

Mantle geochemistry: the message from oceanic volcanism

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Basaltic volcanism 'samples' the Earth's mantle to great depths, because solid-state convection transports deep material into the (shallow) melting region. The isotopic and trace-element chemistry of these basalts shows that the mantle contains several isotopically and chemically distinct components, which reflect its global evolution. This evolution is characterized by upper-mantle depletion of many trace elements, possible replenishment from the deeper, less depleted mantle, and the recycling of oceanic crust and lithosphere, but of only small amounts of continental material.

Geochemists began to study the composition and evolution of the Earth's mantle in the 1960s, when it became clear that plate tectonics is driven by solid-state mantle convection, which carries deep-mantle material upwards until it begins to melt (at about 30–100 km depth). This melt rises to the surface where it extrudes as basaltic lava and delivers a chemical 'message' from the mantle to the geochemist.

When a mantle region melts, it loses **incompatible** (see Box 1 for explanation of professional jargon) trace elements, such as uranium, thorium and potassium, to the melt, which transports them to the oceanic or continental crust. The continental crust now contains about half of the Earth's total inventory of Th and U, leaving at least the upper mantle correspondingly **depleted**. This depleted region is sampled globally by basalts along the 60,000-km-long mid-ocean-ridge system. Other types of volcanism are fed by less depleted or even **enriched** regions in the mantle. A mantle region can 'remember' its depletion or enrichment history, because the accumulation of daughter products of radioactive decay records the changes in parent-to-daughter concentration ratios which occur during melt removal (or addition). Because of this, isotopic measurements have become the major (though not the only) tool of the mantle geochemist. This allows us to 'map' the geochemical structure of the Earth's interior by interpreting the isotopic composition of mantle-derived basalts. Thus isotope geochemistry, having established the chronology of the Earth's accretion and continent formation, is now beginning to decipher its internal differentiation history as well.

I review here the main geochemical evidence bearing on mantle structure and processes, and some of the models based on it. I conclude that much of the chemical heterogeneity evident in oceanic basalts is caused by **recycling** of oceanic, and to a much lesser extent continental, crustal material, which resurfaces predominantly in the '**mantle plumes**' that create volcanic islands. Whether these plumes rise from the base of the upper mantle or the base of the lower mantle remains a hotly debated issue. Earlier reviews of this and related topics may be found in refs 1–9.

Overview of mantle models

In the 1970s, geochemists developed the idea of a chemically layered mantle, with an upper depleted and a lower undepleted (also called **primitive**) layer, because it was found that there is a fundamental geochemical difference between mid-ocean-ridge basalts (**MORB**), which come from mantle regions that are depleted in all incompatible elements, and ocean island basalts (**OIB**), which are less depleted or even enriched. Ocean islands often form long lines of volcanoes of progressively increasing ages, which are created by an apparently stationary heat source ('**hotspot**') under a moving plate¹⁰. Morgan¹¹ proposed that hotspots are created by narrow 'plumes' rising from the deep mantle. The chemical and isotopic

differences between MORB and OIB appeared to indicate that the former come from an upper, depleted layer, whereas the latter rise from a deeper, undepleted layer (see, for example, ref. 12). This is the geochemical 'standard model' shown in Fig. 1a. Apparent support came from geophysical evidence showing a sharp increase in the velocity of seismic waves at a depth of 660 km (the **660-km seismic discontinuity**). This indicated that the mantle consists of two layers, which differ in either chemical or mineralogical composition or both.

This standard model is now untenable because OIB are highly variable in composition, so that they could not be derived from a chemically uniform, primitive layer of the mantle. This has led to a proliferation of speculative models about the origin and distribution of the different types of material in the mantle. Some of these have retained the concept of a two-layer mantle (Fig. 1b): the two convecting layers are kept separate by an intrinsic compositional density contrast or by a negative pressure–temperature slope of an isochemical phase transition at 660 km (ref. 13). Plumes originate from the base of the upper layer but may entrain material 'leaking' from the lower layer^{14,15}. Other models are based on 'whole-mantle' convection (see, for example, ref. 16 and Fig. 1c). In this class of models, **subducted lithosphere** penetrates the 660-km boundary, and all plumes originate from the core–mantle boundary. Recently, hybrid models have been developed in which the two, normally separately convecting layers are intermittently perturbed when sinking pieces of subducted lithosphere and rising plumes occasionally penetrate the 660-km boundary (Fig. 1d; refs 5, 17, 18). It will be seen further below that geochemical mass-balance considerations strongly favour some type of layered convection (models in Fig. 1b or d).

Geological background

The following geological observations and inferences derived from them provide a framework for interpreting the geochemical messages from the mantle:

(1) Mid-ocean ridges migrate laterally in a pattern controlled largely by the surface geometry of the plates. Therefore, they should normally 'sample' the uppermost mantle (that is, the **asthenosphere**), which rises passively under the spreading ridge. Occasionally, a migrating ridge intersects a plume, which rises from the deeper mantle. When this happens, such as on Iceland, oceanic crust of anomalous chemistry and thickness is produced.

(2) Mantle plumes are thought to generate about 20–40 stationary 'hotspots', which are also used as a reference frame to determine absolute plate motions. Plumes probably originate from boundary layers in the mantle^{7,19,20}, which may be located either above the 660-km seismic discontinuity or above the core–mantle boundary (at 2,900 km). In either case, heating from below lowers the density until the layer becomes unstable and forms a rising column or 'plume'.

Box 1 Geochemical and geophysical jargon

Asthenosphere. Relatively soft, hot mantle region (at or near the melting point) underlying the colder, harder **lithosphere**. Its thickness is of the order of 100 km but is poorly defined because stiffness increases gradually with depth.

Depleted (enriched) reservoir. Region in the mantle that is depleted (enriched) in **incompatible elements** relative to a primitive reservoir.

Hotspot. Locus of volcanism that remains nearly stationary relative to the moving lithospheric plates. Classic hotspots form long chains of volcanoes (such as the Hawaiian–Emperor chain) which become progressively older as a function of distance from the presently active volcanism.

Incompatible element. A chemical element that is excluded from solid minerals of the upper mantle and therefore preferentially enters an available melt phase. Reasons for incompatibility include large ionic radius and high ionic charge, both of which cause misfits in the existing crystal structures of mantle minerals. Incompatible elements have, by definition, low **partition coefficients**, usually $D \leq 0.1$.

Lithosphere. Stiff, cold layer comprising the uppermost mantle and overlying crust. The lithosphere is about 100 km thick in oceanic regions and 100–400 km in continental regions. The moving plates created by sea-floor spreading consist of lithosphere.

Mantle plume. Solid-state, narrow upwelling current in the mantle with a diameter of the order of 100 km and originating from a hot, low-density boundary layer located either above the seismic discontinuity at 660 km depth or near the core–mantle boundary at 2,900 km depth.

Metasomatism. Process of changing the bulk chemical composition of a rock, usually by infiltration of an aqueous or carbonaceous fluid or melt.

MORB. Mid-ocean-ridge basalt. MORB forms the upper part of the oceanic crust.

