



## Isotopes, DUPAL, LLSVPs, and Anekantavada



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## ABSTRACT

The mantle perspective provided by radiogenic isotope geochemistry has evolved over the last 40 years. Although the idea of an upper mantle depleted in incompatible elements by extraction of partial melt remains, ideas about the lower mantle have evolved from simple primitive material occupying the lower two-thirds of the mantle to a heterogeneous, multicomponent lower mantle. The lower mantle is sampled by plumes rising from it, and although each is compositionally unique, these plumes can be divided into 5 or 6 genera with the compositional similarity within each suggesting they have evolved in similar ways. The dominant signature in these plumes is that of lithospheric material carried into the deep mantle through subduction, subduction erosion, and continental foundering, and these processes have also polluted and refertilized the depleted upper mantle. The stable isotope geochemistry of these plumes confirms the presence of recycled material, including material derived from the continents, oceans and atmosphere. Noble gas isotope ratios provide a dramatically different perspective: that of reservoirs of noble gases isolated from the convecting mantle for the entire history of the Earth. Neither perspective is likely to be wrong and the conclusion to be drawn is that plumes, at least some of them, draw on reservoirs of both recycled and primitive material from the deep mantle. The difference in noble gas content in the primitive and recycled material may well be such that the primitive noble gas isotopic signature dominates in any mixture of these.

In the meantime, the suprachondritic  $^{142}\text{Nd}/^{144}\text{Nd}$  ratio of the modern mantle has reopened the question of the composition of the Earth and therefore primitive mantle. If this is not entirely a result of nebular isotopic heterogeneity, then “primitive mantle”, defined as the composition that has given rise to the lithosphere and convecting mantle, appears to be depleted in light rare earths, and likely other incompatible elements such as U and Th. This material would have  $\epsilon_{\text{Nd}}$  in the range of 3 to 7, which matches the most common compositions observed in oceanic island basalts, particularly those of the PREMA genera. PREMA cannot be truly primitive mantle, even defined in this way, instead, it appears to consist of balanced mix of recycled enriched and depleted components with only a limited contribution from long-isolated, nearly primitive material.

As the geochemical perspective of the mantle has evolved, so has the geophysical one, and it now reveals a highly heterogeneous lowermost mantle dominated by two large low-shear-wave velocity provinces (LLSVPs) beneath Africa and the South Pacific and associated with the DUPAL anomaly. The latter appears to actually be two anomalies, DUPAL and SOPITA, each closely associated with an LLSVP. Mantle plumes have now been shown to preferentially rise from the margins of these structures, while subduction zones overly apparently cold high-seismic velocity regions surrounding the LLSVPs. The LLSVPs appear to be both hot and dense, and may consist of the PRIMA-like mixture of recycled and primitive material present in many mantle plumes. Geoneutrino studies may eventually resolve some of these questions, including both the total amount of U and Th in the Earth and whether these elements are concentrated within the LLSVPs.

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## 1. Introduction

The Earth's mantle profoundly affects the Earth's surface and therefore life upon it. Convection within the mantle drives continents around on the surface like bumper cars at a carnival. Collisions produce mountain ranges that divert atmospheric currents and block migration and trade routes. Ocean crust subduction produces earthquakes and volcanoes that can produce massive societal disruptions. Subduction and volcanism also modulate atmospheric CO<sub>2</sub> on long time scales, thereby modulating global climate. An understanding of our planet thus requires an understanding of the mantle. Some aspects are reasonably well understood, for example, plate tectonics driven by upper mantle thermal convection. The more remote deeper mantle is far less well understood. Among other things, the deep mantle may be the source of mantle plumes that are responsible for oceanic island volcanoes and perhaps other instances of intraplate volcanism (Morgan, 1971). The compositions of the oceanic island basalts (OIB) differs significantly from lavas erupted elsewhere, such as at mid-ocean ridges and in island arcs. If they are the products of mantle plumes, then they represent a unique sample of deep mantle material. What then can they tell us about the Earth's deep interior? How do we reconcile their geochemistry with what other scientists, including seismologists, mineral physicists, and geodynamicists, have learned about the Earth's deep interior?

According to the Jainist concept of *Anekantavada*, the truth depends on one's point of view, and no single point of view comprises the complete truth (the analogous concept in western philosophical thought is *Perspectivism*, generally attributed to German philosophers Gottfried Leibniz and Friedrich Nietzsche). The point is often made with the Indian parable of the *six blind men and the elephant*, in which six blind men are asked to determine the true nature of an elephant by feeling various parts of its body. One feels the legs and says it is like a tree trunk, one feels the ear and says it is like a leaf, one feels the tail and says it is like a rope, etc. *In trying to understand the nature and evolution of the mantle, scientists are indeed blind: we cannot see through its nearly 2900 km thickness.* In seeking the true nature of the Earth's mantle, scientists have been somewhat like the blind men: seismologists 'feel' regions of hot and cold, low and high density, mineral physicists 'feel' phase changes, trace element and isotope geochemists 'feel' recycled material from the Earth's surface, and noble gas geochemists 'feel' primitive reservoirs. These perspectives are not wrong, merely incomplete. *The task then is to assemble these various perspectives to produce a more complete picture of the mantle, which is the objective of this review.* My own background and the nature of this journal means, of course, this will be primarily a geochemical perspective, but one that relies on seismology, geodynamics, and mineral physics as well.

While it is not yet possible to assemble the entire image, it is becoming clear that it is quite different one from the one imagined a few decades ago of an incompatible element depleted upper mantle

overlying a primitive lower mantle. Radiogenic isotope geochemistry has demonstrated that while extraction of partial melts to form crust has extensively depleted the mantle in incompatible elements, subduction, subduction erosion, and continental foundering has returned incompatible elements to the mantle, locally enriching it above original primitive mantle levels. Stable isotope geochemistry demonstrates that surficial material has been widely recycled into almost all the mantle, including both the upper mantle source of mid-ocean ridge basalts (MORB) and the lower mantle source of mantle plumes. Geophysics, seismology in particular, reveals a highly heterogeneous lower mantle that includes regions dominated by accumulation of cold, subducted oceanic lithosphere as well as large hot, dense upwellings rising hundreds of km above the core-mantle boundary, around which mantle plumes nucleate. Somewhere in the deep mantle, perhaps within upwelling regions, reside regions of primitive material that have remained isolated for nearly all of Earth's history, but which slowly leak into mantle plumes.

Thus *the modern image of the mantle is of one extensively polluted by recycled material, revealing that the Earth's surface is intimately connected with the deep mantle, with subduction carrying surficial material to the base of the mantle and mantle plumes returning it to the surface.* It is an image of a highly heterogeneous and dynamic lower mantle that also appears to preserve within it a primitive noble gas signature of the Earth's creation.

## 2. The radiogenic isotope perspective

### 2.1. The two layer mantle

Geochemists first realized the mantle was heterogeneous more than 50 years ago. Gast et al. (1964) concluded that Pb and Sr isotopic compositions of oceanic island basalts (OIB) from the South Atlantic "indicate the existence of regional variations in the uranium-lead and rubidium-strontium ratios of the upper mantle source of these rocks." As additional data accumulated, mainly <sup>87</sup>Sr/<sup>86</sup>Sr, Hart (1971) concluded that "oceanic-island basalts are derived from a different type of mantle than submarine ridge basalts." This presented something of a dilemma in the case of oceanic islands, such as Iceland, that sat astride mid-ocean ridges. Hart continued, "The mantle which feeds the ridges must pass under the oceanic islands, and yet somehow maintain an identity distinct from that of the mantle which is supplying magma to the oceanic islands."

Morgan (1971) proposed an explanation: Wilson's (1963) hot spots were the surface manifestation of hot convection plumes rising from the deep mantle. Shortly thereafter, Schilling (1973) embraced Morgan's plume model to explain rare earth element patterns Reykjanes Ridge basalts becoming more light rare earth-enriched as Iceland was approached. He found that variations in either extent of melting or fractional crystallization would have to be implausibly large to explain the

data. More importantly, such models could not explain the Sr isotope data of Hart et al. (1973), which was published shortly thereafter. Schilling suggested instead that a “primordial hot mantle plume” rose beneath Iceland and then flowed southward along the Reykjanes Ridge becoming progressively diluted by melts of the “depleted low velocity layer.”

The idea that mantle plumes consisted of “primordial” material was re-enforced by the first Nd isotope studies on oceanic basalts (DePaolo and Wasserburg, 1976a, 1976b; O’Nions et al., 1977; Richard et al., 1976). Unlike the Rb–Sr and U–Th–Pb decay systems studied up to that time, it was reasonable to assume that the Sm/Nd ratio of the bulk silicate Earth was chondritic and therefore that “primordial” or “primitive” material should have a chondritic  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio, i.e.,  $\epsilon_{\text{Nd}} = 0$ . The oceanic basalt Sr–Nd isotope data set, or the “mantle array” as it came to be called, appeared to terminate at  $\epsilon_{\text{Nd}} = 0$ . This led directly to two-layer mantle models with an incompatible element-depleted layer, the source of MORB, overlying a primitive layer, from which mantle plumes arose (Wasserburg and DePaolo, 1979). Mass balance calculations of how much of the mantle must have been depleted to produce the continental crust suggested the depleted layer occupied about 25–50% of the mantle (DePaolo, 1980; Jacobsen and Wasserburg, 1979; O’Nions et al., 1979); the lower range of these estimates corresponded approximately to the mantle above the 670 km seismic discontinuity, fueling suspicion that this was a chemical boundary. Allegre et al. (1979), on the other hand, argued that a “large proportion of the mantle” had undergone differentiation on basis of evaluation of the Sr–Nd isotope data available at the time.

## 2.2. The multi-component mantle

While geochemists focusing on Sr and Nd isotope data were touching one part of the elephant, those focused on Pb isotopes were touching another. The two-layer mantle model had problems from the beginning in that it could not explain Pb isotope ratios. For example, Pb isotope ratios increased along the Reykjanes Ridge, becoming less rather than more primitive toward Iceland (Sun et al., 1975). And as more data become available, it became apparent that (1) some oceanic island basalt (OIB) sources had  $\epsilon_{\text{Nd}}$  values less than zero and (2) the mantle array

was a broad swath that widened toward the high  $^{87}\text{Sr}/^{86}\text{Sr}$ – $\epsilon_{\text{Nd}}$  end (e.g., White and Hofmann, 1982), neither of which could be explained by two-component mixing between a depleted and primitive reservoir. Zindler et al. (1982) proposed that three distinct isotopic components existed in the mantle. As more data accumulated, in particular Pb isotope data from the Society Islands, Samoa, and the Azores, it became apparent that even three components were insufficient to explain the oceanic basalt data set. I suggested that oceanic basalts could be grouped into 5 classes (White, 1985): MORB, St. Helena, Society, Kerguelen, and Hawaii. I wrote that “The five oceanic basalt groups may represent five end-members, or ‘components’ from which all intermediate compositions can be derived by mixing, but it is more likely that each of these groups represents a distinct, internally heterogeneous reservoir or that each group is composed of a number of isotopically, and by inference chemically, similar reservoirs.” The following year, Zindler and Hart (1986) gave these their now familiar names of DMM (MORB), HIMU (St. Helena), EM I (Kerguelen), EM II (Society) and PREMA (Hawaii) and interpreted them as “end-member components”, which differed from my interpretation. The association of these names with isotopic compositions in the present oceanic basalt data set is shown in Figs. 1 through 3.

These groups can also be distinguished on  $\epsilon_{\text{Hf}}$  vs.  $\epsilon_{\text{Nd}}$  plot, but only partly. HIMU oceanic islands plot to the low  $\epsilon_{\text{Hf}}$  side of the array, but EM I and EM II largely overlap, although the EM I field extends to lower  $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$ . The attests to the strong coherence in Lu–Hf and Sm–Nd fractionations, although this breaks down among MORB, particularly those from the North Atlantic (Chauvel and Blichert-Toft, 2001; Patchett and Tastumoto, 1980). There are still too few samples with both  $^{187}\text{Os}/^{188}\text{Os}$  and other radiogenic isotopes to discern systematic differences among these groups.

In that 1985 paper, I wrote “The five groups recognized here should not be regarded as a final enumeration of possible mantle reservoirs. I have attempted only to put the existing data into a general framework; additional data may well require significant modification of this framework and additional ‘groups’.” In fact, I think only minor modification of the framework is necessary, provided we interpret it broadly. It is clear that the “end-member component” interpretation fails, as Stracke (2012) also pointed out. For example, Samoa and the Society Islands

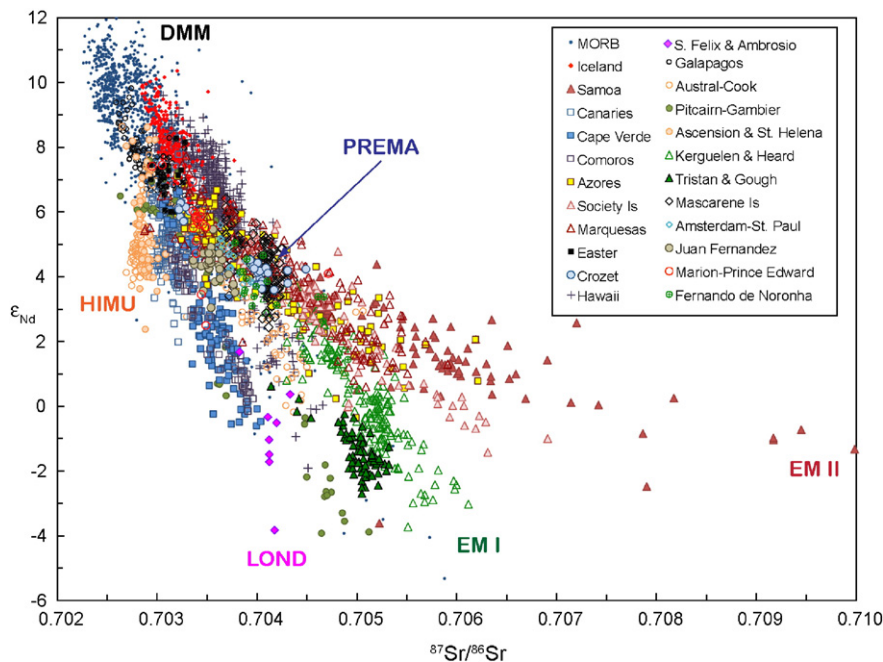


Fig. 1. Sr and Nd isotope data on oceanic basalts. These appears to divide into 6 genera, whose names are shown. Data from the EarthChem databases ([www.earthchem.org](http://www.earthchem.org)). Some Samoan data plot off the figure to higher  $^{87}\text{Sr}/^{86}\text{Sr}$ .

