plume, even though the constraints from U-series isotopes are only for the depths at which melting takes place, and not for the depths at which the upward movement of material commenced.

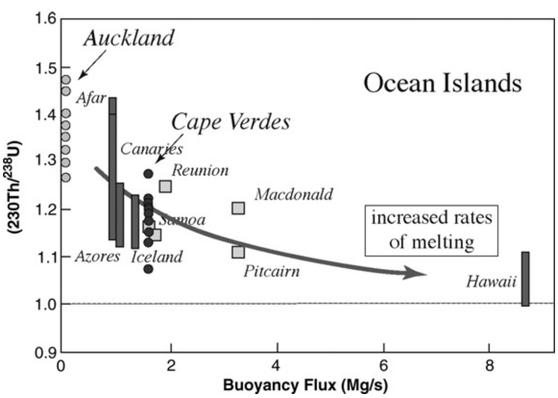

Fig. 3. Plot of ($^{230}Th/^{238}U$) versus buoyancy flux for different hot spots after Chabaux and Allègre (1994). Higher buoyancy fluxes are associated with higher rates of melting and hence lower ($^{230}Th/^{238}U$) values. Data also from Turner et al. (1997), Widom et al. (1997), Sims et al. (1999), Vigier et al., (1999), Thomas et al. (1999), Lundstrom et al. (2003) and Kokfelt et al. (2003).

4. Continental flood basalts and mantle plumes

The most striking outpourings of basalt, at least over the last 250 Myr, are in large igneous provinces, or more specifically in continental areas, continental flood basalts (CFB) (Mahoney and Coffin, 1997). They range in estimated erupted volumes from 0.18×10^6–3×10^6 km^3, but most have suffered significant erosion, and constraining average eruption rates in rocks that are 10s of millions of years old require exceptionally detailed dating programmes. Nonetheless average eruption rates are almost 1 km^3/year, significantly greater than those for other intraplate settings and subduction related magmatism ($\sim 10^{-2}$ to 10^{-3} km^3/year, White et al., 2006). It is tempting to consider one model for all CFB, but there are clear differences in composition and estimated eruption rates. The Deccan CFB has received considerable attention, in part because it was erupted at the K/T boundary, and in part because it is well preserved. There is a main pulse of magmatism at 66–65 Ma, preceded and followed by smaller volumes of magma erupted over an 8 Myr interval. One formation, the Ambenali, has compositions little affected by material from either the mantle or the crust within the continental lithosphere (Lightfoot et al., 1990). Rather its isotope and trace element signals are similar to those generated on Reunion, consistent with derivation from similar sub-lithospheric mantle source regions.

The estimated eruption rates for the main phase of the Deccan CFB are ~ 2 km^3/year, almost two orders of magnitude greater than those on Hawaii. Similar sub-lithospheric source regions have been sampled for the last 65 Myr in a hot spot trace across the Indian Ocean that starts with the Deccan and is now under Reunion. The eruption rates have decreased from ~ 2 km^3/year in the Deccan to $\sim 2.4 \times 10^{-3}$ km^{-3}/year on Reunion (White et al., 2006), and so the effect of the physical anomaly responsible for melting has lessened markedly with time. There is no evidence that these lavas were derived from a more volatile rich source that might have lessened its influence with time, and most interpretations have sought to explain the rates and amounts of melting in terms of excess temperatures. The changes in volumes and eruption rates are consistent with plume models in which most melt generation is associated with emplacement of the plume head, and this decreases with the emplacement of the smaller, albeit hotter tail (Griffiths and Campbell, 1990). However, using the parametization of McKenzie and Bickle (1988) partial melting only takes place beneath the continental lithosphere at significantly elevated temperatures. Thus for a potential temperature of 1480 °C there will be no melting in the asthenosphere if the overlying lithosphere is greater than 100 km thick, and for a thickness of 170 km, melting will not start until the potential temperature exceeds 1630 °C. One consequence is that CFB magmatism may be best developed where the lithosphere has already been thinned significantly, and even in the plume model (e.g. White and McKenzie, 1989), the presence or absence of CFB may reflect the thickness of the overlying lithosphere rather than simply the distribution of plumes (Hawkesworth et al., 1999).