OIB. Ocean island basalt, restricted to islands that are not related to **subduction**. Typical OIB occur on Hawaii, Iceland and the Polynesian islands, but not in so-called island arcs such as the Aleutians, Marianas or Japan.

Partition coefficient. Description of the equilibrium distribution of a trace element between different phases. According to Henry's law, the partition coefficient is independent of the absolute concentration of the trace element. For solid–melt systems, the coefficient is defined as $D = C^{\text{solid}}/C^{\text{melt}}$, where C is the concentration of the trace element in question.

Primitive mantle (sometimes called 'bulk silicate Earth'). Silicate portion of the Earth as it existed after separation of the core but before it was differentiated into crust and present-day mantle. A **primitive reservoir** is any region of the mantle that has retained this composition. The composition of the primitive mantle is inferred from the composition of the stony meteorites known as chondrites^{124,125}.

Recycling. Introduction of (oceanic or continental) crust or lithosphere into the mantle by **subduction** or delamination, storage in the mantle, and reappearance in volcanism.

Sea-floor spreading. Creation of new oceanic lithosphere by solid-mantle upwelling, consequent partial melting, extrusion and cooling of **MORB** at a mid-ocean ridge, and lateral movement of the new lithosphere away from the ridge.

Subduction. Destruction of **lithosphere** by sliding back into the mantle beneath island arcs, often at an angle of 45° and reaching depths of at least 600 km.

660-km seismic discontinuity. A narrow zone of sharp increase in seismic wave velocity at a depth of 660 km. It may be caused by a mineralogical phase change of upper-mantle silicates to denser structures, or by a sharp change in major-element composition.

(3) Not all intra-plate oceanic volcanoes originate from plumes. Thousands²¹ of small, isolated volcanic seamounts litter the oceanic crust and are probably formed by local melting anomalies. In addition, there are 'hot lines' of volcanoes that show no age progression but erupt roughly simultaneously along the entire extent of the line (for example, the Cameroon Line volcanoes²²). Most of these geochemical and melting anomalies probably come from the upper mantle.

(4) Continental flood basalts and oceanic plateaus are, according to some authors²³, formed by the surfacing of a large, mushroom-like head of a 'starting' plume, which has entrained large amounts of mantle material on the way from its origin to the surface. Often, a progressively 'younging' line of volcanoes connects an old flood basalt province (for example, the Deccan Traps of India) with a currently active hotspot (for example, Reunion Island). This is interpreted as the surface expression of the much narrower conduit or 'stem' of the plume, which may be active for over a hundred million years.

(5) **Sea-floor spreading** generates large chemical heterogeneities by extracting melt from the mantle, thereby forming a basaltic crust and a refractory residue. **Subduction** reinjects these heterogeneities back into the mantle, where they are gradually rehomogenized by convection²⁴. Subduction also causes melting, resulting in volcanic 'island arcs', which are ultimately accreted to the continental crust.

The geochemical evidence

To characterize the mantle source regions of basaltic lavas, the geochemist uses a variety of geochemical tracers. Such tracers are either isotope abundance ratios of daughter elements of radioactive nuclides, or concentration ratios of incompatible trace elements. The melt 'copies' these tracer ratios from the source and delivers them to the surface with little or no distortion. In spite of occasional assertions to the contrary, the geochemical tracing approach has withstood the test of time quite well (see, for example refs 1 and 25) and will be used here without apologies. Table 1 shows the radioactive decay systems used in this Review, their half-lives, and (radiogenic to non-radiogenic) isotope ratios of the daughter elements, which will vary as a function of age and parent/daughter element ratio (discussed below). I focus here purely on oceanic basalts (MORB and OIB) rather than mantle xenoliths or volcanic rocks from island arcs or continental regions, because oceanic basalts represent relatively large volumes of mantle and carry the smallest risk of being contaminated during magma transport through the crust to the surface.

Elemental chemistry of MORB, OIB and continental crust.

General chemical characteristics of average continental crust, average oceanic crust (= MORB), and selected OIB are shown in Fig. 2. Concentrations are normalized to those of the **primitive mantle** and plotted in the order of increasing compatibility, which, except for the 'anomalous' elements Nb, Pb and Ti (see below), coincides with the order of descending abundances in the continental crust. All types of crustal rock (MORB, OIB and continental crust) are enriched in incompatible elements (relative to the primitive mantle) because they originate as melts, which concentrate incompatible elements from the mantle. However, in the oceanic crust (= MORB), the most highly incompatible elements (for example, Rb, Ba and Th) are actually relatively depleted in comparison with the moderately incompatible elements (for example Sm and Hf), because this crust is formed by melting of a mantle region that has previously been depleted by extraction of the continental crust⁴. This effect also explains the mutually complementary positive and negative anomalies of Nb and Pb.

Ocean island basalts are much more enriched in incompatible elements than MORB, and they show a large variation in composition. This variability will be especially obvious in the isotopic compositions discussed below. Here I show average concentration patterns for basalts from Mauna Loa (Hawaii) and two of the

isotopically 'extreme' types of mantle plume (see below and Figs 3–6), namely Tubuai, Austral Islands (HIMU) and Tristan–Inaccessible Island (EM-1). (See Isotope taxonomy section, below, for explanation of HIMU, EM-1 and EM-2). Their greater enrichments in incompatible elements cause them superficially to resemble continental crust, but their Nb and Pb anomalies are similar to those of the oceanic crust (= MORB) and opposite to those of the continental crust. Thus, except for their grossly different relative levels of enrichment (which can be explained by differences in the melting process), all these basalt types have fundamentally similar trace-element patterns. In contrast, the trace-element patterns of EM-2 basalts (not shown for reasons of clarity) differ from those of other OIB and resemble that of continental crust (see section on trace-element ratios).