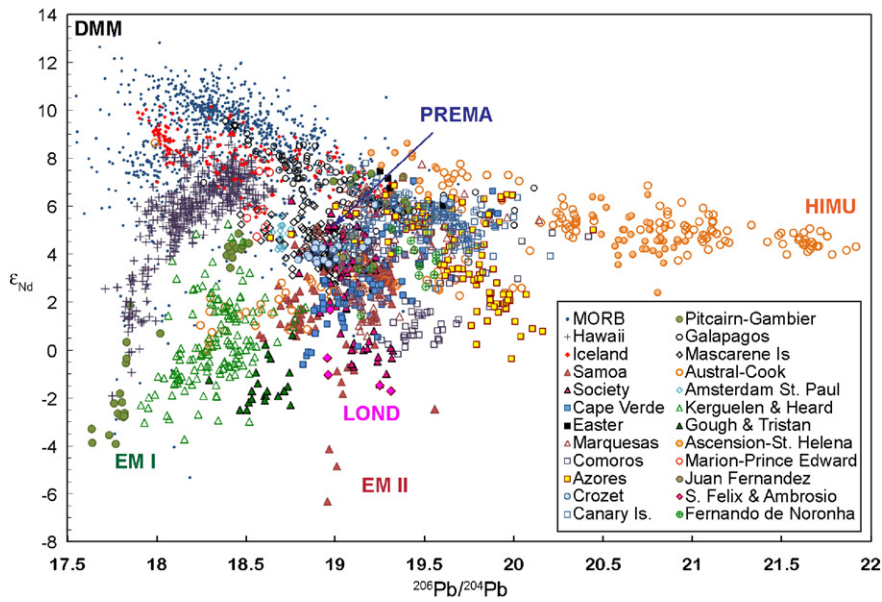


Fig. 2. Nd and Pb isotope data on oceanic basalts. Data from the EarthChem databases.

share the characteristics that define EM II, suggesting their sources have evolved in a similar manner, yet they define distinct arrays in multi-isotope space (Figs. 1–3). Furthermore, one does not observe mixing arrays between, for example, the EM I and EM II components or between EM II and HIMU. Instead, the arrays invariably extend back

toward the central PREMA-DMM region. While it is possible to explain this by first mixing two end-member components, for example HIMU and a Samoa-like EM II and completely homogenizing them, then mixing that mixture incompletely with PREMA to produce the Society array, it is implausible that the first two components would always produce a completely homogeneous mixture when addition of the third end-member does not. Indeed, in Austral-Cook Islands two distinct “components” clearly co-exist: HIMU and EM I. However, instead of forming an array between HIMU and EM I end-members, the Cook-Austral form two arrays, one from EM I and from HIMU that both extend back toward the central PREMA region. It should be noted that Cook-Austral volcanism is complex and at it consists of three hotspot tracks and the HIMU lavas and EM I lavas are associated it with different volcanoes. These observations are particularly clear when the data are viewed in three dimensions, such as video in the Supplementary File 1.

Al Hofmann referred to these isotopic groups as species; the biological analogy may be a good one, but it would be better to think of them as genera, each of which can contain several species. Thus, just as Samoa and the Society Islands are species of EM II, Kerguelen-Heard, Tristan-Gough, and Pitcairn belong to the EM I genus, each defining distinct, but similar, arrays. Extending biological analogy, it is likely that the sources of basalts within each group share a similar, but not identical, evolutionary history.

Additionally, data from the Central Atlantic volcanoes of the Cape Verde and the Canary Islands, the Comoros of the Indian Ocean, and the San Felix and San Ambrosio islands of the eastern south Pacific don't fit well into any of these groups. Hart et al. (1986) had pointed out that the Comoros, San Felix, and San Ambrosio were “misfits” that defined a Sr-Nd isotope array characterized by low  $\epsilon_{Nd}$  for a given  $^{87}Sr/^{86}Sr$  compared to EM I sources, which they named “LoNd” since they appear to have low  $\epsilon_{Nd}$  for a given  $^{87}Sr/^{86}Sr$  (but it could be equally argued that the have low  $^{87}Sr/^{86}Sr$  for a given  $\epsilon_{Nd}$ ). These islands are also distinguished from EM I by having  $^{206}Pb/^{204}Pb > 19$ . I propose that they constitute a 6th genus to be called LOND. While the realization that each island chain is unique might suggest that, rather than introduce yet another genus, we should abandon the White (1985), Zindler and Hart (1986) construct entirely, the similarity of evolutionary history within these genera suggests we should not because it is precisely that evolutionary history we wish to deduce.

Zindler and Hart's analysis differed from mine in another important respect. I defined the fifth group as consisting of Hawaii only, while

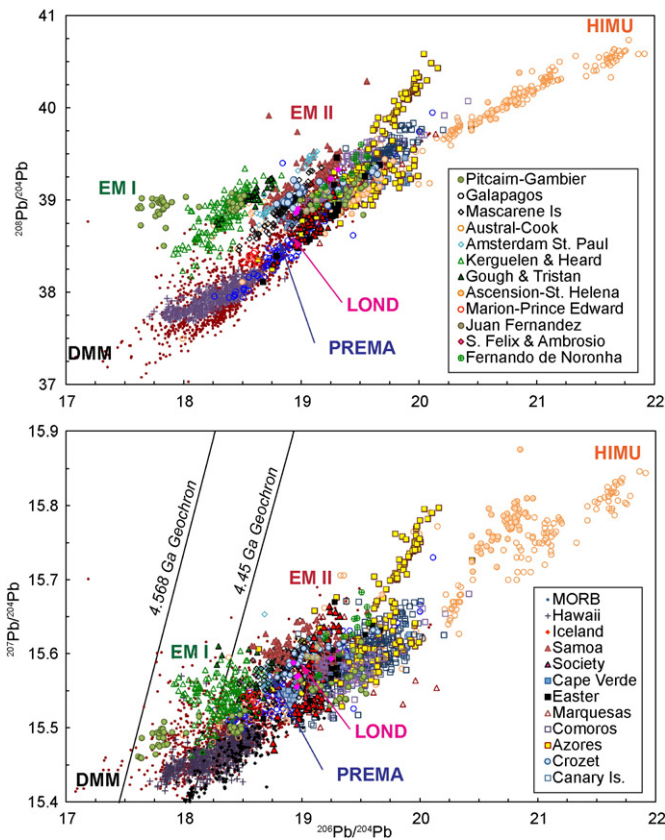


Fig. 3. Pb isotope data on oceanic basalts. Data from the Earthchem databases. Also shown are the two single state isochrons, or Geochrons, calculated assuming the age of the Earth as shown and an initial isotopic composition equal to that in troilite of the Canyon Diablo meteorite.



Zindler and Hart defined their fifth component as having intermediate Pb, Sr and Pb isotopic compositions and called it “Prevalent Mantle” (PREMA) because much of the oceanic basalt radiogenic isotope data plot in this region. With additional data, it is now clear that Hawaii belong in the EM I genus (I had mentioned the EM I-like character of the Koolau volcanics in 1985), and that there does indeed appear to be some sort of prevalent mantle composition. Some mantle plumes, such as Juan Fernandez, Reunion, and Crozet, appear to consist exclusively of this material. Many other oceanic island volcanoes defined arrays that extend toward intermediate compositions, suggesting many or all plumes contain a “common component”, an idea that has subsequently re-emerged in various forms. Hart et al. (1992) called this FOZO, an acronym for Focus Zone, noting that many oceanic basalt arrays pointed toward it in multi-isotope space. They suggested another characteristic of FOZO was high  $^3\text{He}/^4\text{He}$  and that it consisted of lower mantle material entrained by rising plumes. Farley et al. (1992) inferred the existence of a component in the Samoan plume with “high  $^3\text{He}/^4\text{He}$  ratios and intermediate Sr, Nd, and Pb isotopic ratios” that they called “primitive helium mantle” or PHEM and suggested it occurred in other plumes as well. Hanan and Graham (1996), working with Pb isotope ratios in MORB, also inferred the existence of a common component, which they called “C”. They suggested this was also a common component of OIB and was characterized by high  $^3\text{He}/^4\text{He}$  and intermediate Nd, Sr, and Pb isotope ratios. I believe PREMA, FOZO, PHEM, and C all refer to the same thing. However, while many isotope arrays extend from unique compositions back toward intermediate compositions, the region of intersection is far too broad to be considered a component. Nevertheless, “prevalent mantle” seems a term worth retaining, since intermediate isotopic compositions are indeed “prevalent”. Because Zindler and Hart’s (1986) term not only describes it best, but was also first, I will refer to this broad compositional region as PREMA. As these authors all noted, the high  $^3\text{He}/^4\text{He}$  ratios imply this material is less degassed than much of the mantle. While the highest  $^3\text{He}/^4\text{He}$  ratios are associated with PREMA-like ratios of other radiogenic isotopes, the nevertheless correlate poorly with those other radiogenic isotope ratios, again demonstrating that PREMA does not consist of a single component.

Farley et al. noted in reference to PHEM that “this material cannot have been derived from a reservoir completely closed to elemental fractionation for the full 4.55 Ga duration of Earth’s history”. While PREMA non-noble gas radiogenic isotopic compositions do seem less fractionated than other mantle reservoirs, this may only reflect a relatively even balance of depleted and enriched components within this reservoir. I’ll return to the question of the relationship between PREMA and primitive mantle in a subsequent section.

### 2.3. The crustal recycling paradigm

The incompatible element-depleted nature of the MORB source (DMM) had been recognized early. This was readily understood to result from previous extraction of partial melt to form crust (e.g., Gast, 1968; Kay et al., 1970; Tatsumoto, 1966).  $\epsilon_{\text{Nd}}$  of most OIB were positive, suggesting sources that were also incompatible element-depleted relative to the Chondritic Uniform Reservoir (CHUR) model terrestrial composition (I’ll discuss the validity of that model in the following section). As discussed above, that ‘depleted’ signature could be explained at first by mixing of depleted and primitive mantle, but the discovery of OIB with negative  $\epsilon_{\text{Nd}}$  required some mechanism of enriching areas of the mantle in incompatible elements. One explanation was that regions of the mantle could become enriched by reaction with silicate, hydrous, or carbonatitic fluids percolating through them (Vollmer, 1983). There is certainly evidence of such “mantle metasomatism”, particularly in peridotitic xenoliths found in continental volcanics and more rarely in oceanic ones (e.g., Menzies and Murthy, 1980). But while the small-scale effects of mantle metasomatism are real, particularly within the lithosphere, it seemed improbable that fluids could transport

incompatible elements mantle-scale distances and produce enriched regions sufficiently large and persistent to account for the compositions of oceanic island volcanoes.

An obvious source of incompatible element enriched material is the crust and as Armstrong (1968) pointed out earlier on, subduction of oceanic crust and sediment carries this material into the mantle. Allegre et al. (1980) suggested that “recycling of sediments during lithospheric subduction” contributed to mantle heterogeneity; Hawkesworth et al. (1979) suggested “one possible explanation” for the distinctive Sr and Nd isotopic compositions of Saõ Miguel, Azores was “subducted crustal material which has retained its identity in the upper mantle.” Chase (1981) and Hofmann and White (1980, 1982) went further and argued that the mantle plume sources of oceanic island basalts consisted, in part, of subducted oceanic crust that had sunk to the base of the mantle. Others subsequently proposed variations on the recycling theme. McKenzie and O’Nions (1983) suggested subcontinental lithosphere, enriched in incompatible elements by metasomatic fluids rising from below, could “become detached from continental lithosphere, incorporated into convective flow and thereby providing a source for some oceanic island basalts. Niu and O’Hara (2003) and Workman et al. (2004) suggested instead that subducted metasomatized oceanic lithosphere could form the source of incompatible element-enriched plumes. Other mechanisms of supplying enriched crustal material to the mantle include lower crustal foundering or “delamination” (Arndt and Goldstein, 1989; Kay and Kay, 1993) and subduction erosion (Scholl et al., 1980). The importance of these latter processes is generally overlooked by geochemists (papers by Willbold and Stracke (2006) and Willbold and Stracke (2010) are notable exceptions), perhaps because they are difficult to geochemically document and quantify, but Cliff et al. (2009), Stern and Scholl (2010), and Stern (2011) all estimate that these processes produce a combined flux of continental crust to the mantle that exceeds the sediment subduction flux.

Although interpretations of the relative importance of the various mechanisms and the importance of the various components they carry into the mantle differ, it is now widely agreed that recycling of lithosphere, particularly oceanic and continent crust, together with extraction partial melt, the dominant mechanism by which mantle chemical heterogeneity has been produced.