The Parana has often been regarded as an anomalous CFB. Most of the rocks have a strong lithospheric signature (Fig. 4), but it preserves an internal chemical stratigraphy, and exceptionally different chemical units can be linked to different dyke swarms with different orientations. Thus, the volumes of magma erupted through different dyke swarms, for which average amounts of extension can be estimated, can be calculated from the volumes of different magma types in the lava pile. With good chronology it is therefore possible to estimate average rates of extrusion through different dyke swarms with different degrees of extension. This was the basis of models that sought to generate the estimated variations in melt volume through time, and in particular the observation that the main pulse of magmatism took place 4–5 Myr *before* the generation of the oldest oceanic crust in the South Atlantic. Thus there is not a progressive increase in the volumes of magma erupted with increasing amounts of extension at the time of the opening of the South Atlantic, as might be expected if the magmas were primarily derived from a mantle plume. Rather there is a predominantly lithospheric signature in most of the basalts, and Hawkesworth et al. (2000) took the 2 Myr gap between the CFB and oceanic volcanism to mean that the two were derived from different sources, that most of the Parana CFB were derived from the mantle lithosphere, before further extension enabled melting to take place within the plume. In such models the plume provides heat for melting, but magmas from the plume are only recognized late in the evolution of the province.

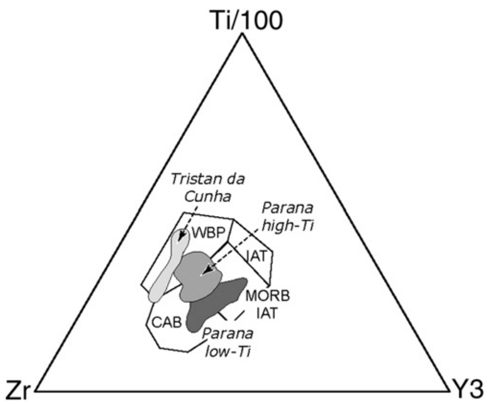

Fig. 4. An Y–Ti–Zr discriminant diagram, after Pearce and Cann (1973), illustrating the shift from the strong lithosphere signal in the Parana continental flood basalts to the more classically within plate compositions of the Tristan da Cunha rocks (Le Roex et al., 1990; Peate, 1997, and references therein).

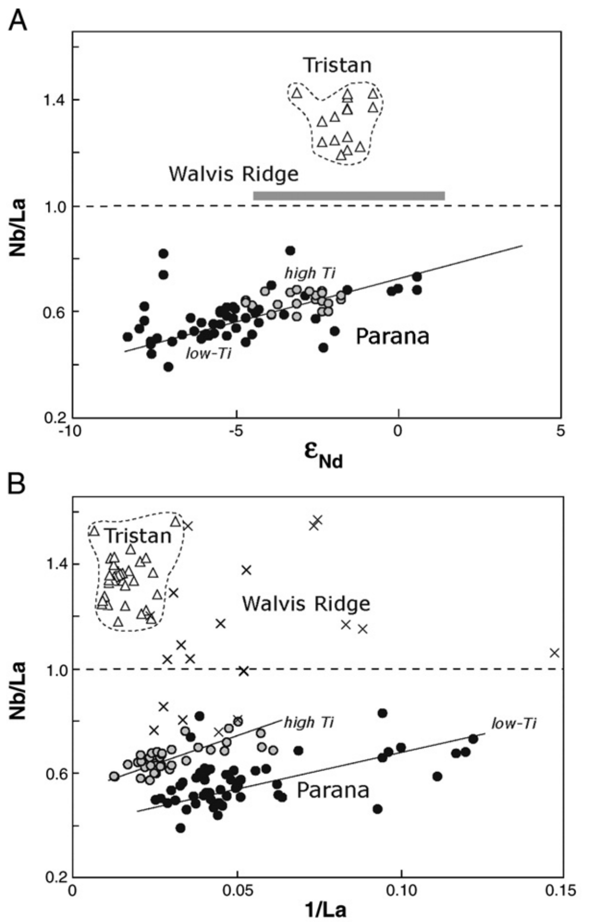

Fig. 5. Plots of Nb/La versus εNd (A) and 1/La (B) for basalts from the Parana, the Walvis Ridge and Tristan da Cunha, which are in the same related magmatic province. Sub-lithosphere melts are inferred to have Nb/La ratios > 1, and Nb/La ratios are not available on the samples from the Walvis Ridge for which there are Nd isotope analyses. Data from Humphris and Thompson (1983), Le Roex et al. (1990), Richardson et al (1982), and Peate (1997) and references therein.