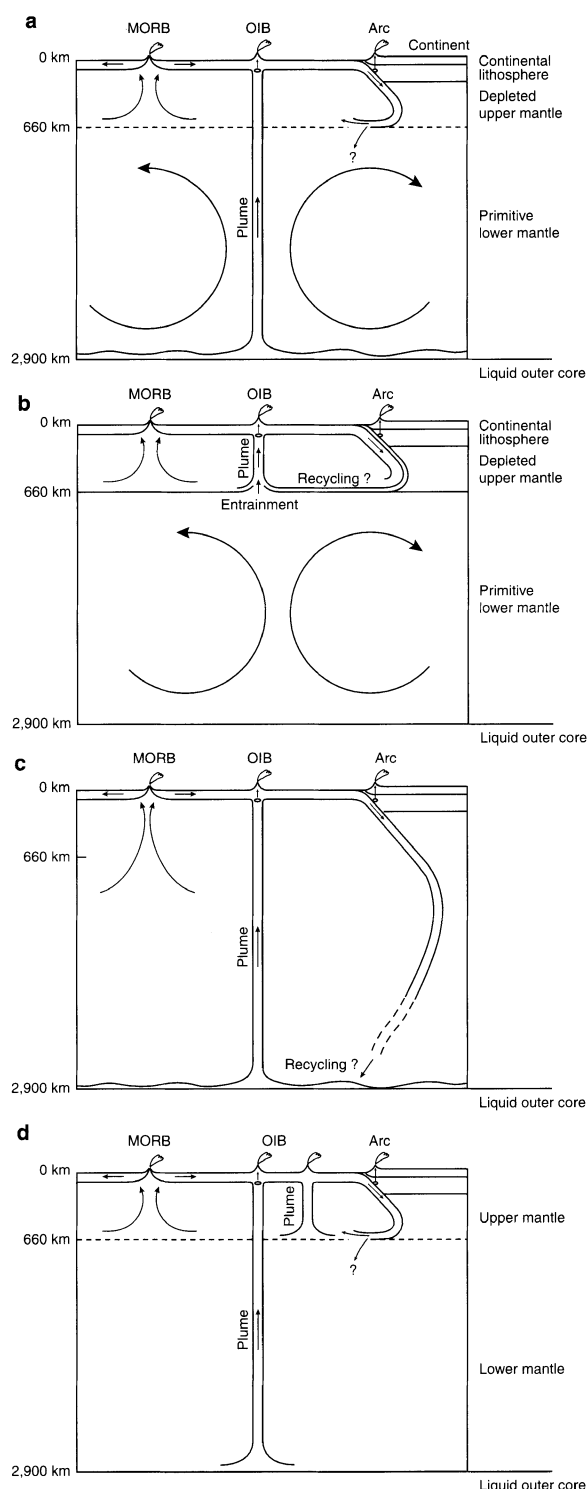
Isotope chemistry. The radioactive parent nuclides listed in Table 1 are all very long-lived, so the daughter isotope ratios reflect the long-term history of the basalt-source reservoirs in the mantle. Figures 3–6 show Sr, Nd and Pb isotope data for over 1,100 samples of MORB and OIB.

Strontium, neodymium and hafnium. Isotope data for Sr and Nd in MORB, OIB and continental crust are summarized in Fig. 3. The MORB points form a relatively tight cluster that defines the upper left-hand corner of the array. In general, $^{143}\text{Nd}/^{144}\text{Nd}$ correlates negatively with $^{87}\text{Sr}/^{86}\text{Sr}$, and positively with $^{176}\text{Hf}/^{177}\text{Hf}$ (not shown). The isotopic composition of the primitive mantle, marked by a square, is normally estimated from this correlation and the Nd value of meteorites²⁶. These correlations are consistent with the relative compatibilities shown in Fig. 2, namely $\text{Rb} < \text{Sr}$, $\text{Sm} > \text{Nd}$, and $\text{Lu} > \text{Hf}$. Thus, mantle regions depleted in incompatible elements have low Rb/Sr and therefore low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, coupled with high Sm/Nd and Lu/Hf , and therefore high $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios. Continental crust, which is enriched in incompatible elements, shows the opposite isotopic signatures. The position of OIB between the depleted MORB source and the continental crust suggests that the OIB sources might just be the result of back-mixing of various types of continental material into the mantle. It will be seen below that this is, for the most part, not the case.

Lead. The Pb isotope data (Fig. 4) are more complex than those for Sr, Nd and Hf, in part because the geochemical behaviour of lead is anomalous (see below and Fig. 2). The U/Pb ratio of the Earth cannot be inferred directly from meteorite data because the silicate portion of the Earth is severely depleted in lead (either because it has been lost from the Earth along with other volatile elements or because much of the lead has entered the core)²⁷. However, possible primitive mantle compositions are constrained to lie along a line (the 'geochron') determined by the age of the mantle. Also shown are estimates for the average upper (UCC) and lower (LCC) continental crust.

Figure 1 Models of mantle circulation. **a**, Old 'standard model' of two-layer circulation. The upper layer has been depleted in incompatible elements by the formation of continental crust. The layers are separated by either an endothermic phase change or by an intrinsic density contrast at a depth of 660 km. Plumes rise from the base of the lower, primitive (or less depleted) layer. The counterflow into the lower layer is not specified. (MORB, mid-ocean-ridge basalt; OIB, ocean island basalt.) **b**, Two-layer circulation with nearly complete isolation between upper and lower layers. Plumes rise from the base of the upper layer but may entrain small amounts of material from the lower layer. Plume sources are created by recycling of oceanic or continental lithosphere, which creates reservoirs that are enriched in incompatible elements. **c**, Whole-mantle, single-layer circulation with plumes rising from the core–mantle boundary. Plume sources are created as in **b**. **d**, Hybrid model, with circulation occurring primarily in two separate layers with small plumes rising from 660 km depth as in **b**, but with limited exchange by means of occasional foundering of subducted lithosphere and rise of strong plumes from the core–mantle boundary.

Two features are noteworthy. (1) The Pb data do not form a simple trend extending from depleted MORB through OIB to the continental crust. Thus, OIB sources cannot be explained simply by back-mixing of continental crust (as might have been inferred from the Sr–Nd–Hf data). (2) Given the relative compatibilities of U and Pb from Fig. 2, Pb isotope data in Fig. 4a for MORB should fall well to the left of the 'geochron' (locus of primitive-mantle Pb compositions). In other words, the Pb data are expected to show roughly the same topology as the Sr–Nd data in Fig. 3, but in fact most MORB data are roughly centred on the geochron, or even lie on its right-hand side. Moreover, the bulk continental crust (located somewhere between UCC and LCC) also lies close to the geochron rather than



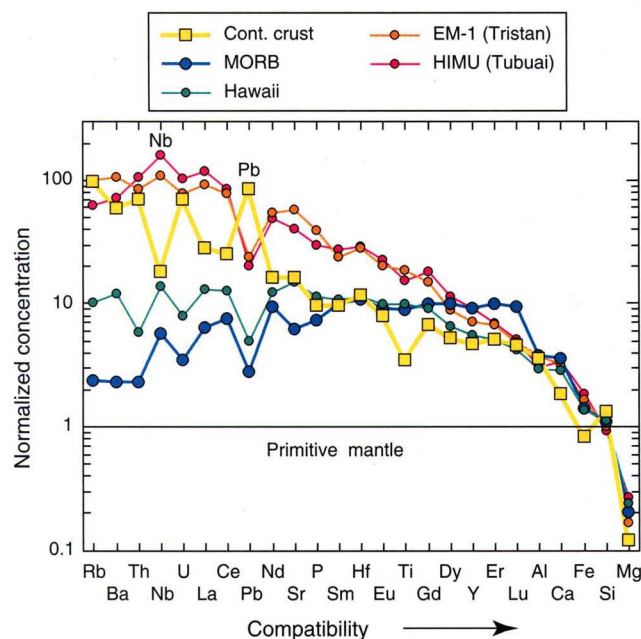


Figure 2 Concentrations of selected trace and major elements, arranged in the order of ascending compatibility and normalized to primitive-mantle concentrations, in average continental crust¹¹⁸, average MORB⁴, average Mauna Loa, Hawaii¹¹⁹, and three types of OIB: average Tristan and Inaccessible islands representing EM-1^{120,121}, and Tubuai representing HIMU islands⁴⁹. The patterns for MORB and the oceanic island basalts differ by their different enrichments (or depletions) in incompatible elements, but they are similar with respect to their positive Nb and negative Pb anomalies. The continental crust has opposite Nb and Pb anomalies. A fourth type of OIB, called EM-2, is similar to continental crust and has been omitted for clarity. (See text for explanations of EM-1, EM-2 and HIMU.)

far on its right-hand side. A solution to this puzzle (the 'lead paradox'²⁸) will be suggested below.