### 2.4. Elusive primitive mantle

The crustal recycling paradigm has largely replaced the early model of a depleted mantle supplying mid-ocean ridges overlying primitive mantle supplying mantle plumes. Yet, the mass balance calculations mentioned above (DePaolo, 1980; Jacobsen and Wasserburg, 1979; O’Nions et al., 1979) remain valid assuming that the silicate Earth has chondritic relative abundances of refractory lithophile elements, particularly Sm and Nd. Furthermore, assuming a bulk silicate Earth potassium content of around 220 ppm, more than half of the  $^{40}\text{Ar}$  produced over Earth’s history remains in the solid Earth and only a fraction of this could be in the continental crust and MORB source mantle (Allègre et al., 1996). However, while a relatively undegassed reservoir appears to contribute noble gases to many plumes, as discussed in Section 4, no OIB, or any other mantle-derived magmas, have the Sr, Nd, Hf, or Pb isotopic characteristics expected of primitive mantle. There are two possible explanations: no substantial reservoir of primitive mantle has survived or primitive mantle does not have the composition we have thought it does.

The discovery that all post-Archean rocks have non-chondritic  $^{142}\text{Nd}/^{144}\text{Nd}$  (Boyett and Carlson, 2005) suggests that “primitive mantle” might have a different composition than we had assumed.  $^{142}\text{Nd}$  was produced by decay of the extinct radionuclide  $^{146}\text{Sm}$  ( $t_{1/2} = 103$  Ma). Many early Archean rocks have excesses or deficits of  $^{142}\text{Nd}$ , demonstrating that the Earth had begun to differentiate before  $^{146}\text{Sm}$  became extinct (e.g., Caro et al., 2003; Harper and Jacobsen, 1992; O’Neil et al.,

2008), but if the bulk silicate Earth has chondritic relative abundances of refractory lithophile elements, an implicit feature of many compositional models (e.g., McDonough and Sun, 1995), it should have a chondritic Sm/Nd ratio and chondritic  $^{142}\text{Nd}/^{144}\text{Nd}$ . Instead, all modern mantle derived materials have  $^{142}\text{Nd}/^{144}\text{Nd}$  about 18 ppm higher than the average in ordinary chondrites. Boyet and Carlson (2005) explained this conundrum as a consequence of very early differentiation of the Earth into an incompatible element-enriched reservoir (the Early Enriched Reservoir or EER) and an early depleted one (EDR). In that model, the EER, constituting only a few percent of the mass of the Earth, formed as a basaltic crust of a magma ocean sunk to the base of the mantle while the EDR gave rise to the modern continental lithosphere and the convecting mantle, which together constitute the “observable” Earth. The EER, if it exists, must have remained sequestered for all of Earth’s history. Murphy et al. (2010) calculated that even a small contribution from the hypothesized EER should produce a measurable anomaly in  $^{142}\text{Nd}/^{144}\text{Nd}$ , yet no measurable variation has been observed any post-Archean rocks (Jackson and Carlson, 2012; Murphy et al., 2010). Even if the EER were contributing a fraction too small to detect in a particular sample, a continual bleed of this material into the EDR should result in an observable shift in  $^{142}\text{Nd}/^{144}\text{Nd}$  over time, but this is also not observed. Other arguments against this scenario are described in Campbell and O’Neill (2012).

There are several alternative explanations to the  $^{142}\text{Nd}/^{144}\text{Nd}$  conundrum. The first possibility is that the solar nebula was isotopically heterogeneous as a result of incomplete mixing of s-process nuclides produced in red-giants, such as  $^{142}\text{Nd}$ , and r-process nuclides produced in supernovae, such as  $^{143}\text{Nd}$  and  $^{144}\text{Nd}$ . Observed isotopic heterogeneity in chondrites supports this possibility (e.g., Andreasen and Sharma, 2006; Boyet and Gannoun, 2013; Carlson et al., 2007; Huang et al., 2013). Indeed, as Fig. 4 shows, while ordinary chondrites have  $^{142}\text{Nd}/^{144}\text{Nd}$  on average 18 ppm lower than the modern terrestrial value, carbonaceous chondrites have average  $^{142}\text{Nd}/^{144}\text{Nd}$  roughly 40 ppm lower and enstatite chondrites have average  $^{142}\text{Nd}/^{144}\text{Nd}$  only about 10 ppm lower and the range in enstatite chondrites overlaps the terrestrial value (Gannoun et al., 2011; Qin et al., 2011). While enstatite chondrites do share some isotopic features with the Earth (e.g., Javoy et al., 2010), there are other problems with building the Earth out of enstatite chondritic material, including the very different Mg/Sr ratios and Si isotope composition of enstatite chondrites (Fitoussi and Bourdon, 2012). It is nonetheless possible that we do not have a complete inventory of planetary building blocks, i.e., chondrites, and that some chondrite class may still have the right combination of chemical and isotopic compositions matching Earth’s.

Another alternative is that the Earth does not have a chondritic inventory of refractory lithophile elements as a consequence of collisional erosion of primitive basaltic crusts that formed from partial melts on planetary embryos that accreted to form the Earth (Caro et al., 2008; O’Neill and Palme, 2008). As O’Neill and Palme pointed out, the Earth has a higher Fe/Mg ratio than chondrites and they argued that this resulted from preferential loss of silicate mantles relative to cores during collisions between planetary embryos. This view is supported by a growing body of evidence that the accretion process is not conservative (e.g., Agnor and Asphaug, 2004; Bonsor et al., 2015; Marcus et al., 2009; Stewart and Leinhardt, 2012). Collisions between planetary embryos result not just in mergers, but also in disruptions, partial accretion, or partial erosion depending on the mass ratio of the objects, the ratio of impact velocity to escape velocity, and impact angle. In modeling the process, Stewart and Leinhardt (2012) found perfect mergers occur in a minority of collisions and that on average collisions result in preferential loss of the silicate portions of planetary embryos, resulting in a core-to-mantle mass ratio increase of > 10%. Bonsor et al. (2015) found even larger increases in core-to-mantle ratios in the growth of planetesimals (~160 km radius) to protoplanets (~1000 km radius). These models do not have sufficient resolution to explore the fate of the crusts of these bodies, but it seems reasonable to infer that they would be even more

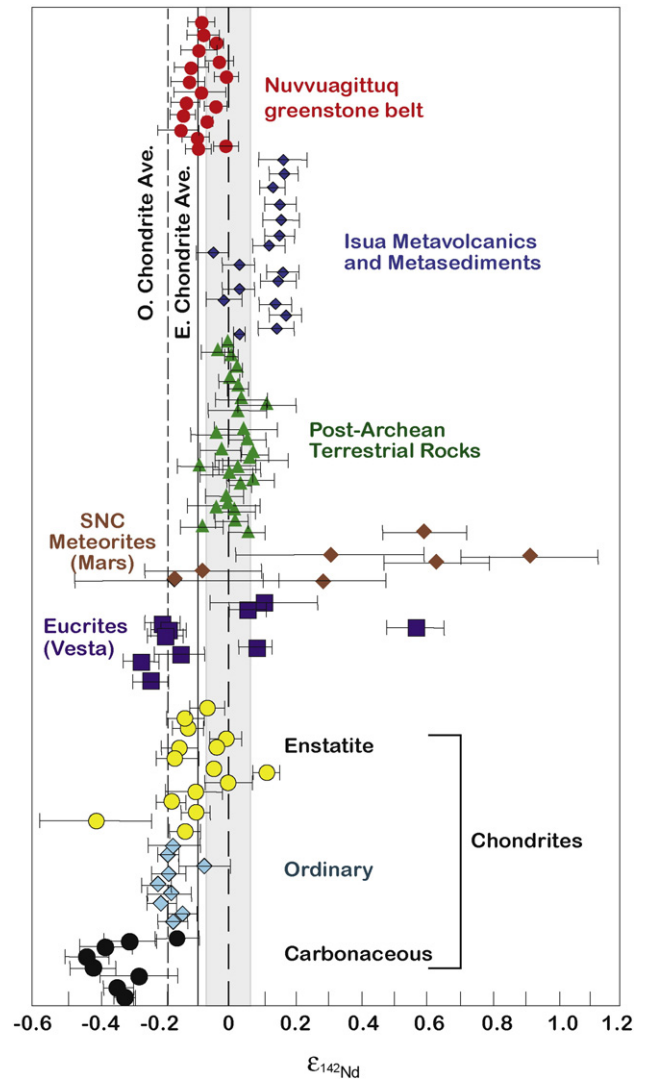


Fig. 4.  $\epsilon_{142\text{Nd}}$  in terrestrial and solar system materials.  $\epsilon_{142\text{Nd}}$  is the relative deviation in the  $^{142}\text{Nd}/^{144}\text{Nd}$  ratio from a terrestrial laboratory standard in parts in 10,000. All post-Archean terrestrial rocks are identical within error to the laboratory standard.

readily lost than mantles. Other evidence of collisional erosion includes the excess of iron meteorites and asteroids over achondritic ones: iron meteorites provide evidence of at least 60 disrupted differentiated planetesimals, but there are far fewer classes of achondrites and there are ~40 identified M-class (metal-rich) asteroids but less than 30 olivine- or pyroxene-dominated (A, V, and J class) asteroids (Burbine et al., 1996). Collisional disruption should reasonably produce more silicate fragments than metallic ones, suggesting the silicate mantles of those disrupted bodies have been, in the words of Burbine et al. (1996), “battered to bits” and either blown out of the system by stellar winds or spiral into the star through Poynting–Robertson drag. Huang et al. (2013) argued that a  $^{143}\text{Nd}/^{144}\text{Nd}$  mass balance between mantle and crust requires a chondritic  $^{143}\text{Nd}/^{144}\text{Nd}$  for the bulk silicate Earth. Their mass balance, however, involves several debatable assumptions, including an estimate of  $^{147}\text{Sm}/^{144}\text{Nd}$  in the MORB source that significantly lower than previous estimates (Gale et al., 2013; Salters and Stracke, 2004; Workman and Hart, 2005) and a particularly low estimate for the age of the continental crust.

The third alternative is that the core contains some of the Earth’s inventory of rare earths and core-mantle differentiation has left the mantle with a suprachondritic Sm/Nd (Wohlert and Wood, 2015). Partitioning experiments of Wohlert and Wood (2015) demonstrated that under highly reducing conditions in which the silicate FeO content

approaches 1%, normally highly lithophile elements such as the rare earths, Ti, Ta, Nb, and U can partition somewhat into a sulfide melt phase in equilibrium with a silicate melt. Because Nd partitions more readily into the sulfide phase than Sm, this would leave the mantle with a suprachondritic Sm/Nd. While these elements would not partition into a sulfide melt at the oxygen fugacity of the terrestrial mantle, Wohlers and Wood hypothesized a growing Earth accreting a planetary embryo similar to Mercury that had already differentiated into silicate mantle and metal/sulfide core under reducing conditions. If the core of that body merged with the Earth's core without re-equilibration, this could leave the Earth's mantle with a slightly suprachondritic Sm/Nd. An attractive feature of this idea is that the core formed in this way would contain some U, and a lesser amount of Th, providing some 2 to 2.4 TW to power the geodynamo, whose energy source is otherwise enigmatic. However, even if this reduced planetary embryo constituted 50% of the mass of the Earth, this scenario could not account for the ~18 ppm difference in  $^{142}\text{Nd}/^{144}\text{Nd}$  between the Earth and ordinary chondrites. To account for the smaller ~10 ppm difference between the Earth and enstatite chondrites would require the mass of the accreted reduced body be >35% of the Earth and would leave the silicate Earth with a Th/U ratio greater than 4.25, which seems unlikely given the Th/U ratios observed in the reservoirs comprising the silicate Earth (Paul et al., 2003).

These possibilities are not mutually exclusive; it is entirely possible that the suprachondritic terrestrial  $^{142}\text{Nd}/^{144}\text{Nd}$  is a consequence of a combination of them. For example, the isotopic compositions of O, Ti, and Cr in enstatite chondrites better match terrestrial values than those of ordinary chondrites, yet even assuming the Earth formed from material with an enstatite chondrite-like  $^{142}\text{Nd}/^{144}\text{Nd}$ , a 10 ppm difference remains between enstatite chondrites and Earth, which could be accounted for either by collisional erosion, partitioning of some Nd into the core, or a high  $^{142}\text{Nd}/^{144}\text{Nd}$  reservoir in the deep mantle. Similarly, accretion of a Mercury-like body might plausibly explain part of the excess  $^{142}\text{Nd}$ , but has great difficulty explaining all of it.

Indeed, Boujibar et al. (2015) have recently suggested just such a combination of factors to explain the Earth's unique composition. They argue that the Earth formed from enstatite chondrite-like planetary embryos based on isotopic composition. During their growth, heating resulting from a combination of impacts and short-lived radionuclides such as  $^{26}\text{Al}$  led to partial melting and formation of Si-rich proto-crusts. Impacts then eroded the proto-crusts, ultimately raising the Earth's Mg/Si ratio to its present value and decreasing the Earth's incompatible element inventory. The model focuses on major element chemistry and it is unclear whether it can explain the difference between the terrestrial  $^{142}\text{Nd}/^{144}\text{Nd}$  and the average of enstatite chondrites, but that avenue certainly seems worth exploring.