An alternative model is that the lithosphere signal in the Parana basalts was introduced by contamination of magmas derived from below the lithosphere, as from a mantle plume. The lithosphere tends to be characterized by low εNd and Nb/La ratios, and (Peate, 1997) noted that εNd decreased with Nb/La ratios in the high- and low-Ti Parana basalts (Fig. 5A). Such trends might be modelled by progressive lithosphere contamination of plume derived melts which are inferred to have relatively high Nb/La. The data in Fig. 5 indicate that the Nd isotope ratios of the high Nb/La end-member, i.e. with Nb/La = 1 similar to Nb/La in primitive mantle, are ϵNd of ~ +7 to +8. Such Nd isotope values are higher than those that characterize more recent eruptions from Tristan da Cunha (Fig. 5A), but they are similar to those in many oceanic basalts. However, a plot of Nb/La versus 1/La highlights that the end-member with Nb/La = 1 also has very low La abundances. The logical implication of contamination models is that they are easier to invoke if the initial magmas have low incompatible element contents, and in the case of the Parana these would be ~ 5 to ~ 9 ppm for La (Fig. 5B). Such values compare with 3 ppm La in average MORB, 24 ppm in average Walvis Ridge basalts, and 72 ppm in the Tristan da Cunha rocks.

Gallagher and Hawkesworth (1994) highlighted the decrease in estimated melt generation rates of over an order of magnitude from the Parana CFB, down the Walvis Ridge and the Rio Grande Rise to near the mid-Atlantic ridge at the present day. In models in which magma from the sub-lithospheric mantle is variably contaminated in the lithosphere, the La contents of these sub-lithospheric magmas increase from 5 ppm to 72 ppm as the rates of melt generation decrease (Fig. 5B). In the simplest partial melting model of primitive mantle, the degrees of melting decrease from ~ 11% to 0.8%, and these are minimum values, because the isotope data indicate that the high Nb/La end-member to the Parana was depleted relative to bulk earth (Fig. 5A). Nonetheless, the 11% melting needs to have taken place beneath a lithosphere that was at least 130 km thick, and as the lithosphere thinned in response to continental break-up the rates and degrees of melting decreased markedly. Thus, in models in which most of the melt comes from the plume the potential temperature in the plume under the Parana appears to have been at least 1600 °C, and this would have to have decreased markedly by the time continental separation took place (Gallagher and Hawkesworth, 1994). The temperatures in the tail of a plume are thought to be higher than those in the plume head, although the volume of hot mantle is much smaller, and such models offer little explanation for the cessation of the main phase of CFB magmatism 2 Myr before the onset of oceanic magmatism (Hawkesworth et al., 2000).

5. Deep mantle signatures

Constraining the depths of origin of the source regions for basalts remains extremely difficult. Broadly three approaches have been used. One is to infer depths from the chemical signatures of minerals that are only stable over particular depth ranges, for example, amphibole (e.g. Hawkesworth et al., 1990; Class and Goldstein, 1997). A second relies on models in which the lower mantle is more primitive, and less degassed, and high $^3He/^4He$ ratios have been frequently taken to be indicative of deep mantle source regions (Kurz et al., 1982; Farley et al., 1992). A third approach is to say that irrespective of models for the evolution of the mantle, some distinctive compositions are only present at certain depths, such as in the core.

5.1. Noble gases

Noble gases have long been used to characterize intraplate and mid-ocean ridge lavas. The $^3He/^4He$ ratios of MORB have been widely regarded as being relatively constant with $R/R_A = 8 \pm 1$, where R_A is the $^3He/^4He$ ratio of air (Hilton and Porcelli, 2003), although unfiltered data seem to suggest a much greater variance that may range up to R/R_A values of ~ 20 R_A (Anderson, 2000; Meibom et al., 2003). Analyses of OIB range towards even higher R/R_A values of up to 50 R_A in lavas that are associated with hot spots, as on Baffin Island (Stuart et al., 2003).

$^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ display distinct arrays where MORB plot along a mixing line between air and a presumed solar composition (Trieloff et al., 2000). OIB, on the other hand, tend to plot along slopes with higher $^{20}Ne/^{22}Ne$ for any given $^{21}Ne/^{22}Ne$, which implies higher time-integrated $^{21}Ne/(U+Th)$ ratios in their source.