Correlations between Pb and other isotopes. Figure 5 shows relationships between $^{206}\text{Pb}/^{204}\text{Pb}$ and Sr isotope ratios. Although these isotope ratios correlate positively in MORB from the Atlantic and Pacific oceans, they do not correlate in MORB from the Indian Ocean and in the overall OIB–MORB array. This indicates that U–Pb and Th–Pb systems in the different mantle reservoirs evolve rather differently from the Rb–Sr (and Sm–Nd and Lu–Hf) systems.

In contrast, the parameter $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ (the ratio of the radiogenic additions to the initial terrestrial lead, defined as $\{(^{208}\text{Pb}/^{204}\text{Pb}) - (^{208}\text{Pb}/^{204}\text{Pb})_{\text{init}}\} / \{(^{206}\text{Pb}/^{204}\text{Pb}) - (^{206}\text{Pb}/^{204}\text{Pb})_{\text{init}}\}$) does correlate with $^{143}\text{Nd}/^{144}\text{Nd}$ (and with Sr and Hf isotopes); see Fig. 6. This parameter depends primarily on Th/U (and age) but not on U/Pb or Th/Pb. The topology of Fig. 6 is rather similar to that of Fig. 3. This means that Th/U correlates with Sm/Nd (as well as with Lu/Hf and Rb/Sr) in mantle evolution, but U/Pb and Th/Pb do not. This identifies Pb (rather than Th or U) as the anomalous element²⁹. **Osmium.** Recent improvements in analytical methods have made osmium isotope analyses of oceanic basalts feasible. The primitive-mantle value of $^{187}\text{Os}/^{188}\text{Os}$ (or $^{187}\text{Os}/^{186}\text{Os}$) is identical or similar to the meteorite value^{30,31}. This means that the Earth's mantle has the same Re/Os ratio as meteorites, which is best explained by continued infall of meteoritic material after the main accretion and core formation of the Earth. Current results indicate the presence of higher-than-primitive $^{187}\text{Os}/^{188}\text{Os}$ in many OIB^{32–35}. Basalts have much higher (up to a factor of a hundred or more) Re/Os ratios than their mantle sources, so that growth of $^{187}\text{Os}/^{188}\text{Os}$ in the oceanic crust is quite rapid. Therefore, Os isotopes should furnish an

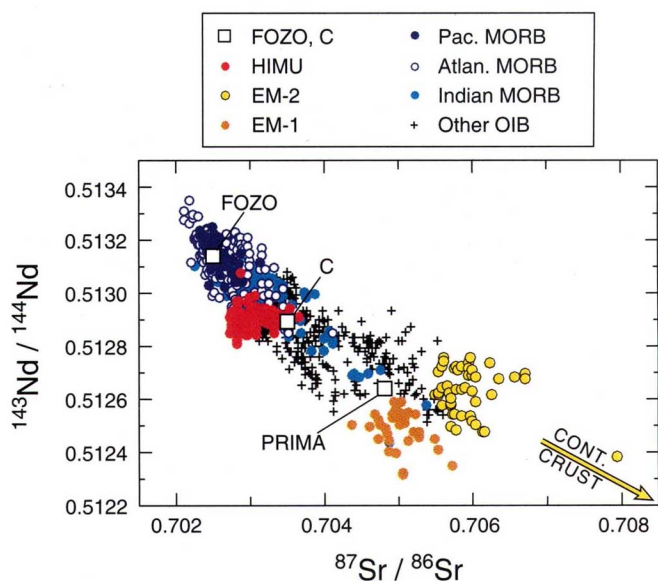


Figure 3 Nd and Sr isotopic compositions, assembled from literature sources, of MORB and OIB, with extreme HIMU, EM-1 and EM-2 samples marked in red, brown and yellow colours, respectively. Only those samples are shown for which Pb isotope data are also available (see Figs 4–6). HIMU samples are arbitrarily defined by having $^{206}\text{Pb}/^{204}\text{Pb} \leq 20$ (Fig. 4). EM-1 and EM-2 samples are also arbitrarily defined by their low $^{143}\text{Nd}/^{144}\text{Nd}$ and high $^{87}\text{Sr}/^{86}\text{Sr}$ values as shown on this diagram. The arrow points to the composition of average continental crust ($^{87}\text{Sr}/^{86}\text{Sr} = 0.72$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.5118$). Also marked are the compositions representing the primitive mantle (PRIMA) and the proposed common mantle components of most plumes 'FOZO'¹⁶ and 'C'⁴⁰. See Supplementary Information for references used in compiling Figs 3–7.

excellent tracer for recycled basaltic material in the mantle and current results have generally been interpreted in this way. Mantle xenoliths from ancient subcontinental lithosphere have consistently lower-than-primitive $^{187}\text{Os}/^{188}\text{Os}$ values³⁶, and this constitutes an excellent potential tracer for recycled ancient lithosphere. However, no such low Os values have been found in oceanic basalts as yet.

Noble gas isotopes. The radiogenic nuclides ^4He and ^{40}Ar are produced by the decay of U and Th, and ^{40}K , respectively, and may be degassed from the Earth's interior into the atmosphere. The accumulation of ^{40}Ar in the atmosphere will be further discussed in the section on mass-balance considerations. Oceanic basalts also contain the non-radiogenic isotopes ^3He and ^{36}Ar (as well as Ne, Kr and Xe). Atmospheric helium is not recycled into the mantle because it is continually lost to space from the atmosphere, and nearly all ^3He now coming out the mantle is primordial, thus demonstrating that the Earth has never been completely degassed. (This nearly universally accepted view has been challenged by Anderson³⁷, who suggested that cosmic-dust-derived ^3He has been supplied to the mantle through subduction of pelagic sediments. However, high $^3\text{He}/^4\text{He}$ ratios do not correlate with other tracers of recycled subducted sediments in OIB³⁸, a fact that seriously weakens Anderson's argument.)

Relative to the atmospheric $^3\text{He}/^4\text{He}$ ratio ($R_A \equiv (^3\text{He}/^4\text{He})_{\text{atm}} = 1.4 \times 10^{-6}$), continental crust has low ratios ($^3\text{He}/^4\text{He} \approx 0.01 R_A$) because it is enriched in Th and U, which produce ^4He during decay. MORB have rather uniform values of $(8 \pm 1) R_A$ (ref. 39), and OIB range from 5 to $30 R_A$ (ref. 40). The existence of high- $^3\text{He}/^4\text{He}$ islands (Hawaii, Iceland, Bouvet, Galápagos, Easter, Juan Fernandez, Pitcairn, Samoa, Reunion and Heard islands; see, for example, ref. 40) is consistent with the layered-mantle model: plumes

might rise directly from the lower, high- $^3\text{He}/^4\text{He}$ reservoir through the upper, low- $^3\text{He}/^4\text{He}$ layer^{38,41–43}, or they might start from the base of the upper layer, in which case the helium must migrate into the plume source from the lower mantle^{2,44}.