The important point is that unless nebular isotopic heterogeneity is the sole cause of high terrestrial  $^{142}\text{Nd}/^{144}\text{Nd}$ , then "primitive mantle" – which I will define as the material from which the modern observable mantle and crust have evolved – has a composition different from what geochemists have long assumed. In either the EER or collisional erosion hypothesis, "primitive mantle" defined in this way is depleted in the more incompatible lithophile elements and has higher  $\epsilon_{\text{Nd}}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  than the canonical values of 0 and 0.705, respectively. If the Mercury-like component theory of Wohlers and Wood (2015) is correct, then primitive mantle also has  $\epsilon_{\text{Nd}}$  greater than 0, but other isotopic compositions cannot be predicted in the absence of experimental data on the relevant elements. Caro and Bourdon (2010) calculate  $\epsilon_{\text{Nd}}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\epsilon_{\text{Hf}}$  of primitive mantle to be 6.9, 0.703, and +12, respectively, assuming the terrestrial  $^{147}\text{Sm}/^{144}\text{Nd}$  is 6% higher than chondritic (needed to explain the 18 ppm excess  $^{142}\text{Nd}/^{144}\text{Nd}$  relative to ordinary chondrites). Assuming instead that the Earth formed from enstatite chondrite-like precursors, as (Boujibar et al., 2015) do,  $^{147}\text{Sm}/^{144}\text{Nd}$  needs to be only 3% higher than chondritic and I calculated these values to be  $\epsilon_{\text{Nd}} = +3.6$ ,  $^{87}\text{Sr}/^{86}\text{Sr} = 0.704$  and  $\epsilon_{\text{Hf}} = +6.4$  (White, 2013). If this composition, with  $\epsilon_{\text{Nd}}$  between 3 and 7, is indeed primitive mantle,

it explains some of the features of mantle geochemistry that have been enigmatic up to now, some of which other have already pointed out by others (Campbell and O'Neill, 2012; Caro and Bourdon, 2010; Jackson and Jellinek, 2013; Jellinek and Jackson, 2015):

- $\epsilon_{\text{Nd}}$  values of +3.6 to +7 are the ones most commonly observed in OIB.
- As discussed in Section 4, OIB with  $\epsilon_{\text{Nd}}$  values in this range have the highest  $^3\text{He}/^4\text{He}$ , suggesting they contain a relatively undegassed or primitive component.
- The "missing" argon conundrum is resolved as the K content of the silicate Earth is reduced and with it the amount of  $^{40}\text{Ar}$  produced so that nearly all resides in the atmosphere.
- Rare earth patterns in many OIB are strongly light rare earth-enriched relative to chondrites yet they have positive  $\epsilon_{\text{Nd}}$ . This requires either extraordinarily small extents of melting, often implausibly small, or a source evolution that includes strong light rare earth-depletion followed by quite recent enrichment. An evolution that begins with light rare earth depletion relative to chondrites allows the enrichment event to be older and more modest.
- Rather than occupying 65 to 75% of the mantle, mass balance calculations show that the primitive mantle occupies <30% of the mantle, consistent with geophysical evidence of whole mantle convection now demonstrated through seismic tomography as discussed in Section 5. Thus, in addition to primitive mantle being different than what we had assumed, little or none of it may have survived.



### 3. Stable isotope perspective

#### 3.1. Oxygen, carbon, nitrogen, and sulfur

Somewhat later, stable isotope geochemists began to provide yet another perspective of the mantle. This work trailed that of radiogenic isotope geochemists because stable isotope variations in the mantle are small, and useful data required development of higher precision analytical techniques as well as overcoming other obstacles. Isotopic fractionations occurring at mantle or magmatic temperatures tend to be small because isotopic fractionation decreases with the square of temperature and the variety of atomic environments and bonds in mantle minerals is limited. A much greater variety of phases are present at the Earth's surface and that, along with much lower temperatures, results in much greater isotopic fractionation. Because of this, stable isotopes can be used as tracers of surficial material in the mantle. Taylor and Sheppard (1986) expressed it this way: "igneous rocks whose oxygen isotopic compositions show significant variations from the primordial value (+6) must either have been affected by low temperature processes, or must contain a component that was at one time at the surface of the Earth." This presents both an opportunity and obstacles because it requires identifying and avoiding those samples that have been affected by secondary low-temperature processes. In addition, volatile elements such as H, C, N, and, to a lesser degree, S, undergo fractionation during magma degassing. Finally, while the mantle signal can be compromised for all isotope systems when magmas assimilate crustal material, some elements, such as B and Cl, are extremely sensitive to this process. Thus in contrast to radiogenic isotopes, stable isotopes basalts do not always provide a representative sample of mantle material.

Using laser fluorination technique that allowed analysis of pristine small grains, Matthey et al. (1994) showed that the  $\delta^{18}\text{O}_{\text{SMOW}}$  value of typical mantle peridotites was about +5.5 (a bit lower than the previous accepted value of +5.7 to 6). Eiler et al. (2000) used this technique to show that  $\delta^{16}\text{O}$  in fresh MORB glasses was not uniform and correlated positively with  $\text{K}_2\text{O}$  and incompatible element ratios such as La/Sm, K/U, and  $\text{K}_2\text{O}/\text{H}_2\text{O}$  (the latter is important because it is the opposite of what one would expect if low-temperature secondary alteration were the



cause). They concluded this reflected real variation in mantle oxygen isotopic composition and resulted from recycling of surficial material into the mantle. A subsequent study by Cooper et al. (2004) showed that  $\delta^{18}\text{O}_{\text{SMOW}}$  also correlated positively with  $^{87}\text{Sr}/^{86}\text{Sr}$  and negatively with  $^{143}\text{Nd}/^{144}\text{Nd}$  in MORB from the Mid-Atlantic Ridge, confirming the earlier conclusions.

The range observed in  $\delta^{18}\text{O}_{\text{SMOW}}$  in MORB is, however, small, a few tenths per mil. Much larger variation in oxygen isotope ratios, including values both well above and well below the nominal mantle value, have been found in eclogite xenoliths from kimberlites (e.g., MacGregor and Manton, 1986; Pernet-Fisher et al., 2014; Smart et al., 2014), clearly indicating subduction carries isotopically heterogeneous oxygen into the mantle (e.g., Carmody et al., 2013). Furthermore, diamonds of the eclogite paragenesis are also highly variable in carbon (Mattey, 1987) and nitrogen (Marty and Dauphas, 2003) isotopic compositions.

Farquhar et al. (2002) reported mass-independently fractionated sulfur in diamond sulfide inclusions. Mass-independent fractionation (MIF) sulfur is common in sedimentary and hydrothermal sulfides and sulfates in rocks older than 2.3 Ga, but disappears completely by 2.0 Ga (Farquhar et al., 2000; Farquhar and Wing, 2003). Mass independent fractionation appears to result from ultraviolet photolysis in the atmosphere (see review of Thiemens, 2006). Farquhar and Wing argued that in the absence of oxygen and ozone in the Archean atmosphere, ultraviolet radiation could penetrate through the whole atmosphere and fractionate atmospheric sulfur, but not after oxygenation of the atmosphere around 2.3 to 2.4 Ga. Thus, the diamonds analyzed by Farquhar et al. (2002) apparently contain sulfur that had cycled through the atmosphere in the Archean or earliest Proterozoic and was subsequently subducted and stored in the subcontinental lithosphere.

All of these, however, are derived from the subcontinental lithosphere, leaving unclear the question of whether such material is carried into the deep mantle. That question was answered by Walter et al. (2011), who reported strongly negative  $\delta^{13}\text{C}$  values in diamonds from a Cretaceous Brazilian kimberlite. This isotopically light carbon strongly suggests an origin as biologically produced organic matter. Significantly, the diamonds contain inclusions matching the compositions of basaltic phases in lower mantle, such as 'Ca-perovskite' ( $\text{CaSiO}_3$ ), calcium ferrite, and bridgmanite. Walter et al. concluded that ancient oceanic crust had been subducted into the deep mantle, then carried more than 500 to 1000 km upward beneath Brazil by a Cretaceous mantle plume. More recently, Ickert et al. (2015) reported  $\delta^{18}\text{O}$  ratios ranging from +8.6 to +10 in majorite inclusions in Jagersfontein (South Africa) diamonds with  $\delta^{13}\text{C}$  ranging from -17.4 to -23. The  $\delta^{13}\text{C}$  values are strongly suggestive of a biological origin of the carbon, the  $\delta^{18}\text{O}$  clearly suggest they derived from material that had reacted with water at or near the surface of the Earth, and the compositions of the inclusions suggest they formed at depths of 500 km, well within the mantle transition zone.

Eiler et al. (1997) reported  $\delta^{16}\text{O}_{\text{SMOW}}$  values are as high as 6.1‰ in basalts from the Society Islands and concluded that the Society Islands mantle source contained up to 5% of a sedimentary component, assuming a  $\delta^{16}\text{O}_{\text{SMOW}}$  of +15‰ for the sediment. Elevated  $\delta^{16}\text{O}$  also occurs in Samoan peridotite xenoliths and Eiler et al. suggested that they too could contain a recycled sedimentary component. Subsequently, Workman et al. (2008) reported variations of  $\delta^{16}\text{O}$  in olivines in Samoan lavas that correlated positively with  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  and incompatible element ratios, confirming the presence of recycled material in the source of Samoan lavas.

Eiler et al. (1997) also found that some basalts from HIMU island chains had low  $\delta^{16}\text{O}_{\text{SMOW}}$ , which they suggested reflected assimilation of hydrothermally altered material in the volcanic edifice. However, Cabral et al. (2013) reported MIF sulfur in olivine sulfide inclusions from one of these islands, Mangaia of the Cook-Austral chain (Fig. 5). In particular, the negative  $\Delta^{33}\text{S}$  observed in these inclusions is also characteristic of Archean hydrothermal sulfides, which suggests that the low  $\delta^{16}\text{O}$  values observed by Eiler et al. reflect the presence of very ancient recycled hydrothermally altered oceanic crust rather than modern

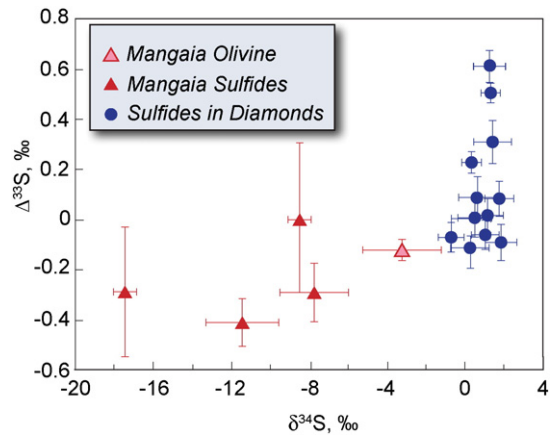


Fig. 5. Sulfur isotope ratios in sulfide inclusions in olivines (triangles) from Mangaia, Austral-Cook Islands (Cabral et al., 2013) and in diamonds (circles) from the Orapa kimberlite pipe in Botswana (Farquhar et al., 2002).

assimilation. The MIF sulfur is particularly important because, in addition to unequivocally demonstrating the presence of recycled oceanic crust in mantle, it constrains the age of this material to be 2.3 Ga or older and unlike MIF sulfur in diamonds, the sulfur in Mangaia olivines must have come from the convecting mantle, most likely the deep mantle.

Although they did not find evidence of mass independent fractionation, Labidi et al. (2015) found that  $\delta^{34}\text{S}_{\text{CDT}}$  in the reduced sulfur fraction of Samoan lavas ranged from +0.11‰ to +2.79‰. Importantly,  $\delta^{34}\text{S}$  in the reduced sulfur (more than 75% of total S) correlates with  $^{87}\text{Sr}/^{86}\text{Sr}$  in glasses (Fig. 6). They argued the correlation “requires the EM-2 endmember to be relatively S-rich, and only sediments can account for these isotopic characteristics.”

### 3.2. Unconventional isotopes: U, Li, Mg, and Fe

Over the last 15 to 25 years, stable isotope geochemistry has expanded from a short list of light elements whose isotopic composition could be determined in gas source mass spectrometers to an array of multi-isotopic elements. For the most part, fractionation of the isotopes of these elements depend on the same factors in the same way as the traditional light stable isotopes, meaning we can usually expect small fractionations at under mantle conditions. However, for heavier elements, such as U, the size and shape of the nucleus can affect electron energy and consequently affect isotopic fractionation, and the effect of this nuclear field shift can be larger and of opposite sign to the vibrational

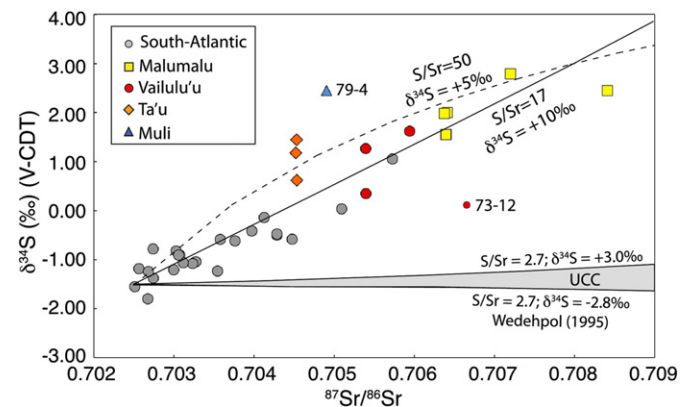


Fig. 6.  $\delta^{34}\text{S}_{\text{CDT}}$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  in lavas from Samoan volcanoes (Malumalu, Vailulu'u, Ta'u, and Muli) and MORB from the South Atlantic. Also shown are mixing curves between a mantle component and potential sedimentary or upper crustal end-members with distinct  $\delta^{34}\text{S}$  and S/Sr ratios from Labidi et al. (2015).



energy term that is the principle source of temperature dependence in isotopic fractionations (Bigeleisen, 1996a, 1996b).