The He and Ne isotope ratios of MORB and OIB also indicate that these magmas are derived from different source reservoirs in the mantle. A common interpretation has been to invoke a layered mantle in which the lower mantle is less degassed and therefore has more primitive noble gas signatures. The lower mantle is consequently invoked as the source of high $^3He/^4He$ OIB, with the implication that such OIB are associated with plumes from the deep mantle (Kurz et al., 1982; Farley et al., 1992; Allègre and Moreira, 2004). This interpretation was initially linked to the assumption that noble gases have D_{He} and $D_{Ne} \ll D_U$ and D_{Th}, however, recent experimental data suggests that D_{He} might actually be greater than D_U and D_{Th} (Parman et al., 2005). Furthermore, Ellam and Stuart (2004) and Class and Goldstein (2005) point out that OIB with the highest R_A values have trace element data that are more in accordance with a depleted MORB-like mantle component, and hence suggest that a long term undegassed mantle source is unnecessary. This also seems to be consistent with the observation that OIB have higher $^{20}Ne/^{22}Ne$ for any given $^{21}Ne/^{22}Ne$, if $D_{Ne} > D_U$, D_{Th}. Rare gases in oceanic basalts are therefore interpreted in terms of pockets of undegassed mantle, and in terms of variable contributions from recycled crust, and as such they arguably contribute less than was initially perceived to whether certain OIB are linked to plumes from the deep mantle (e.g. Allègre and Moreira, 2004).

5.2. Pt–Re–Os and W isotopes

The core–mantle boundary is associated with a marked chemical change from the silicate mantle to the metallic core, and distinctive material may also be present in the D″ layer at the base of the mantle (Tolstikhin and Hofmann, 2005). A chemical signal from either the metallic core or the D″ layer in intraplate basalts might therefore be taken as evidence that the source of those basalts had been at the core/mantle boundary. It is tempting then to infer that material was transferred from the core/mantle boundary in a mantle plume, although strictly speaking geochemistry provides little constraint as to *when* the source material of the basalts was at the core/mantle boundary. The core is much denser than the silicate mantle, but oxygen saturation in the core enables siderophile elements to be released back into the mantle (Walker et al., 2002; Walter and Elliott, 2006). Following the development of improved techniques for the analysis of Os and W isotope ratios, recent discussions have been concerned with whether contributions from the core might be detected in intraplate basalts.

A contribution from the core is most likely to be recognized using siderophile elements such as platinum (Pt), rhenium (Re), osmium (Os) and tungsten (W), which are strongly enriched in the core relative to the mantle. Even a very small core contribution (<0.5%) in mantle peridotite would result in a significant isotope imprint on the mixture, if the core has a unique siderophile element isotope signature (Walker et al., 1995; Brandon et al., 1998, 1999, 2003; Schersten et al., 2004). Core contributions have been invoked on the basis of radiogenic and positively correlated $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ ratios and high Fe/Mn ratios in basalts, and they should be apparent from variations in W isotopes (Brandon et al., 1998, 1999, 2003; Humayun et al., 2004; Schersten et al., 2004).

5.2.1. Pt–Re–Os

Pt–Re–Os isotopes are particularly sensitive to contributions from the core because these elements are very much more abundant in the core than in the mantle (Walker et al., 1995; Brandon et al., 2003). The isotope ratios of Os reflect Pt/Os and Re/Os fractionation in the core and these ratios are assumed to be higher in the outer core (see below; Walker et al., 1995). ^{190}Pt decays to ^{186}Os and ^{187}Re decays to ^{187}Os, and so with time elevated Pt/Os and Re/Os ratios result in high $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ ratios in the outer core (Walker et al., 1995). Pt, Re and Os are refractory elements and they occur in broadly chondritic relative proportions in the bulk Earth. This will also be true for the bulk core since these elements were almost totally partitioned into core, and it follows that the inferred elevated Pt/Os and Re/Os ratios in the outer core are the products of core differentiation processes. The values of the $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ ratios in the outer core therefore depend on the degree of Pt–Re–Os fractionation between the Earth's inner and outer cores, and when that took place.

The crystallisation history of the Earth's core depends on its latent heat, the heat flux across the core/mantle boundary and the presence of heat producing radioactive elements. For example, potassium may be present to a few hundred parts per million in the core (Murthy et al., 2003), and the associated radioactivity might mean that the inner core started crystallising earlier. Results from thermal models for the onset of inner core crystallisation are uncertain, but they typically indicate that inner core crystallisation started later than 2.2 Ga (Labrosse et al., 2001; Labrosse, 2003; Nimmo et al., 2004; Butler et al., 2005; Nakagawa and Tackley, 2005) although one scenario extends the date back to 3.3 Ga (Nakagawa and Tackley, 2005).