Neon isotope data from basalts are still scarce because of experimental difficulties. Recent work has shown that Ne from the Hawaiian plume and from MORB have different $^{21}\text{Ne}/^{22}\text{Ne}$ and $^{20}\text{Ne}/^{22}\text{Ne}$ correlations, indicating the presence of a high- ^{20}Ne reservoir⁴⁵ in the plume source and a high- ^{21}Ne reservoir in the MORB source⁴⁶. Both components form mixing lines with a low- $^{21}\text{Ne}/^{22}\text{Ne}$ and $^{20}\text{Ne}/^{22}\text{Ne}$ reservoir of atmospheric origin. This provides additional evidence for a layered mantle with restricted exchange between layers.

Isotope taxonomy. The deviations from simple linear correlations in Figs 3–6 are not random but show systematic regularities^{1,14,47}, which are illustrated in these figures by colour coding. For example, all samples possessing $^{206}\text{Pb}/^{204}\text{Pb} \geq 20$ (Fig. 4) are shown as red dots and labelled ‘HIMU’ (see key in Fig. 3). They also form well-defined clusters on isotope diagrams not involving the element lead (Figs 3, 5, 6), even though they do not form an obvious endmember in them. Samples with this ‘isotopic colour’ occur in several oceanic islands in completely different parts of the world. This isotopic–chemical regularity demonstrates the existence of reproducible differentiation processes in the mantle and justifies the isotopic taxonomy discussed in the following paragraphs.

Zindler and Hart¹ suggested that the mantle contains the following isotopically extreme ‘mantle components’ (Figs 3–5), which contribute to the (usually mixed) sources of oceanic basalts. (1) HIMU (‘high μ ’; $\mu = ^{238}\text{U}/^{204}\text{Pb}$) has the highest Pb ratios and the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ of any OIB (almost as low as MORB). Examples are St Helena, Austral Islands, Balleny Islands and the Azores. (2) EM-1 (‘enriched mantle 1’) occupies the lower left-hand corner of the Sr–Nd array (Fig. 3), and is concentrated in the right-hand corner of the $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ –Nd array (Fig. 6), and the upper left-hand corner of the Pb–Pb array (Fig. 4b). Representatives are the Pitcairn and Tristan hotspots. (3) EM-2 (‘enriched mantle 2’) has the highest $^{87}\text{Sr}/^{86}\text{Sr}$ and relatively high $^{207}\text{Pb}/^{204}\text{Pb}$ ratios. Representatives are the Societies and Samoa hotspots. (4) DMM (‘depleted MORB mantle’) is not specifically marked on the figures. It is defined by the most depleted MORB samples with the highest $^{143}\text{Nd}/^{144}\text{Nd}$ and the lowest $^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios.

Many of the isotope data arrays for individual islands or hotspots are roughly linear, indicating that they represent mixtures of a more

enriched and a more depleted component originally thought to be the DMM. However, recently published data (for example, refs 38, 48, 49) show arrays in which DMM is clearly not a mixing end-member. This has led to the definition of a new component, called FOZO (‘focal zone’)¹⁶, whose composition is defined by the point of convergence, in three-dimensional isotope diagrams, of linear data arrays for individual ocean islands. A similar point of convergence of isotope arrays for MORB defines the component C (‘common’)⁴⁰. In the two-dimensional diagrams shown here, the convergence of HIMU and MORB arrays is most clearly seen in Fig. 4b.

There is much current debate about the meaning of this taxonomy. Authors disagree as to whether the linear isotopic trends seen in many hotspots are caused by the existence of two components in the plume source^{6,49}, whether isotopically distinct but internally uniform plume sources are mixed during ascent by entraining relatively depleted lower-mantle material^{16,18}, possibly producing a zoned plume⁵⁰, or whether similarly uniform plumes are mixed only with upper-mantle asthenosphere and/or lithosphere⁵¹. In general, individual hotspots contain only a limited range of isotopic compositions and most hotspots have distinct isotopic ‘flavours’. On a much larger geographical scale, EM-1 and EM-2 compositions are concentrated in OIB just south of the Equator. This feature has been called the ‘DUPAL anomaly’⁵² and has been correlated with large-scale seismic anomalies in the lowermost mantle. Also, nearly all Indian Ocean MORB have distinctly high $^{208}\text{Pb}/^{204}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ values relative to Pacific and Atlantic MORB (Figs 4–6). All of this provides strong evidence that the different isotopic flavours are not randomly distributed in the mantle but can be mapped. Nevertheless, conclusive interpretations are hard to come by because we cannot look into the mantle directly but must rely on simulations³³ or correlations between geophysical and geochemical observations. Until recently, the spatial resolution of both geophysical observations such as seismic tomography and numerical convection ‘experiments’ has been insufficient to ‘see’ or model relatively small features such as plumes. However, this resolution is improving rapidly and much progress can be expected within the coming decade.

Quite distinct from the spatial distribution of plume sources and other heterogeneities within the mantle is ‘Darwin’s question’: what is the origin of the isotopic mantle species? To answer this, we must consider other aspects of mantle chemistry, in particular the concentration ratios of highly incompatible elements, which characterize the different species and should help to identify the

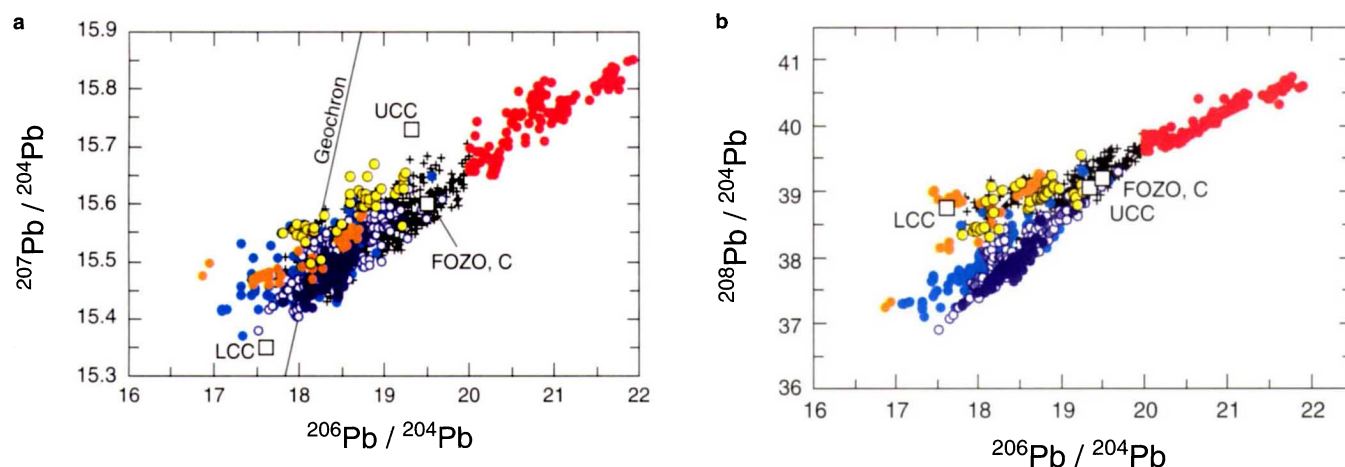


Figure 4 Pb isotopes for the samples shown in Fig. 3, using the same colour code. The solid line labelled ‘geochron’ in **a** marks the locus of possible primitive mantle values assuming an overall age of the mantle of 4.50 Gyr (refs 27, 122). UCC

and LCC mark average compositions of upper and lower continental crust, respectively¹²³.