Seawater-basalt interaction results in uranium enrichment of the oceanic crust (e.g., Staudigel, 2014). Andersen et al. (2015) found that altered oceanic crust has variable  $\delta^{238}\text{U}$ : the upper hundred meters has  $\delta^{238}\text{U}$  slightly lighter than seawater while the deeper parts of the ocean crust contain isotopically heavy U. Uranium is likely taken up in the upper crust under oxic conditions, in which U is in the +6 state, as it is in seawater, with little fractionation. Uptake in the lower crust, however, occurs under conditions in which the U is reduced to the +4 state and a significant isotopic fractionation is associated with the reduction, with  $^{238}\text{U}$  preferentially partitioning into the reduced phase. Andersen et al. (2015) also found that U in subduction-related volcanics was isotopically light, similar to that of the upper oceanic crust. They argued that U in subduction-related volcanics was derived from the dehydrating uppermost part of the subducting oceanic crust with the isotopically heavier U carried deeper into the mantle. This fractionation would not have occurred in the early Earth, because U at the surface of the Earth would have been in the reduced  $\text{U}^{4+}$  state, immobile, and present only in very low concentrations in seawater. The first step toward oxygenation of the surface occurred around 2.4 Ga, but the deep ocean is unlikely to become oxidizing until around 600 Ma (Lyons et al., 2014).

Anderson et al. also found that the  $\delta^{238}\text{U}$  of MORB and OIB differ, albeit slightly, with OIB having  $\delta^{238}\text{U}$  similar to meteorites, and, presumably, to bulk Earth values, while MORB are slightly  $^{238}\text{U}$ -enriched. They argue that isotopically U heavy in recycled deep oceanic crust has extensively polluted the upper mantle MORB source during the Phanerozoic while OIB sources contain Precambrian recycled material with unfractionated uranium. As they point out, this is consistent with the presence of MIF sulfur in Mangaia olivines as well as Precambrian model ages implied by oceanic basalts  $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$  data.

Other non-traditional stable isotopes provide additional evidence of a recycled component in OIB sources. Low temperature alteration of the oceanic crust appears to involve uptake of Li from seawater ( $\delta^7\text{Li} = +31\%$ ; Misra and Froelich, 2012) and a consequent increase in both Li concentration and  $\delta^7\text{Li}$ , with altered MORB having an average  $\delta^7\text{Li}$  of  $+11.3\%$  compared to  $\delta^7\text{Li} = +3.7 \pm 1$  for fresh MORB (Chan et al., 1992; Elliott et al., 2006; Tomascak et al., 2008) and  $2.96 \pm 0.77$  for chondrites and presumably primitive mantle (Pogge von Strandmann et al., 2011). In contrast, hydrothermal metamorphism extracts Li from basalt such that both Li concentration and  $\delta^7\text{Li}$  decrease in the process (Chan et al., 2002). The net effect of low and high temperature seawater interaction is not entirely clear, but appears to result in a net decrease in Li concentration and  $\delta^7\text{Li}$  of the oceanic crust (Misra and Froelich, 2012).  $\delta^7\text{Li}$  of clastic sediment tends to be lighter ( $-3$  to  $+5\%$ ) than that of biogenic sediment ( $+6$  to  $+15$ ) so that subducting sediment varies among subduction zones from about  $-1$  to  $+9\%$  (Plank, 2014). Thus, subducting lithosphere carries both isotopically light and heavy Li into the primitive mantle.

When potentially altered samples are filtered out,  $\delta^7\text{Li}$  correlates significantly with  $^{206}\text{Pb}/^{204}\text{Pb}$  ( $r = 0.57$ ;  $n = 202$ ,  $r_{\text{crit},0.05} = 0.01$ ) and  $\epsilon_{\text{Nd}}$  ( $r = -0.13$ ;  $n = 209$ ,  $r_{\text{crit},0.05} = 0.009$ ) in oceanic basalts and values both below and above the primitive mantle value occur (Fig. 7). Correlations within individual island chains, or within MORB, are generally not statistically significant (perhaps due to limited data) with two exceptions. Hawaiian basalts show a particularly large range in  $\delta^7\text{Li}$ , which correlates significantly with  $^{206}\text{Pb}/^{204}\text{Pb}$  but not  $\epsilon_{\text{Nd}}$ . Volcanoes of the Loa trend have, on average, lower  $\delta^7\text{Li}$  than volcanoes of the Kea trend and the post-shield and rejuvenescent stage lavas have systematically lower  $\delta^7\text{Li}$  than both Loa and Kea shield lavas (Harrison et al., 2015). There is also a statistically significant  $\delta^7\text{Li}$ – $^{206}\text{Pb}/^{204}\text{Pb}$  correlation in the Austral–Cook Islands data set, as Chan et al. (2009) noted. In contrast to the isotopically heavy lithium observed in HIMU lavas, EM I and EM II type lavas from Pitcairn, the Koolau Series of Oahu, the Societies, Marquesas, and Azores tend to exhibit decreasing  $^7\text{Li}$  with

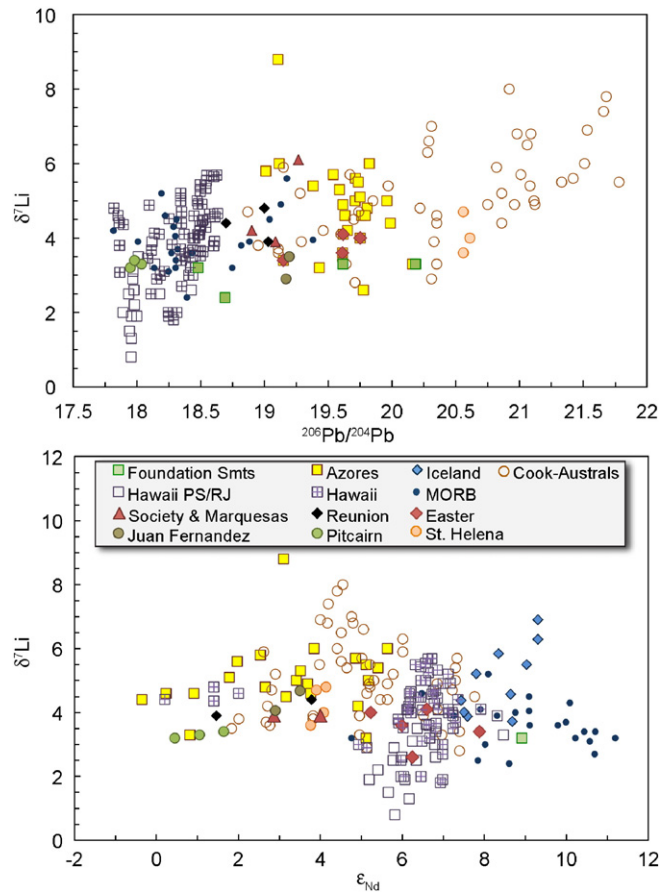


Fig. 7. Li, Pb, and Nd isotope ratios in oceanic basalts. Data from Nishio et al. (2005), Elliott et al. (2006), Nishio et al. (2007), Tomascak et al. (2008), Chan et al. (2009), Magna et al. (2011), Krienitz et al. (2012), Genske et al. (2014), and Harrison et al. (2015). Potentially altered samples, assessed from authors' descriptions, water content, etc., have been excluded. Note that the Hawaiian post-shield and rejuvenescent stage lavas (labeled Hawaii PS/RJ) are distinct from the shield stage lavas (labeled Hawaii).

decreasing  $\epsilon_{\text{Nd}}$ , suggesting the presence of a continental or marine sedimentary component. Krienitz et al. (2012) concluded that "The Li contents and isotope characteristics of HIMU-type lavas are consistent with recycling of altered and dehydrated oceanic crust, whereas those of the EM1-type lavas can be attributed to sediment recycling." While it is certainly speculative at this point to associate specific Li isotopic compositions in OIB with specific crustal components, the Li isotope data nonetheless provide evidence that the mantle has been extensively polluted by material from the surface of the Earth.

Mg and Fe isotopes may also provide evidence of recycling of surficial material into the mantle, but this remains tentative at this stage. Both  $\delta^{26}\text{Mg}$  and  $\delta^{57}\text{Fe}$  exhibit small but significant variations in oceanic basalts and basalts from the Society Islands have statistically significantly higher  $\delta^{26}\text{Mg}$  and  $\delta^{57}\text{Fe}$  than in both Hawaii and MORB (Teng et al., 2010, 2013) ( $\delta^{26}\text{Mg}$ : Society Is. =  $-0.29 \pm 0.03\%$ , Hawaii =  $-0.24 \pm 0.03\%$ , MORB =  $-0.25 \pm 0.03\%$ ;  $\delta^{57}\text{Fe}_{\text{IRMM-14}}$ : Society =  $+0.20 \pm 0.05\%$ , Hawaii =  $+0.13 \pm 0.04\%$ , MORB =  $+0.15 \pm 0.03\%$ ). Furthermore, Mg and Fe isotopes in these basalts appear to be anti-correlated. While some fractionation occurs during partial melting and fractional crystallization, this cannot readily explain the above differences.

The Fe isotope variation may be due in part to fractionation that occurs between pyroxene and olivine due to differences in bonding environment. Williams and Bizimis (2014) found that iron in garnet pyroxenites from Hawaii is on average isotopically heavy ( $\delta^{57}\text{Fe}_{\text{IRMM-14}} = +0.10$  to  $+0.27\%$ ) compared to depleted peridotites ( $-0.34$  to  $+0.14\%$ ), primitive mantle ( $\sim +0.14\%$ ), and MORB ( $\sim +0.16\%$ ).

They also found that  $\delta^{57}\text{Fe}$  inversely correlates with several indicators of melt depletion in Oahu peridotites and pyroxenites as well as  $\epsilon_{\text{Hf}}$  (Fig. 8). They suggested that the isotopically heavy iron observed in some OIB, notably the Society and Austral Islands, is due to the presence of pyroxenites, perhaps derived from recycled oceanic crust in the sources of these islands.

Huang et al. (2011a) analyzed Hawaiian lavas and found that  $\delta^{42}/^{44}\text{Ca}_{\text{SRM915a}}$  in lavas of Koolau volcano (Oahu) ranged from 0.34 to 0.40‰, significantly lower than the estimated bulk silicate Earth or primitive mantle value of  $\sim +50\%$ . In addition, they found that calcium isotope ratios correlated inversely with  $^{87}\text{Sr}/^{86}\text{Sr}$  and with Sr/Nb ratios, although not with other trace element ratios. Huang et al. argued that the calcium isotope variations and these correlations reflected the presence of marine carbonates in ancient recycled oceanic crust in the Hawaiian mantle plume.

Thus, stable isotope geochemistry clearly confirms the importance of recycling of crust material in creating mantle heterogeneity, as others have argued (e.g., Hofmann, 1997; Stracke, 2012).

#### 4. The noble gas perspective

Noble gas geochemists have touched yet another part of the elephant, so to speak, and provided yet another, and in some ways quite different, perspective. The noble gases, being volatile, are highly depleted in the Earth and, being inert, do not participate in chemical reactions in the mantle (Xe may be an exception, Sanloup et al., 2011). They are of interest nevertheless because all exhibit isotopic variations due to radioactive decay and related nuclear reactions (although Kr is produced by fission, isotopic variations in the mantle have yet to be demonstrated). Helium is, of course, produced by alpha decay and argon is produced by potassium decay. Xenon isotopes vary due to uranium fission as well as decay of the extinct radionuclides  $^{244}\text{Pu}$  and  $^{129}\text{I}$ . Ne isotopes are produced by reactions of O and Mg with alpha particles and neutrons produced by other radioactive decays. In addition, noble gas isotope ratios can vary due mass dependent, and perhaps other types of, fractionation.

Noble gas isotopic analysis presents its own set of challenges. First, the abundance of these elements in the Earth is extremely low, and much of the Earth's inventory of several of them is in the atmosphere. Second, they are quickly lost from subaerially erupted lavas through degassing, but some gas is retained in submarine and subglacial lavas as well as in olivine phenocrysts. Third, atmospheric contamination is ubiquitous, except for He, which means that the isotope ratios most different from the atmospheric value are generally the most significant. Finally, ingrowth of radiogenic  $^4\text{He}$  can lower and cosmogenic production of  $^3\text{He}$  can increase the  $^3\text{He}/^4\text{He}$

ratio over time, although the latter is important only within the top meter of the Earth's surface.

#### 4.1. Helium

Helium is unique among elements because it is the only one for which the Earth is not a closed system: it continually leaks to space from the top of the atmosphere and is replaced by gas leaking from the solid Earth resulting in an atmospheric residence time of He of only a few million years (the exact value is uncertain). Most atmospheric He is radiogenic  $^4\text{He}$ : the atmospheric  $^3\text{He}/^4\text{He}$  ratio is  $1.384 \times 10^{-6}$  compared to a primordial (pre-deuterium burning) ratio of  $1.66 \times 10^{-4}$  and a solar wind ratio of  $4.63 \times 10^{-4}$ . In the subsequent discussion, I will use the R/R<sub>A</sub> notation for He isotope ratios, which is the  $^3\text{He}/^4\text{He}$  ratio divided by the atmospheric ratio. Helium in the continental crust is more radiogenic than atmospheric He (R/R<sub>A</sub>  $\approx 0.1$ ). Clarke et al. (1969) found that helium in Pacific deep water was less radiogenic than atmospheric and they suspected that the source of this helium was the mantle. This was confirmed by high  $^3\text{He}/^4\text{He}$  ratios in dredged basalts (Lupton and Craig, 1975) and xenoliths (Tolstikhin et al., 1974). Kaneoka and Takoaka (1978) reported R/R<sub>A</sub> values in olivines from Hawaiian lavas ranging from 8 to 18, clearly confirming the mantle was a reservoir of less radiogenic He. Kurz and Jenkins (1981) found that MORB from all oceans had a "remarkably constant" R/R<sub>A</sub> of 8 (the mean value of over 500 analyses in the PetDB database is now  $8.8 \pm 2.5$ ). Kurz et al. (1982) showed that both higher and lower  $^3\text{He}/^4\text{He}$  ratios than MORB occurred in OIB and that  $^3\text{He}/^4\text{He}$  in MORB increased along the Mid-Atlantic Ridge toward Iceland (reaching values of 17 R/R<sub>A</sub>) but decreased to  $<7$  R/R<sub>A</sub> in the vicinity of the Azores. Subsequently, ratios in excess of 30 R/R<sub>A</sub> have been reported in basalts from Iceland, the Galápagos, and Hawaii (Fig. 8) and ratios as high as 50 R/R<sub>A</sub> were reported in early Cenozoic Iceland mantle plume picrites on Baffin Island (Starkey et al., 2009; Stuart et al., 2003). Because He is lost from the mantle during melting and subsequent degassing and because  $^4\text{He}$  is replaced by radioactive decay but  $^3\text{He}$  is not, these high  $^3\text{He}/^4\text{He}$  ratios indicate that some OIB sources tap a relatively primordial, less degassed mantle reservoir, most likely in the deep mantle. Porcelli and Elliott (2008) argued, persuasively, that  $^3\text{He}/^4\text{He}$  ratios as high as 50 R/R<sub>A</sub> "can only be preserved if located in domains that are not modified by convective mixing or diffusive homogenization" over the last 3 Ga.