The low pressure crystallisation of iron meteorite fractionates the PGE such that Pt and Re are enriched relative to Os in the residual liquids (Walker et al., 1995). Inner core crystallisation would fractionate Pt–Re–Os in the same fashion if the observed iron meteorite partitioning characteristics are valid at core pressures, and would result in an outer core that has suprachondritic Pt/Os and Re/Os ratios. Elevated Pt/Os and Re/Os ratios will result in higher $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ ratios than average mantle or bulk core. A core contribution to the mantle should therefore result in positively correlated $^{187}Os/^{188}Os$ (commonly expressed as γOs, which is the percent deviation from the chondrite reference, (Shirey and Walker, 1998)) and $^{186}Os/^{188}Os$ ratios, where the slope and variation in isotope ratios depend on the timing and degree of inner core crystallisation and the magnitude of the contribution.

Positively correlated $^{187}Os/^{188}Os$–$^{186}Os/^{188}Os$ arrays are observed in recent Hawaiian picrites (Brandon et al., 1998, 1999) and 89 Ma old Gorgona komatiites (Brandon et al., 2003). Suprachondritic individual isotope analyses have also been reported from the 250 Ma Siberian trap (Walker et al., 1997) and as an isochron initial ratio for the 2.8 Ga Kostomuksha komatiites (Puchtel et al., 2005). These data were interpreted in terms of a core contribution, and Brandon et al. (2003) infer a present day outer core composition of γOs = 17.5 and $^{186}Os/^{188}Os = 0.119870$. This interpretation of the observed isotope correlations indicate that the average outer core Pt/Re ratio is in the range of ~55–86 depending on when the inner core crystallised (Brandon et al., 2003), and crystallization had to start no later than 3.4 Gyr ago, which contrasts with most of the thermal models (Puchtel et al., 2005).

Meibom and Frei (2002) and Meibom et al. (2004) reported suprachondritic $^{186}Os/^{188}Os$ ratios for PGE alloys, which are thought to be representative of the upper mantle and not easily reconciled with an outer core origin, and interpreted them as the product of common upper mantle fractionation processes. Walker et al. (2005) did not find suprachondritic $^{186}Os/^{188}Os$ ratios in alloys from the same region and the reasons for this discrepancy is unclear. Nonetheless, mantle sulphides and PGE alloys can display fractionated PGE patterns that depend on whether they occur as silicate inclusions or interstitial grains and on the degrees of mantle melting involved (Alard et al., 2000; Bockrath et al., 2004). Further work is required to elucidate the importance of indigenous mantle processes that affect HSE fractionation due to e.g. sulphide or alloys, which play an important role in regulating the highly siderophile elements in the mantle. Fig. 6 summarises measured Pt/Os and Re/Os ratios in komatiites and sediments, mantle peridotites, chromites from ophiolites, chondrites and Fe–Mn crusts, and compares these with the relative fractionation in Pt/Os and Re/Os implied by the $^{186}Os/^{188}Os$–$^{187}Os/^{188}Os$ data from Hawaii (Brandon et al., 1998). There are wide variations in measured Pt/Os and Re/Os ratios, and clearly if such materials are isolated for significant periods of time they will result in variable Os-isotope ratios. This highlights the tension between presuming that enriched $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ values require contributions from the core, when they might alternatively be due to the recycling of crustal materials, such as Fe–Mn crusts, and/or to mantle enrichment processes that result, for example, in clinopyroxenite veins in peridotite (Buchl et al., 2002; Sobolev et al., 2005). Strikingly the latter would result in the enriched Os-isotope ratios seen in Hawaii (Brandon et al., 1998, 1999) in just 150 Myr, although such signals would presumably be diluted during partial melting of veined peridotite.