Table 1 Long-lived radioactive decay series used as tracers

Parent nuclide	Daughter nuclide	Half-life (yr)	Tracer ratio (radiogenic/ nonradiogenic)
^{147}Sm	^{143}Nd	106×10^9	$^{143}\text{Nd}/^{144}\text{Nd}$
^{87}Rb	^{87}Sr	48.8×10^9	$^{87}\text{Sr}/^{86}\text{Sr}$
^{176}Lu	^{176}Hf	35.7×10^9	$^{176}\text{Hf}/^{177}\text{Hf}$
^{187}Re	^{187}Os	45.6×10^9	$^{187}\text{Os}/^{188}\text{Os}$
^{40}K	^{40}Ar	1.25×10^9	$^{40}\text{Ar}/^{36}\text{Ar}$
^{232}Th	^{208}Pb	14.01×10^9	$^{208}\text{Pb}/^{204}\text{Pb}$
^{238}U	^{206}Pb	4.468×10^9	$^{206}\text{Pb}/^{204}\text{Pb}$
^{235}U	^{207}Pb	0.738×10^9	$^{207}\text{Pb}/^{204}\text{Pb}$

processes that ultimately created the isotopic differences.

Trace element ratios. Concentration ratios (hereafter called ‘ratios’) of incompatible trace elements can serve as tracers of source chemistry and complement the information gained from radiogenic isotopes. However, they must be used with care because, unlike isotope ratios, they may be fractionated during igneous processes. The ratio of two elements in a melt in equilibrium with its solid residue is given by

$$\frac{C_1}{C_2} = \frac{D_2(1-F) + F \cdot C_{1,0}}{D_1(1-F) + F \cdot C_{2,0}}$$

where C_1 and C_2 are the concentrations in the melt, $C_{1,0}$ and $C_{2,0}$ the concentrations in the original source, D_1 and D_2 the bulk partition coefficients, $D \equiv C_{\text{solid}}/C_{\text{liquid}}$, and F is the melt fraction. If $D_{1,2} \ll F$, that is, if the elements are highly incompatible or the melt fraction is large, the first term on the right-hand side vanishes and one obtains $C_1/C_2 \approx C_{1,0}/C_{2,0}$, so that the ratio in the melt will be the same as the ratio in the source. Such trace-element ratios can be just as useful as isotope ratios in serving as tracers of mantle chemistry.

Indicators of source depletion. The bulk partition coefficients of the most highly incompatible elements increase in the approximate order $\text{Ba} \approx \text{Rb} \leq \text{Th} < \text{U} \approx \text{K} < \text{La} < \text{Ce}$. Therefore, Ba/La , Rb/La , Th/U and Th/La ratios in basalts are generally greater than (or equal to) the respective source ratios. Thus, when these ratios are less than the primitive-mantle values, they document a previous depletion of the source rocks. This effect produces the leftward-descending branch in the MORB pattern seen in Fig. 2. A relative depletion for Rb and Ba is also seen in the Tubuai pattern; it is characteristic of all HIMU basalts and distinguishes them from EM-type basalts. It is consistent with the low Rb/Sr of HIMU sources inferred from their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, which indicate a ‘depleted heritage’ for both MORB and HIMU sources.

Globally ‘uniform’ ratios and the significance of Nb, Ta and Pb. Certain trace-element ratios are comparatively uniform in most oceanic basalts, irrespective of their absolute concentrations, which may range over two orders of magnitude from the most depleted MORB to the most enriched OIB. In such cases, the bulk partition coefficients of the two elements involved are nearly identical, or both are much smaller than the melt fraction F (see above)⁵⁴. Such uniform ratios include Ba/Rb , K/U (except in HIMU basalts), Nb/Ta , Zr/Hf , Y/Ho , Ti/Sm , Sn/Sm and P/Nd (see, for example, refs 55–57). These ratios are also similar in the average continental crust, and for the highly refractory element pairs Nb – Ta , Zr – Hf and Y – Ho , they are identical to the respective (‘chondritic’) ratios of the primitive mantle (see Box 1).

Some ratios, namely $\text{Nb}/\text{U} \approx 47$, $\text{Ta}/\text{U} \approx 2.7$ and $\text{Ce}/\text{Pb} \approx 25$ are similar in MORB and OIB, but their values are much higher than those of the continental crust and island arc volcanics (by factors of 4–5) and those estimated for the primitive mantle (by factors of 1.5–2.5)⁵⁴. The significance of this result is fourfold: (1) it shows that ocean island basalts do not sample predominantly primitive mantle reservoirs; (2) it links the origins of MORB and OIB sources; (3) it confirms independently the link between island arc magmatism and formation of continental crust as a consequence of plate

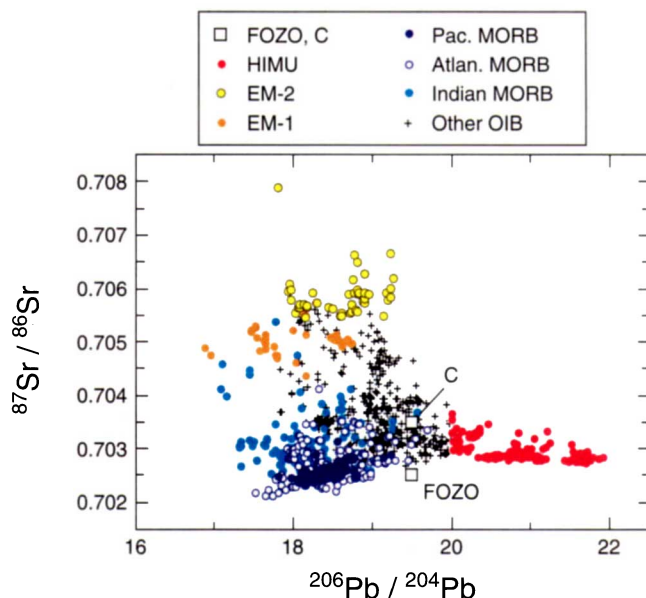


Figure 5 $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for the same samples as in Figs 3 and 4.

tectonic processes⁵⁸; (4) it provides excellent tracers to test for the presence of recycled continental crust in OIB sources.