Helium isotope ratios do not correlate with other radiogenic isotope ratios in oceanic basalts overall (Fig. 9), suggesting that noble gas

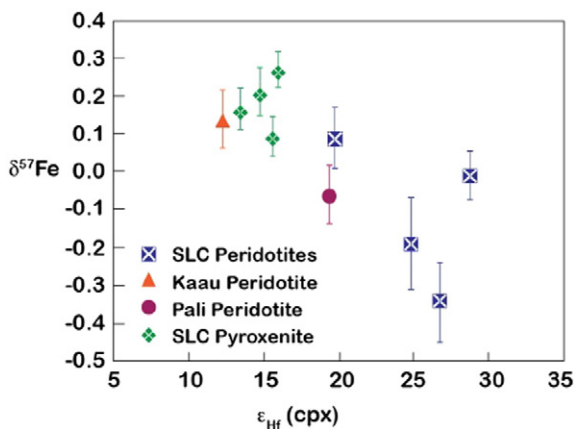


Fig. 8. Hf and Fe isotopes in peridotite and pyroxenite xenoliths from the Salt Lake Crater, Pali, and Kaau vents of the Honolulu Volcanic Series of Hawaii. Data from Williams and Bizimis (2014).

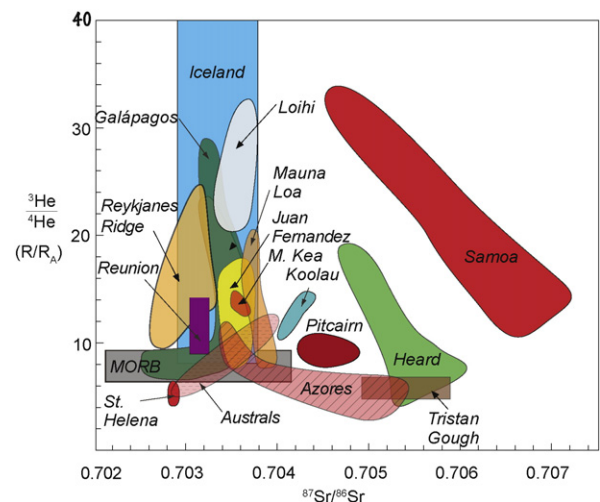
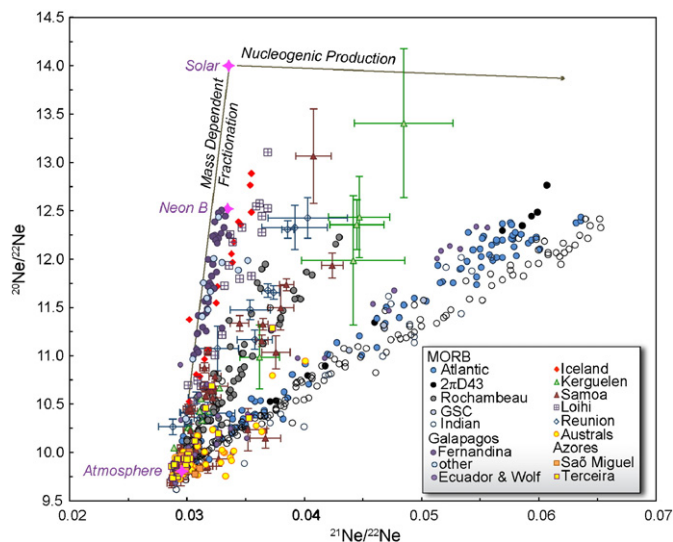


Fig. 9. He isotope ratios as a function of  $^{87}\text{Sr}/^{86}\text{Sr}$  in OIB. There is no overall correlation, but the highest  $^3\text{He}/^4\text{He}$  ratios are associated with intermediate  $^{87}\text{Sr}/^{86}\text{Sr}$ . After Graham (2002).

geochemists are indeed feeling an entirely different part of the elephant. Local correlations, however, are observed in along some mid-ocean ridge segments (e.g., Graham et al., 2014), individual islands and island groups (e.g., examples cited in Moreira, 2013), and individual volcanoes (e.g., Kurz and Kammer, 1991). However, as I mentioned in Section 2.4 and several others have pointed out (e.g., Class and Goldstein, 2005; Farley et al., 1992), the highest  $^3\text{He}/^4\text{He}$  ratios tend to be associated with intermediate Sr, Nd, and Pb isotope ratios. It stretched credulity to argue that this is coincidental; instead, it strongly suggests the least modified mantle is depleted in incompatible elements relative to chondrites.

#### 4.2. Neon

Neon isotopic composition varies significantly in the Earth as a consequence of both mass dependent fractionation and the secondary nuclear reactions mentioned above. Unlike He, the atmosphere contains significant amounts of Ne, so atmospheric contamination is ubiquitous. This observation combined with the low abundance of Ne in the mantle makes analysis of Ne isotope ratios difficult and data of useful precision only started to become available in the late 1980s. Fig. 10 summarizes the currently available data. Neon in MORB and OIB define correlations that extend from the atmospheric value to higher  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$ . These correlations result from dilution (mainly through contamination) of mantle neon by atmospheric neon. Hence it is the highest  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  in each data set that are most significant. Atmospheric neon differs from solar wind Ne as a consequence of mass-dependent fractionation, i.e., preferential loss of  $^{20}\text{Ne}$  and  $^{21}\text{Ne}$  relative to  $^{22}\text{Ne}$  in proportion to mass difference. The meteoritic “Neon B” component is also fractionated relative to solar wind, but far less so than atmospheric neon. The first observation is that mantle neon, both from MORB and OIB, is far less fractionated, and therefore more solar-like, than atmospheric Ne, with  $^{20}\text{Ne}/^{22}\text{Ne}$  values that in some cases exceed the meteoritic Neon B value. The second observation is that mantle Ne is enriched in  $^{21}\text{Ne}$  compared to atmospheric, meteoritic, and solar Ne as a consequence of nuclear reactions; the extent of this enrichment is effectively a measure of the  $(\text{U} + \text{Th})/\text{Ne}$  ratio in mantle source.  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios are generally higher in MORB than



**Fig. 10.** Neon isotope data in oceanic basalts. For clarity, error bars are shown only for the data from Reunion (Staudacher et al., 1990), Samoa (Jackson et al., 2009), and Kerguelen (Valbracht et al., 1996) as these data are less precise than the remaining data. Other data are from Valbracht et al. (1997), Madureira et al. (2005), Hopp and Trieloff (2005), Doucet et al. (2006), Raquin et al. (2008), Raquin and Moreira (2009), Kurz et al. (2009), Hanyu et al. (2011), Mukhopadhyay (2012), Tucker et al. (2012), Parai et al. (2012), Moreira et al. (2012), and Petó et al. (2013).

OIB, implying the MORB source is more degassed than OIB sources, with a few exceptions. Ne isotopic compositions from the Australs suggest that the source is as or more degassed than the MORB source. The Galapagos submarine basalts show a wide variation in  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios; basalts from Volcan Fernandina have low  $^{21}\text{Ne}/^{22}\text{Ne}$  (Kurz et al., 2009), as do those from an eastern seamount (Raquin and Moreira, 2009), while those from Volcan Ecuador and Volcan Wolf have  $^{21}\text{Ne}/^{22}\text{Ne}$  close to MORB. The variation within the Galapagos is consistent with radiogenic isotope ratios, as Ecuador and Wolf basalts have more MORB-like Sr, Nd, Pb, and Hf isotope ratios than Fernandina (Blichert-Toft and White, 2001; White et al., 1993). In addition to Fernandina, submarine basalts from Loihi, Hawaii (e.g., Valbracht et al., 1997) and subglacial basalts from Iceland (e.g., Mukhopadhyay, 2012) have Ne isotopic compositions that plot close to a mass dependent fractionation line passing through the solar wind composition, indicative of a relatively undegassed source. Data on olivine separates from basalts of Kerguelen and Reunion are less precise (mainly due to smaller quantities of gas), but nevertheless define mixing lines between an atmospheric component and one with lower  $(\text{U} + \text{Th})/\text{Ne}$  than MORB, implying their sources are also less degassed than the MORB source. Data from Samoa (from olivines in both subaerial and submarine lavas, Jackson et al., 2009) show greater scatter; this is perhaps to be expected since He and radiogenic isotope ratios from Samoa suggest a mixture of recycled and undegassed components in the Samoan plume. Similarly, data from the Azores are also quite variable, with the Ne isotope ratios from Saõ Miguel (which has the most radiogenic Sr) generally close to the atmospheric value.

With far more limited data available, Honda et al. (1993) found that  $^3\text{He}/^4\text{He}$  ratios correlated with the slope of data set on the  $^{20}\text{Ne}/^{22}\text{Ne}$ – $^{21}\text{Ne}/^{22}\text{Ne}$  plot. This relationship continues to hold: volcanoes and chains with the highest  $^3\text{He}/^4\text{He}$  ratios, such as Iceland, Loihi, and Fernandina, plot along steep slopes while MORB and islands and chains with lower  $^3\text{He}/^4\text{He}$ , such as Ecuador and the Australs, plot along lines of lower slope. The relation results from both  $^4\text{He}$  and  $^{21}\text{Ne}$  being produced as a consequence of decay of Th and U. This correlation requires that the  $^3\text{He}/^{22}\text{Ne}$  ratio vary between mantle reservoirs, with  $^3\text{He}/^{22}\text{Ne}$  being highest in the MORB source and lowest in the source of OIB with the highest  $^3\text{He}/^4\text{He}$  ratios, such as the Galapagos and Iceland and it appears impossible to produce these variations by partial melting or crustal recycling (Tucker and Mukhopadhyay, 2014).

#### 4.3. Argon

Argon isotopes also suggest MORB and OIB tap different reservoirs. Argon is a major atmospheric gas, and nearly all of it is radiogenic  $^{40}\text{Ar}$  that has been produced by decay of  $^{40}\text{K}$  over Earth's history. This testifies to continuing outgassing of the Earth's interior.  $^{40}\text{Ar}/^{36}\text{Ar}$  as high as 40,000 have been measured in MORB (Burnard et al., 1997; Raquin et al., 2008), far higher than the atmospheric value of 296.16 (Mark et al., 2011). Maximum  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios in OIB are much lower. Although the lower ratios could be a result of contamination, an estimate of the maximum  $^{40}\text{Ar}/^{36}\text{Ar}$  can be obtained from the correlation of  $^{40}\text{Ar}/^{36}\text{Ar}$  with  $^{20}\text{Ne}/^{22}\text{Ne}$  and assuming either a solar or meteoritic (i.e., Neon B) value for the mantle. Using this approach suggests  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios of around 8000 for Hawaii, around 10,750 for Iceland, and 40,000 to 60,000 for MORB (Moreira, 2013; Mukhopadhyay, 2012; Trieloff et al., 2003). Ar isotope ratios also show clear correlations with  $^3\text{He}/^4\text{He}$  (e.g., Moreira, 2013). Thus Ar isotopes suggest that the mantle plumes that produce OIB, or at least some of them, tap a significantly less degassed reservoir than MORB, consistent with He and Ne isotopes.

#### 4.4. Xenon

Of the noble gases, Xe is the rarest, the most challenging to analyze, has the most complex behavior, has the most isotopes, and is the one that offers the greatest potential insights into Earth's early evolution.



Because of the former factors, high quality data is limited; in addition to data on MORB, useful Xe isotope data are available only from one subglacial Icelandic basalt, submarine basalts from Loihi Seamount, Hawaii, xenoliths from Reunion, and olivines from Samoa. While limited, this dataset is nonetheless highly informative. Xe isotope ratios vary as a consequence of beta decay of the extinct  $^{129}\text{I}$  ( $t_{1/2} = 15.7 \text{ Ma}$ ) producing  $^{129}\text{Xe}$ , fission of  $^{238}\text{U}$  and extinct  $^{244}\text{Pu}$  ( $t_{1/2} = 82 \text{ Ma}$ ) producing  $^{131}\text{Xe}$ ,  $^{132}\text{Xe}$ ,  $^{134}\text{Xe}$ , and  $^{136}\text{Xe}$ , and mass fractionation. As with the other noble gases, nearly all samples are contaminated by atmospheric Xe, so it is the ratios most offset from the atmospheric value that are significant (which is not to imply that any particular mantle reservoir is necessarily isotopically homogeneous). Fig. 11 shows that Xe in MORB is more radiogenic than in OIB, and both are more radiogenic than atmospheric Xe. Several inferences can be drawn from this. First, the unradiogenic nature of the atmosphere suggests either it formed very early through outgassing of the mantle or has an entirely different origin than Xe in the solid Earth. Second, the difference between MORB and OIB indicates higher time-integrated I/Xe and (U + Pu)/Xe in the MORB source, implying it is more degassed than OIB sources. Third, and more significantly, because of the short half-life of  $^{129}\text{I}$  (and  $^{244}\text{Pu}$ ), this difference must have been established very early in Earth's history and sustained ever since. Indeed, Mukhopadhyay (2012) argues that "Because  $^{129}\text{I}$  became extinct about 100 million years after the formation of the Solar System, OIB and MORB mantle sources must have differentiated by 4.45 billion years ago and subsequent mixing must have been limited." Furthermore, he finds that "The Iceland plume source also has a higher proportion of Pu- to U-derived fission Xe, requiring the plume source to be less degassed than MORBs."