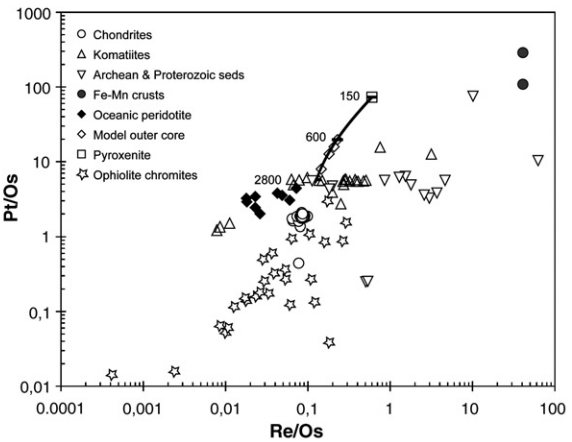

Fig. 6. A plot of Re/Os ratio versus Pt/Os ratio for chondrites, (Brandon et al., 2005; Horan et al., 2003) komatiites (Puchtel and Humayun, 2005), Archean and Proterozoic sediments (Siebert et al., 2005), Fe–Mn crusts (Baker and Jensen, 2004), oceanic peridotites (Snow and Schmidt, 1998), model outer core (Brandon et al., 2003), clinopyroxenite (Buchl et al., 2002) and ophiolite chromites (Frei et al., 2006). The curve represents the Re–Pt–Os ratios and time required after (instant) fractionation from a chondrite precursor to develop the maximum coupled Os-isotope enrichments observed in Hawaiian lavas. Tick marks for 150, 600 and 2800 My are rarely indicated. Note that outer core values are grossly underestimated as the curve does not account for prolonged crystallisation history, which is the case for the core (c.f. Brandon et al., 2003).

5.2.2. Hf–W

An independent test of a contribution from the core is provided by the extinct Hf–W isotope system. ^{182}Hf was extant for the first ~60 Myr of solar system history and it decayed to ^{182}W. Thus subsequent mantle processes that fractionate Hf/W ratios do not have any effect on the isotope composition of W, since that can only be altered by mixing material from reservoirs that fractionated very early in the Earth's history while ^{182}Hf was still extant. The number of such potential reservoirs within the Earth is strongly limited, possibly to just two, the core and the silicate Earth. Additional sources could include extraterrestrial material that commonly has different W isotope ratios from the parts of the silicate Earth that we can currently sample (Horan et al., 1998; Kleine et al., 2002; Yin et al., 2002; Kleine et al., 2004; Scherstén et al., 2006).

The Hf/W ratio of the primitive mantle was strongly increased due to the siderophilic behaviour of W during core formation (Newsom et al., 1996). Hf and W are both refractory elements and it is generally assumed that the bulk Earth is chondritic with respect to its Hf/W ratio. W enrichment of the Earth's core is ~30 times that in the primitive mantle and W appears to be isotopically homogenous in the Earth's mantle (Schoenberg et al., 2002;

Scherstén et al., 2004). This implies that the convective mantle that is currently sampled in the generation of basalts has been well mixed since ^{182}Hf became extinct ~60 Myr after solar system formation. The mantle ^{182}W/^{184}W ratio is higher than that of chondrites by approximately 2ϵ values, where ϵ is the deviation in parts per ten thousand from the average chondrite ratio (Kleine et al., 2002; Schoenberg et al., 2002; Yin et al., 2002; Scherstén et al., 2004; Kleine et al., 2004). Mass balance requires the core to have a slightly lower W isotope ratio than bulk chondrites, i.e. ~2ϵ units lower than the mantle.

A core contribution should therefore lower the ^{182}W/^{184}W ratio in any mixed core–mantle source rock. The size of the shift depends on the concentration and isotope contrasts between the core and mantle. The latter is reasonably constrained to be ~2ϵ, but the differences in element concentrations are more difficult to tie down. Current estimates for the abundance of W in the silicate Earth following the depletion in W due to core formation range between 10 and 21 ppb with a best estimate of 16 ppb (Newsom et al., 1996). W also behaves as an incompatible element during partial melting of the mantle, much like La or Th. Thus W is enriched in the melt, and the residual mantle has reduced W contents. This is important as it might increase or decrease the difference in the W abundances between the core and the mantle. The continental crust has high W contents of ~1000 ppb, and so generation of the crust lowered the average mantle concentration to ~8 ppb. It is possible that the W content of the lower mantle might range up to 19 ppb if (a) W depletion due to core formation was minimal and (b) the continental crust was largely derived from the upper mantle (Newsom et al., 1996; Scherstén et al., 2004). W might be moderately compatible in the inner core and so crystallisation of the inner core will lower the W content in the outer core and hence decrease the contrast in W contents between the core and the mantle. Crystallization of the inner core will not affect the W isotopic composition of the outer core as the Hf concentration of the core can be safely assumed to be zero, and all ^{182}Hf was extinct by the time of onset of inner core crystallisation. In this discussion it is assumed that any decrease in ϵW due to a contribution from the core, should be associated with a correlated increase in ^{186}Os/^{188}Os and ^{187}Os/^{188}Os.