Questions about the ‘constancy’ of these ratios and the above interpretation have recently been raised^{59,60}. The validity of the use of Nb/U as an important tracer of mantle sources is reaffirmed here by a new compilation, shown in Fig. 7, of Nb/U versus $^{143}\text{Nd}/^{144}\text{Nd}$ (expressed as ϵ_{Nd} ; see legend for definition). This shows average values for basalts from 33 ocean islands (or hotspots) and MORB, compiled from high-quality data published mostly since 1986. The great majority of all these basalt suites have average Nb/U between 40 and 60, independent of the source depletion or enrichment expressed by ϵ_{Nd} , and are in good agreement with the value of 47 ± 10 proposed in 1986⁵⁴. This is significantly higher than the primitive mantle ratio of $\text{Nb}/\text{U} = 30$ and the mean value of $\text{Nb}/\text{U} \approx 10$ for continental crust and island arc rocks. Thus, most of the sampled mantle has been enriched in Nb (and Ta, which has similar properties to Nb) relative to U and other similarly incompatible elements. Possible mechanisms for this enrichment are discussed in the final section preceding the conclusion.

Figure 7 shows that normal OIB, including the HIMU islands and EM-1 islands, representing the full range of Nd-isotopic compositions in OIB, have Nb/U ratios very close to those of average MORB. Therefore, these OIB types cannot be generated by mixtures of depleted mantle and either primitive mantle or recycled continental crust (although the slightly low Nb/U ratios of EM-1 basalts permit the presence of a small sedimentary component; see below).

Obvious exceptions are the extreme EM-2 OIB from the Society and Marquesas hotspots (selected by having the highest $^{87}\text{Sr}/^{86}\text{Sr}$ at each hotspot) and the highly anomalous MORB from segment 3 of the Chile ridge (ref. 61 and E. Klein, unpublished data). This confirms that, except for EM-2, all types of oceanic basalt and their sources have very similar Nb/U values, which are significantly higher than primitive-mantle Nb/U . EM-2 OIB, and Chile ridge MORB are unique in that they, and only they, lie on mixing trajectories between DMM or HIMU mantle and average continental crust (probably in the form of mantle-recycled sediments).

An analogous but converse relationship holds for lead. Using Ce/Pb as a tracer, Hofmann *et al.*⁵⁴ and Newsom *et al.*⁶² showed that lead is systematically depleted in oceanic basalts, but overabundant in island arc rocks and continental crust (see also Fig. 2). A compilation of recent, more extensive data⁶³ shows that the bulk partition

coefficient of Pb is closer to that of Nd than to that of Ce. Therefore, although Ce/Pb (or better, Nd/Pb) ratios scatter considerably more than Nb/U ratios⁵⁹, they nevertheless appear to be good tracers of source ratios. For reasons of clarity, no example of an EM-2 basalt is shown on Fig. 2. However, on the Society Island (EM-2) hotspot, Ce/Pb and Nd/Pb ratios are anomalously low and well correlated with Nb/U and ⁸⁷Sr/⁸⁶Sr (refs 64–66), confirming the inference that EM-2 OIB, but not other OIB, contain small but significant amounts of recycled material of continental origin. The reasons for the anomalous behaviour of lead will be discussed in the section on the ‘lead paradox’ below.

Mass fraction of depleted mantle

By calculating how much of the mantle must be depleted in order to account for the incompatible-element enrichment in the continental crust, one can estimate how much of the mantle could still be chemically primitive. The mass fraction of the depleted mantle, X_d , is given by

$$X_d = \{X_c C_c (R_d - R_c) / (C_p (R_d - R_p))\} - X_c$$

where the subscripts d, c and p refer to depleted mantle, continental crust and primitive mantle, respectively, R is a ratio such as ¹⁴³Nd/¹⁴⁴Nd or Nb/U, and C is the concentration of the element in the denominator of R . Initial results based on Nd isotopes (for example, ref. 67) indicated depleted-reservoir sizes between 25% and 30% of the mantle. This corresponds to the mass of the mantle above the 660-km discontinuity and is thus consistent with the layered mantle model. However, other authors estimated the proportion of depleted mantle to be considerably larger, between 30% and 90% (for example, refs 1, 68–70), depending on specific assumptions about the composition of the continental crust and depending on the inclusion or omission of the OIB source reservoir(s).

Perhaps the best-constrained mass balance is that for radiogenic argon. Approximately 40% of the ⁴⁰Ar produced from ⁴⁰K in 4.5 Gyr of Earth history now resides in the atmosphere; only about 10% is in the continental crust and the depleted upper mantle, and the remaining 50% must still be in the lower mantle⁷¹. In terms of the above equation, this corresponds to $X_d = 0.5$. This is significantly greater than the mass fraction of the mantle above 660 km (about 0.27) but much less than the entire mantle. Thus, although the lower mantle is certainly no longer primitive, it is substantially less degassed, and thus probably also less depleted in incompatible elements, than the upper mantle (which has lost almost all of its ⁴⁰Ar). This constitutes a strong argument against simple whole-mantle convection, because such a circulation type would be expected to cause similar levels of degassing throughout the entire mantle.

Ages of mantle heterogeneities

The isotopic heterogeneities shown in Figs 3–6 require time to develop, particularly in view of the extremely long half-lives of the parent nuclides. If the parent/daughter ratio and the increase in radiogenic daughter nuclide were known, the age of a heterogeneity could be calculated. In practice, this is difficult for mantle domains, because the parent/daughter ratios of the mantle sources are generally not preserved in the basalts. Lead is an exception, because the production ratio of ²⁰⁷Pb/²⁰⁶Pb depends only on time, so that the slope of a straight line in ²⁰⁷Pb/²⁰⁴Pb–²⁰⁶Pb/²⁰⁴Pb space can be interpreted to yield the age of a single U–Pb differentiation event. Thus, if the OIB source regions had been formed in a single event, the slope of the correlation line in Fig. 4a would mean that this event occurred about 2 Gyr ago. However, continuous differentiation and remixing processes have been shown to produce data arrays with a similar slope (yielding an apparent age of 2 Gyr), even though the actual mean differentiation age of the individual mantle sources is only about 1–1.3 Gyr (refs 53, 72). Only the oldest members of the

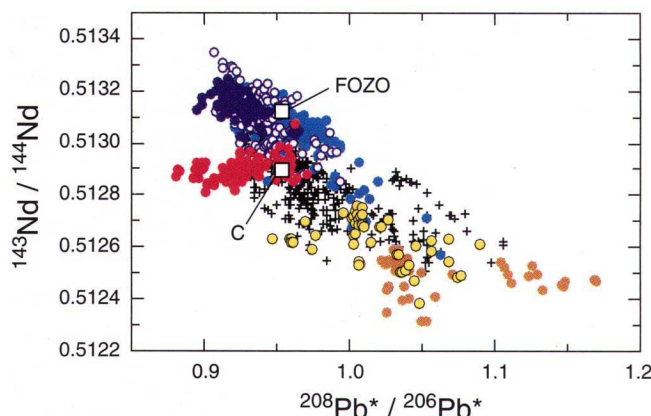


Figure 6 ¹⁴³Nd/¹⁴⁴Nd versus ²⁰⁸Pb*/²⁰⁶Pb* for the same samples as in Figs 3–5 (Here ²⁰⁸Pb*/²⁰⁶Pb* = {(²⁰⁸Pb/²⁰⁴Pb) – (²⁰⁸Pb/²⁰⁴Pb)_{init}} / {(²⁰⁶Pb/²⁰⁴Pb) – (²⁰⁶Pb/²⁰⁴Pb)_{init}}, where the subscript ‘init.’ designates the initial composition of the primitive mantle 4.5 Gyr ago).

club, the HIMU source regions with the highest ²⁰⁶Pb/²⁰⁴Pb values, were formed about 2 Gyr ago. Thus, the timescale observed for ‘oceanic’ mantle differentiation is likely to be significantly shorter than the mean age of the continental crust (about 2–2.5 Gyr; ref. 58).