Thus the perspective provided by noble gas isotopes differs as much from that of other radiogenic and stable isotopes as the feel of an elephant's trunk does from its ear. While the latter provide a picture of a mantle extensively polluted by material recycled from the Earth's crust, the former provides a picture incompletely degassed mantle reservoirs isolated for nearly all of Earth's history. The problem is then to reconcile those perspectives. Before attempting to do so, we need to consider a last perspective, namely that of geophysics.

## 5. The geophysical perspective

Much of what we know about the mantle comes from the investigation of teleseismic waves, principally, but not exclusively, their velocities

as they travel through the mantle. Seismic velocities depend on a combination of rigidity and density, and these can be related to pressure, temperature, and composition through mineral physics. The compositional dependence is ambiguous over the range of plausible mantle compositions (and certainly trace element and isotopic composition have no influence), so any relationships between mantle seismic structure and the geochemical properties can only be indirectly inferred. Furthermore, because the wavelength of teleseismic waves is long, spatial resolution is weak, particularly in the deep mantle, although reflections off the core-mantle boundary provide somewhat better illumination in the deepest mantle. Nevertheless, any effort to understand mantle geochemical structure and evolution must necessarily consider mantle seismic structure.

The mantle perspective provided by seismology in the mid-twentieth century was largely one of rock of uniform composition whose seismic velocities increased continuously due to self-compression (Bullen, 1949). The exceptions were velocity discontinuities in the region of 400 to 700 km that were subsequently shown to be due to phase changes (Ito and Takahashi, 1989; Liu, 1976; Ringwood, 1966) and the lowermost 200 km or so of mantle, known as D", where velocity gradients were anomalous (Julian and Sangupta, 1973). The initial focus was on refining a radial seismic velocity and density model of the mantle, but by the time seismologists agreed on one, the PREM model (Dziewonski and Anderson, 1981), their focus had already begun shifting to examining azimuthal variations from it. Evidence of significant lateral variation in seismic velocities began to emerge (e.g., Dziewonski et al., 1977; Jordan, 1975; Masters et al., 1982) and it became clear that the lowermost mantle was highly heterogeneous. The D" region proved to be particularly curious as it is characterized by an anti-correlation between s-wave and bulk sound velocity (Su and Dziewonski, 1997) and a marked increase in s-wave horizontal anisotropy (Kustowski et al., 2008; Panning and Romanowicz, 2006). Discontinuous regions of anomalously slow s-wave velocity beneath South Africa and the South Central Pacific (Dziewonski, 1984) in and above D" also began to come into focus. These in turn were surrounded by regions of anomalously fast seismic velocity that seemed to relate to convection-driven geoid anomalies (Busse, 1983), subduction history, and hot spot distribution (Ricard et al., 1993; Richards and Engebretson, 1992). Dziewonski (1984) originally referred to the seismically slow regions as "superplumes", but they have come to be known as "large slow shear-wave velocity provinces" or LLSVPs (Lay et al., 2006).

Although details of various tomographic models differ, the seismic velocity structure of the lower mantle now seems reasonably well defined; as Dziewonski et al. (2010) stated in reference to these models, "Global models of mantle shear velocity anomalies have reached maturity", meaning that they "have resolved, on the global scale, the dominant large-wavelength anomalies." They show the LLSVPs to have sharp boundaries and the velocity contrast with the surrounding mantle is difficult to explain by temperature alone, suggesting they are intrinsically denser than average mantle (Garnero and McNamara, 2008). The South Pacific LLSVP extends at least 400 km above the core-mantle boundary while the African LLSVP extends at least 1000 km above it. Together, they cover a substantial (approaching 50%) fraction of the core-mantle boundary, but represent only a small fraction (~2 to 8%) of total mantle volume (Hernlund and Houser, 2008; Šrámek et al., 2013). There had been speculation about a possible seismic boundary at about 1600 km depth in the mantle (Kellogg et al., 1999; van der Hilst and Karason, 1999), but it now seems this may simply have been a smeared seismic signature of the tops of the LLSVPs, which are indistinct, and may resolve into multiple upwellings (Schubert et al., 2004).

Torsvik et al. (2008), among others, pointed out that hot spots appear to be preferentially located on the margins of the LLSVPs and the LLSVPs appear to have been stationary for hundreds of millions of years based on plate reconstructions and the position of large igneous provinces through time. Curious small, thin regions within the D" region,

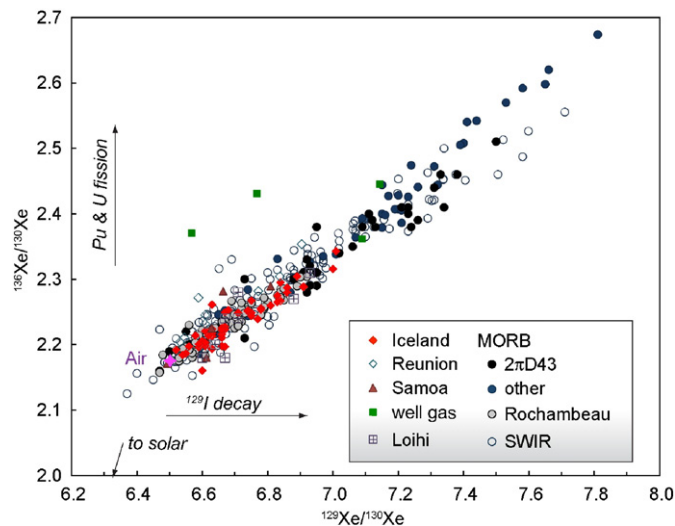


Fig. 11.  $^{136}\text{Xe}/^{130}\text{Xe}$  vs.  $^{129}\text{Xe}/^{130}\text{Xe}$  in oceanic basalts and well gases from New Mexico, USA. Maximum values in MORB are greater than in OIB. Data from Poreda and Farley (1992), Kunz et al. (1998), Trieloff et al. (2000), Hopp and Trieloff (2005), Holland and Ballentine (2006), Tucker et al. (2012), Parai et al. (2012), Mukhopadhyay (2012), and Petó et al. (2013).

called “ultra-low velocity zones” or ULVZs also appear to be preferentially located beneath the margins of the LLSVPs (Garnero and McNamara, 2008). The *s*- and *p*-wave velocity reductions in the ULVZs are so great that some have speculated they are regions of partial melting (e.g., Williams and Garnero, 1996).

Considerable progress has been made on understanding the mantle transition region between 400 and 800 km and its effect on mantle convection. It is clear that the increase in seismic velocity in the region results entirely, or nearly so, from a series of phase changes, the most important of which is the transition from ringwoodite (a high pressure phase of olivine), in which silicon is tetrahedrally coordinated to bridgmanite ((Mg,Fe) SiO<sub>3</sub>), in which silicon is octahedrally coordinated, and (Mg,Fe)O. The Clayperon slope is negative (Ito and Takahashi, 1989), which has the effect of impeding convection across the boundary. Ringwood (1982) suggested that oceanic crust and lithosphere could not penetrate the transition zone because basaltic compositions, which are rich in Ca-perovskite in the lower mantle, undergo the tetrahedral-octahedral transition at greater depth, making basalt relatively buoyant in this region. However, Hirose et al. (1999) found that the transformation in basaltic lithology is complete by around 27 GPa, earlier than previously believed, and that the Clayperon slope for the majorite garnet–Ca-perovskite transformation is positive, and consequently the overall pressure–temperature Clayperon slope is positive for basalt compositions. The seismic evidence that subducted lithosphere passes through the transition zone is now overwhelming, as seismic imaging showing them descending into the deep mantle (Fig. 12) and accumulating at its base mantle (Konishi et al., 2009; Ritsema et al., 2011), although some slabs may temporarily stagnate in the transition zone (e.g., Fukao et al., 1992).

Mantle plumes were thought to have radii on the order of 100 km, comparable to the wavelengths of seismic waves used in deep mantle tomography. Consequently, imaging plumes beneath the transition zone has proved difficult. In the last decade, however, several studies have imaged thermal anomalies beneath hot spots extending downward into the deep mantle (Wolfe et al., 2009, 2011). Other studies have found that the transition zone is thinner beneath hotspots, which is expected to occur when hot mantle upwells through it (Courtier et al., 2007), because the phase change at 670 km has a negative Clayperon slope and is deflected upward while the 410 km phase change has a positive Clayperon slope is consequently deflected downward. Montelli et al. (2004, 2006) reported slow velocity anomalies under some 17 hotspots that extended well into the deep mantle, and in some cases to the base of it. These results, however, were controversial as there is some tendency for the finite frequency technique used to smear anomalies vertically (Van Der Hilst and De Hoop, 2005). Recently, however, French and Romanowicz (2015), using a different technique that includes analysis of both seismic wave velocities and waveforms, have “clearly resolved” seismic *s*-wave anomalies extending into the lowermost mantle beneath 20 oceanic hotspots. They appear to be

broader than 200 km, although the exact width cannot be determined, and are possibly intrinsically dense. All of them are located within the borders of the African and Pacific LLSVPs. They are rooted in wide regions (500–800 km diameter) of strongly negative velocity anomalies at the base of the mantle. These patches coincide with large ULVZ's for the Hawaiian, Samoan, and Icelandic plumes. The conduits are nearly vertical in the lower mantle, but in some cases bend or thin above 1000 km, consistent with their being deflected by the more vigorous convection of the shallow mantle.

Thus the geophysical perspective of the mantle has evolved as well over the last several decades. There is no evidence of a layered structure that many geochemists hypothesized and the existence of whole mantle convection, with subducted oceanic lithosphere sinking into the deepest mantle, is firmly established. This convection, however, is not necessarily steady-state, as, for example, slabs might pass through the 670 km discontinuity in occasional cascades (e.g., Maruyama et al., 2007). The lowermost mantle appears to be at least as complex, if not more so, as the uppermost mantle with clear evidence of strong lateral heterogeneity. Wilson's (1963) hotspots are underlain by hot, and possibly dense, columns that extend to the base of the mantle and are reasonably interpreted as the plumes envisioned by Morgan (1971). The plumes in turn appear to be associated with large regions of slow *s*-wave velocity that are likely both hot and dense. The problem is then to reconcile this perspective with the various geochemical ones.

## 6. Merging perspectives

### 6.1. Plumes, DUPAL, and LLSVPs

The perspectives from radiogenic isotope and stable isotope geochemistry seem well aligned: they provide a picture of a mantle both incompatible-element depleted through crust formation and heavily polluted and refertilized by that same crustal material returned to the mantle through the plate-tectonic driven processes of subduction, subduction erosion, and continental foundering. These data provide little evidence for the existence of an extensive reservoir of primitive mantle that geochemists hypothesized some decades ago, at least if primitive mantle has  $\epsilon_{Nd} = 0$ . However, as DePaolo (1980) noted, “if the Sm/Nd ratio of the Earth were different from that assumed by 5% or more, it could require changes in the conclusions given here and elsewhere” with respect to the volumes of primitive mantle surviving. The suprachondritic <sup>142</sup>Nd/<sup>144</sup>Nd suggests that the terrestrial Sm/Nd ratio might indeed significantly exceed the chondritic value. If the bulk silicate Earth has  $\epsilon_{Nd}$  in the range of 3 to 7, this greatly reduces the potential volume of surviving primitive mantle. Furthermore, this compositional range corresponds with the most common Nd isotopic compositions among OIB (Figs. 1 and 2).

Reconciling the noble gas isotope perspective with the other geochemical perspectives is more difficult. In contrast to the picture of a

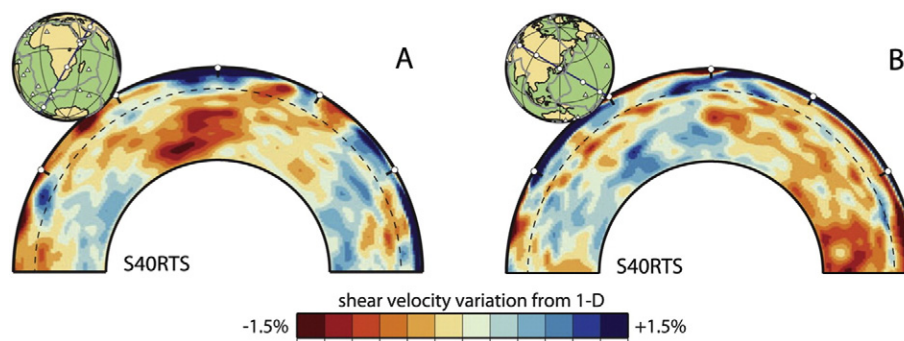


Fig. 12. Tomographic model S40RTS of Ritsema et al. (2011) showing subducted lithosphere (blue) descending into the deep mantle and the two LLSVPs (red) beneath Africa and the Central South Pacific. From Ritsema et al. (2011).

mantle heavily polluted by recycled crustal material, the noble gas isotope perspective, with some exceptions, is one of ancient, long-isolated reservoirs. As mentioned earlier, He isotope ratios as high as 50 R/R<sub>A</sub> require long isolation from other mantle reservoirs. Xenon isotopic compositions suggest that some of the xenon in the Iceland mantle plume has been isolated from the MORB source reservoir since the first 100 Ma of solar system history – the entire history of the Earth – with only limited mixing between them. Indeed, Mukhopadhyay (2012) concluded that “Earth’s mantle accreted volatiles from at least two separate sources and that neither the Moon-forming impact nor 4.45 billion years of mantle convection has erased the signature of Earth’s heterogeneous accretion and early differentiation.” Tucker and Mukhopadhyay (2014) argue that the factor of 3 to 4 higher <sup>3</sup>He/<sup>22</sup>Ne ratio in MORB compared with many OIB is a consequence of multiple early outgassing events, presumably associated with extensive melting during impacts as the Earth grew. They further argue that subsequent impacts, such as the Moon-forming event, could not have entirely melted the mantle.