Using estimates of the average W contents of the core and the mantle, Scherstén et al. (2004) predicted a decrease in ϵW of up to 0.5ϵ for a core contribution of ~0.5 wt.% as suggested by Brandon et al. (2003). Such an anomaly should be readily resolved at the current analytical precision, but Hawaiian lavas, including new samples of some of those analysed by Brandon et al., 1998, 1999) have ϵW = 0.0 ± 0.1, and no negative anomalies could be resolved (Scherstén et al., 2004). Scherstén et al. (2004) therefore concluded that there is no support from W isotopes for a core contribution in the source of these Hawaiian lavas.

Is it possible that the W null result for the Hawaiian lavas is due to insufficient analytical sensitivity? As already mentioned, W is strongly incompatible and enriched in partial melts of the mantle, sediments and the continental crust. A recycled component would therefore dramatically increase the W content of the mantle that might have mixed with material from the core. This would reduce the difference in the W concentrations of the core and mantle material such that the W isotope effects from a core contribution might become too small to resolve. Brandon and Walker (2005) modelled a 5% contribution of a recycled component with 1100 ppb W and ϵW = 0. This increases the mantle W abundance from 8 ppb in the preferred model of Scherstén et al. (2004) to 62.6 ppb, and is sufficient to lower core–mantle concentration contrast so that the current analytical precision for W is insufficient to resolve the calculated anomalies.

But how might such a proposed increase in W in the mantle component be tested? We infer that such an increase in the W concentration of the Hawaiian source will be reflected in melts with relatively high W contents. W/Th ratios display very small ranges in silicate rocks of very different origins (Newsom et al., 1996), and so it appears that W behaves very similarly to Th during partial melting and melt differentiation. The paucity of W data for Hawaiian rocks is therefore compensated by the use of Th as an analogue for W. Using the Hawaiian picrite data from Norman and Garcia (1999) and three W data points from Becker et al. (2004), the effects of fractional crystallisation were stripped off by adding or removing a Fo_{88} olivine component to correct the Th and W concentrations to that of a primary lava with 16 wt.% MgO (Norman and Garcia, 1999). W concentrations were estimated assuming primitive melt W/Th ratios = 0.25. This value is higher than that of the average mantle and so it increases the estimated W value in the mantle source. Nonetheless, the scatter of the Hawaiian data is consistent with a source concentration of between 8 and 12 ppb W (Fig. 7), highlighting that the source had not been enriched in W by the addition of a recycled component. From the discussion above this implies that the W isotope sensitivity should be sufficient to detect a core contribution in the Hawaiian basalts (Brandon and Walker, 2005).

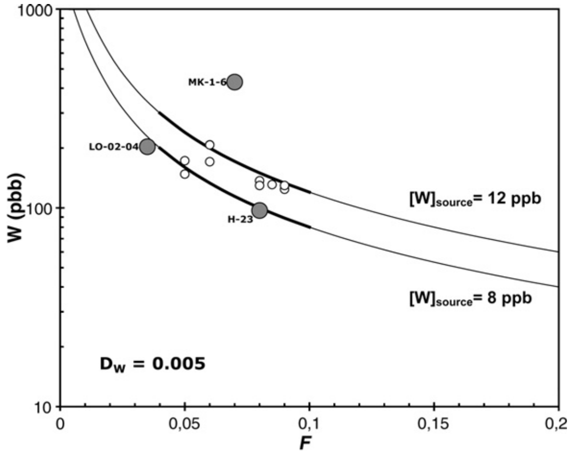

Fig. 7. A plot of fractional melting versus tungsten melt concentration assuming incremental aggregated melting. The two curves represent melt sources of 8 to 12 ppb W, and the bold part of each curve represents the inferred degree of melting for Hawaiian picrites (Norman and Garcia, 1999). The three W data from Becker et al. (2004) for Hawaiian picrites are plotted with large grey circles, and the remaining data were inferred from the Th-concentrations of (Norman and Garcia, 1999). For discussion see text.

5.2.3. Mn-crust component

Mn-crusts have very high Pt/Os ratios that could produce very radiogenic $^{186}Os/^{188}Os$-ratios (Baker and Jensen, 2004) (Fig. 6). The coupled $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ enrichments have therefore been ascribed to a recycled Mn-crust component (Ravizza et al., 2001; Baker and Jensen, 2004; Scherstén et al., 2004). Both combined Nd–Hf and Tl isotope systematics lend further support for a Mn-crust/pelagic sediment component in the Hawaiian lavas (Blichert-Toft et al., 1999; Nielsen et al., 2006). However, Tl-isotopes, which should be very sensitive to the Mn-crust component, which has high Tl-concentrations and distinct Tl isotope ratios, are not simply correlated with $^{186}Os/^{188}Os$-ratios, and this has been taken to invalidate the Mn-crust model for explaining the enriched $^{186}Os/^{188}Os$-ratios (Nielsen et al., 2006).

5.2.4. Hidden reservoir

It has been recognized for some time that the ϵNd–ϵHf array for mantle-derived rocks does not go through the estimate for chondrites, which is required by the chondrite Earth model (Blichert-Toft and Albarede, 1997). This led to the suggestion of the existence of a reservoir that was isolated from the convective mantle for an extensive part of the Earth's history. Tantalising evidence for such a reservoir recently emerged with the demonstration that $^{142}Nd/^{144}Nd$ in the upper mantle is higher than in chondrites (Boyet and Carlson, 2005). The $^{142}Nd/^{144}Nd$ ratio is modulated by short-lived decay of the presently extinct isotope ^{146}Sm, and higher $^{142}Nd/^{144}Nd$ ratios in the mantle than in chondrite require either that the bulk Earth is non-chondritic, or there is a terrestrial reservoir that formed early in Earth's history while ^{146}Sm was extant. Boyet and Carlson (2005) argue for such a depleted reservoir and that it was formed by the generation of mafic crust through partial mantle melting in the first ~30 Myr of Earth history. This crust was subsequently subducted, perhaps to the base of the mantle, and the undulating seismic anomalies above the core–mantle boundary in the D″ layer remain a strong candidate for such a reservoir. It has further been suggested that this model could explain noble gas isotope systematics (Tolstikhin and Hofmann, 2005; Tolstikhin et al., 2006).

An interesting prediction from the suggestion that the D″ layer might contain a contribution from this old crust is that mantle plumes derived from the D″ layer might carry ancient signals such as sub-chondritic $^{142}Nd/^{144}Nd$ ratios that would result from the sub-chondritic Sm/Nd ratios in the first 30 Myr of Earth history. Such $^{142}Nd/^{144}Nd$ anomalies might in turn be expected to be associated with slightly negative ϵW, as this reservoir is predicted to have formed sub-chondritic Hf/W ratios while ^{182}Hf was also extant. Boyet et al. (2005) searched for $^{142}Nd/^{144}Nd$ anomalies in a number of intraplate basalts, including Hawaiian lavas, but reported no anomalies, which is consistent with the current W data. It is not obvious that such a reservoir would evolve such that it could explain coupled $^{186}Os/^{188}Os$ and γOs enrichments, but correlated ϵW–$^{186}Os/^{188}Os$ or ϵW–$^{142}Nd/^{144}Nd$ might provide better tests for contributions from either the core or a 'hidden reservoir'.

6. Summary

Mantle plumes are physical features, and they might be identified geochemically if they are either derived from, or entrain material that has a distinctive geochemical fingerprint. They tend to be associated with anomalous volumes of magma, but they have too often been invoked because the erupted basalts have a within plate signature, in some cases because it is difficult to constrain the volumes of magma or the rates of eruption in older geological terrains. U-series isotopes in basalts are sensitive to variations in the upwelling rates of their mantle source rocks, and so these have been used to invoke upward movements that may be associated with mantle plumes. There is considerable interest in the possibility of identifying a core contribution in intraplate lavas as it would provide evidence for a deep origin of the source rock. A classic mantle plume might then be the only viable mechanism to explain such signals if they are uniquely recognized in intraplate basalts. However, the PGE are highly variable in both mantle-derived rocks and in crustal rocks that might be recycled back into the mantle, and so it remains difficult to establish that enriched Os-isotope signals are necessarily due to a core contribution (Fig 6). Attempts to detect a core contribution using W isotopes have so far proved unsuccessful, but there is also considerable current interest in whether old signatures, such as sub-chondritic $^{142}Nd/^{144}Nd$ ratios have been preserved in mantle domains isolated from very early in Earth history.

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