The isolation between the DMM and OIB reservoirs is not, however, inconsistent with radiogenic isotope evidence. As Hart et al. (1992) pointed out, multi-isotope systematics preclude significant amounts of depleted MORB source material in OIB, although OIB sources do contain incompatible element-depleted material. This is true also of the sources of rejuvenescent-phase volcanism on Hawaii and elsewhere; while this material has an isotopically depleted signature compared to the shield building sources, it is distinct from the MORB source (e.g., White, 2010). Furthermore, the noble gas isotope data do not preclude admixtures of recycled material from the Earth’s surface in either OIB or MORB sources, both because the lightest noble gases can probably not survive the subduction zone barrier and because recycled components are difficult to distinguish from recent atmospheric contamination (Sarda, 2004; Staudacher and Allègre, 1988). The resolution then must be that many mantle plumes carry both a recycled and relatively primitive component to the surface. Assuming the convecting mantle has been extensively and repeatedly melted and degassed, it is easy to imagine the noble gas contents of a primitive mantle reservoir having orders of magnitude higher noble gas contents, so that only a quite small contribution from such a reservoir would be sufficient for the primitive noble gas signatures to swamp that of degassed or recycled ones.

Curiously, the estimated composition of non-chondritic primitive mantle, such as the SCHEM model composition of Caro and Bourdon (2010) or the one derived from enstatite chondrite <sup>142</sup>Nd/<sup>144</sup>Nd value (White, 2013) approximates the Nd and Sr isotopic composition of the PREMA component in OIB, as Nobre Silva et al. (2013) previously noted. PREMA is, however, not a plausible primitive mantle composition in Pb isotope space. The maximum age of lunar rocks provides a minimum age for the Earth of about 4.45 Ga. Consequently, the Pb isotopic composition of the Earth must lie between a 4.45 Ga single-stage isochron and 4.568 Ga isochron, or *Geochron*. The Pb isotopic composition of PREMA appears to lie to the high <sup>206</sup>Pb/<sup>204</sup>Pb side of this (Fig. 3). Furthermore, essentially all OIB, including those of the PREMA genera, have trace element compositions, particularly ratios such as Nb/U and Pb/Ce, inconsistent with primitive mantle. Finally, OIB with PREMA-like compositions, including those from Hawaii and Iceland, often have non-primitive stable isotopic compositions. Nevertheless, the radiogenic isotopic composition of PREMA most closely approximates that of primitive mantle, assuming primitive mantle has non-chondritic Sm/Nd. A reasonable interpretation of PREMA is that it is a well-stirred mixture of a variety of materials, including approximately balanced contributions of depleted and recycled enriched components (e.g., Stracke et al., 2006) in addition to an admixture of anciently isolated mantle carrying the relatively primitive noble gas signature.

We must now reconcile the geochemical and geophysical perspectives. This begins, perhaps, with Hart (1984), who noted an apparent geographic relationship between his “DUPAL anomaly” and the geoid anomalies of Busse (1983). Castillo (1988) pointed that the

DUPAL anomaly was also geographically related to Dziewonski’s (1984) slow seismic velocity anomalies, which we now recognize as the two LLSVPs. Staudigel et al. (1991) also recognized the association of the many hot spot tracks in the Central South Pacific with slow seismic velocity anomalies and referred to the region as the South Pacific Isotope and Thermal Anomaly (SOPITA). In fact, the DUPAL signature in the region of the African LLSVP (i.e., the South Atlantic and Indian) is isotopically distinct from the predominant isotopic signature in the South Pacific: EM I compositions predominate in the former while EM II predominate in the latter. Thus DUPAL appears to resolve into two distinct anomalies (I suggest the Pacific one be called SOPITA), each loosely associated with a LLSVP. SOPTIA: EM2 and SAITIA: EM1

Lateral isotopic heterogeneity in some oceanic island chains, such as Hawaii, Galapagos, and Marquesas, has long been recognized (e.g., Desonie et al., 1993; Tatsumoto, 1978; White et al., 1993) and has been more recently recognized in a number of other ones, including Samoa (Jackson et al., 2014), the Societies (Payne et al., 2013), the Azores (Beier et al., 2010), and Tristan da Cunha-Gough (Rohde et al., 2013). Farnetani et al. (2012) showed that simple lateral compositional variation in the plume source region could map into more complex lateral and radial variation within the plume and generate the pattern of spatial and temporal variation seen in Hawaiian volcanoes. Several recent papers have speculated on the role that the LLSVPs might have in producing this lateral heterogeneity (e.g., Harpp et al., 2014; Weis et al., 2011). Huang et al. (2011b) suggested that the zonation in the Samoan and Marquesas chains “reflect their respective positions relative to the Pacific” LLSVP and “that isotopically enriched material is preferentially distributed in the lower mantle of the Southern Hemisphere, within the Pacific” LLSVP.

The question thus becomes, what are the LLSVPs? Garnero and McNamara (2008) suggested they could consist of hot, intrinsically dense material swept into upwelling regions by mantle convection. They speculated that a trade-off between thermal buoyancy and intrinsic chemical density “can yield long-lived stable structures” and that the dense material might be subducted basaltic crust that has “accumulated throughout Earth’s history” or residues of early mantle differentiation that have persisted throughout geologic time. If they are the latter, then it is tempting to speculate that they comprise the EER proposed by (Boyet and Carlson, 2005) to balance the terrestrial Sm/Nd budget.

If the LLSVPs are the reservoir of the primitive noble gases observed in many mantle plumes, they could not also be the putative EER because the contributed primitive material would produce a slow decrease in the <sup>142</sup>Nd/<sup>144</sup>Nd of the observable mantle over geologic time. A model proposed by Tolstikhin and Hofmann (2005) might at first seem a solution. In their model a primitive early-formed and noble gas-rich layer similar to the EER of Boyet and Carlson (2005) forms within D’ and primitive noble gases then diffuse from D’ into the overlying mantle and then into upwelling plumes. Since the diffusion of Nd should be negligible on the relevant scales, such a layer could slowly release primitive helium but not <sup>142</sup>Nd-poor neodymium. However, while large-scale diffusion of light noble gases into the convecting mantle might be plausible, large-scale solid-state diffusion of heavier ones, Xe in particular, seems improbable. Diffusivity of Xe in water is an order of magnitude less than that of He (Ballentine et al., 2002). The difference is likely to be far greater in solids because the small He atom can diffuse by the interstitial mechanism, while much larger Xe atoms can diffuse only by much slower mechanisms such as vacancy exchange. The heavy noble gas signature thus likely requires advection and mixing of primitive material into plumes, although the fraction of primitive material might nonetheless be small. Thus the LLSVP’s could not be both the reservoir of primitive noble gases and the low <sup>142</sup>Nd/<sup>144</sup>Nd reservoir.

A particularly intriguing possibility was proposed by Li et al. (2014), namely that the LLSVPs consist of both dense residues of early mantle differentiation and subducted oceanic crust. In their geodynamic model subduction and convection sweep an initial, dense primitive layer at the base of the mantle into ‘thermochemical piles’. Subducted



oceanic crust is episodically flushed into the more primitive reservoir and stirred into it through internal convection in the pile. The fraction of oceanic crust in the piles eventually reaches 1% to more than 15%, depending on viscosity and buoyancy contrasts. Mantle plumes form on top of the piles consist of a mixture of ambient deep mantle, relatively recently subducted oceanic crust, and primitive material and older oceanic crust from the LLSVPs and the fraction of primitive material in the LLSVPs diminishes slowly over time. Adapting this model to the radiogenic and stable isotopic observations, plumes of the PREMA genus would contain relatively large fractions of material from the LLSVP's while plumes of the other genera would contain only secondary amounts of LLSVP material.

At this point, beyond noting that the LLSVPs are likely denser and therefore likely richer in iron than surrounding mantle, we can only speculate about their composition. We can also only speculate on whether plumes contain material derived from the LLSVPs, although there is already a fairly strong circumstantial case for this possibility. What now appears to be established from seismology is that mantle plumes are associated with the LLSVPs, preferentially nucleating around their margins.

### 6.2. Another perspective from geoneutrinos?

Evidence of a connection between LLSVPs, primitive reservoirs, and mantle plumes is presently circumstantial (as well as circumferential, since the latter seem associated with the margins of LLSVPs). One new line of research, another blind man touching yet another part of the elephant so to speak, is counting geoneutrinos produced principally by beta decays of U and Th daughters. In principle, such studies should eventually be able to constrain the total U and Th content of the Earth and thus discriminate between collisional erosion models (which predict low U and Th content) and alternative explanations for the  $^{142}\text{Nd}$  conundrum. Unfortunately, neutrinos interact so weakly with matter that only a vanishingly small fraction are detected, so the data come slowly. Results to-date from the two operating geoneutrino detectors are inconclusive. Results from the 1 kt Japanese Kamland detector based on 116 detected geoneutrinos constrain the terrestrial heat production from U and Th to be 8 to 22 TW (Gando et al., 2013). This is consistent with either the conventional estimates of terrestrial composition based on the chondritic model or an Earth depleted in heat producing elements by collision erosion (White, 2013; Jackson and Jellinek, 2013), although the extreme case of O'Neill and Palme (2008) falls at the lower limit. The higher heat production often assumed in geodynamic models (e.g., Turcotte and Schubert, 2002) is excluded. The most recent results from the 278 t detector in Borexino, Italy provide almost the opposite result. Based on 24 detected geoneutrinos, they estimate a U + Th heat production of 23–36 TW, which would encompass both the conventional chondritic models and the higher heat production in geodynamic models (Agostini et al., 2015). As these experiments continue and the SNO+ detector in Sudbury, Ontario begins to contribute results, the accumulation of data should eventually place much better constraints on terrestrial Th and U concentrations and thus distinguish between these models. A large mobile submarine detector, such as the proposed Hanohano detector, could achieve even better constraints. By placing the detector in the ocean, the near-field flux from continental crust would be eliminated and by accumulating data at various sites in the ocean it would be possible to gain the spatial resolution needed to determine whether U and Th are concentrated in the LLSVPs, as would be the case in the Boyet and Carlson model (Dye, 2012; Šrámek et al., 2013).

### 6.3. Remaining problems

Mysteries remain, however. For example, if all or most genera of plumes are flavored by recycled material from the Earth's surface, why do their isotopic flavors differ in the way they do: some with highly

radiogenic Sr and unradiogenic Pb; others with the opposite, etc.? Why are the plumes containing the clearest primitive noble gas signatures, such as Iceland, Hawaii, and the Galapagos, more displaced from the LLSVPs than one with the clearest radiogenic and stable isotope signatures of recycled material, such as Samoa, the Societies, and the Australis? As more hands are placed on different parts of the elephant, answers to these questions should become clearer.

There are several areas, in addition to the geoneutrino studies discussed above, where additional research could contribute to resolution of these questions, including:

- More detailed numerical simulation of planet accretion processes that include planetary differentiation and can resolve crusts from mantles are needed to fully evaluate the collisional erosion hypothesis.
- Far too often, noble gas and other radiogenic isotope analyses are carried out of different samples. We need more an extensive data set that includes He, Ne, Ar, and Xe isotopic analyses as well as Sr, Nd, Pb, etc. to look for local correlations between these variables that could elucidate the source of the primitive noble gas signature. We also need better constraints on the concentrations of noble gases in these long isolated reservoirs containing the relatively primitive noble gas signature. That would enable tests of models such as that of Li et al. (2014) in which the LLSVPs are mixtures of recycled and primitive components.
- Stable isotope data on OIB are quite limited, this is even more true for some elements that have given tantalizing hints that important insights might be derived from them: sulfur, iron, magnesium calcium, and uranium. New studies, however, should insure that other isotope and chemical data be obtained on the same samples.
- What is the major element chemistry and lithology of mantle plumes? I have reviewed this question elsewhere (White, 2010, 2015), but have not discussed it here for lack of space. The question is of great importance, not only because lithologic heterogeneity will influence melting products (e.g., Hirschmann et al., 2003; Sobolev et al., 2005), but also because the density of plumes and hence both their buoyancy and seismic properties depends on major element chemistry. For example, Hauri (1996) argued that the Hawaiian plume is iron-rich compared to the MORB source. This would be consistent with derivation of some material from the apparently dense Pacific LLSVP as well as hints that this and other plumes maybe intrinsically denser than surrounding mantle (French and Romanowicz, 2015). In addition, advances in mineral physics studies that could help clarify the relative contributions of temperature and chemistry to seismic wave velocity variations in the deep mantle. At this point, it appears both contribute, but the relative contributions are very poorly constrained.
- We very much need better constraints on subduction erosion, particularly the composition of material being eroded and how much of this material survives into the deep mantle. This is a very difficult problem from a geochemical perspective because constraining the composition of something that is no longer there can only be done indirectly.
- Continued refinement of analysis of seismic waves as well as increasingly sophisticated geodynamic modeling should, of course, continue to provide new insights into the relationship between heterogeneity in the deep mantle and the generation of mantle plumes.

At this point, we can say that the deep mantle appears intimately connected to the Earth's surface through mantle plumes carrying material to the surface and subduction returning material to the deep mantle. At the same time, the deep mantle also appears to retain a memory of the Earth's earliest days.

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