Evaluation of geochemical mantle models

The large body of geochemical data reviewed above demonstrates that the Earth’s mantle has been partially depleted in incompatible elements by the formation of the continental crust, which has extracted roughly half of the total budget of highly incompatible elements from the mantle. This residual, depleted mantle is chemically heterogeneous on local, regional and global scales. Convective stirring has not homogenized the mantle, presumably because near-surface processes such as partial melting and subduction continue to reintroduce chemical and isotopic heterogeneities. The most highly depleted, and least heterogeneous region is located in the upper 660 km of the mantle and produces MORB by passive upwelling and partial melting. Plumes are more heterogeneous in composition and presumably originate from a boundary layer somewhere beneath this upper-mantle reservoir. There is a continuing debate about the existence of layered mantle convection. Layering may have been caused by an intrinsic, compositional density stratification that originated through crystallization of an early ‘magma ocean’ formed during segregation of the core⁷³. Current evidence from mineral physics⁷⁴ and experimental evidence on crystal–liquid partitioning of high-pressure minerals^{75,76} does not favour this model and probably precludes the survival of this type of mantle stratification. Layered convection may also be caused by the endothermic nature of the phase change from upper-mantle peridotite to a lower-mantle perovskite–wüstite mineralogy¹³. In this case, the major-element compositions of the upper and lower mantle may be the same, but the trace element and isotopic chemistry of the two reservoirs may differ drastically because of crust formation from the upper mantle (see section on mass fraction of depleted mantle).

Layered mantle, primitive OIB sources. This is the original ‘standard’ model (Fig. 1a) in its simplest form^{12,77}. Plumes rise from the primitive lower layer and mix with the upper, depleted layer on their way to the surface. This model is no longer tenable because (1) OIB sources require more than just two source components; (2) most OIB have distinctly non-primitive Pb isotopes to the right of the ‘geochron’ (Fig. 4a); (3) some OIB sources have lower-than-primitive ¹⁴³Nd/¹⁴⁴Nd ratios (Fig. 3); and (4) Nb/U and Ce/Pb (or Nd/Pb) ratios in OIB require non-primitive sources (Fig. 7).

Several authors have nevertheless recently proposed that some

OIB may be derived from primitive (or slightly depleted) sources (for example, refs 38, 42, 43). A particularly popular candidate is Hawaiian volcanism, especially the tholeiites from Oahu, Lanai and Kahoolawe. Basalts from these islands have close-to-primitive isotopic compositions of Sr, Nd, Hf and Pb (for example, ref. 78), and some Hawaiian volcanoes have high $^3\text{He}/^4\text{He}$ ratios^{41,79}. However, every Hawaiian volcano investigated so far shows the same Nb–Ta excess (and Pb deficiency)⁸⁰ that characterizes other OIB, and this precludes the derivation of Hawaiian volcanism from a primitive source.

In subsequent variants^{14,15,81–83} of the two-layer model, plumes originate from the base of the upper mantle, but they entrain small amounts of primitive (or slightly depleted) noble-gas-rich material from the lower mantle, which imparts the high $^3\text{He}/^4\text{He}$ and $^{20}\text{Ne}/^{22}\text{Ne}$ (Fig. 1b). There are two difficulties with these models. First it is not obvious why some plume types, particularly the HIMU types⁴⁰, should be consistently free of entrained, ^3He - and ^{20}Ne -rich lower-mantle material. Second, the amounts of lower-mantle material calculated from noble-gas evolution models are extremely low⁸³ and appear to be inconsistent with the mass of the less-depleted mantle derived from most recent mass-balance estimates (see above).

Other layered mantle models. Anderson (see, for example, refs 84, 85) has proposed some thought-provoking alternatives to the more conventional models. He suggested that the upper mantle is internally differentiated into a lower, garnetiferous, incompatible-element-depleted ‘piclogite’ layer above 660 km (the MORB source), and an upper (above 220 km), enriched peridotite layer, the ‘perisphere’, which is also the OIB source. Evidence for such an enriched layer is found in many young rifts, which typically deliver OIB-type magmas. However, the opening of the Red Sea shows that this enriched rift magmatism is soon replaced by normally depleted MORB magmatism, suggesting that the enriched perisphere is at best a thin veneer of enriched material that may well produce some of the unusual types of OIB, such as the Cameroon Line ‘hot line’ volcanoes⁵⁹, but could not sustain voluminous, long-lived, hotspot-type magmatism such as the Hawaiian–Emperor chain. Furthermore, there is scant evidence for the existence of such a perisphere in intra-oceanic regions, because laterally moving mid-ocean ridges, or ridge jumps, generally sample an ordinary, depleted MORB-type mantle rather than an enriched perisphere supposedly located in the uppermost mantle region. Finally, recent seismic imaging has traced the thermal anomaly beneath Iceland to a depth of 400 km and a diameter of about 100 km (ref. 86), indicating that the Iceland hotspot represents a mantle plume originating from at least 400 km depth. These features are difficult to reconcile with the perisphere model.

Whole-mantle convection models. In these models, the 660-km seismic discontinuity represents little or no barrier to convection. Geophysical support for this comes from evidence for deep, high-seismic-velocity structures (for example, ref. 87), interpreted as subducted lithosphere in the lower mantle, and from the fixed locations of hotspots, which appear to require that plumes originate in a lower-mantle region that has a much higher viscosity and moves much more slowly than does the upper mantle⁸⁸. It is also argued that flood basalt provinces, which are erupted during geologically very brief time spans and attain enormous volumes and lateral extent (about 2,000 km), are produced by plume heads that could have attained such dimensions only by thermal entrainment during plume ascent through the full depth of the mantle⁸⁹. Geochemical arguments are based on the so-called ‘FOZO’¹⁶ or ‘C’⁴⁰ isotopic component, which appears to be common to many plumes and differs isotopically from the MORB source. FOZO is thought to reside in the lower mantle where it is entrained by plumes rising from the core–mantle boundary¹⁶.

Metasomatic models. Metasomatism has been popular with many workers as a mechanism for enriching the upper mantle in incom-

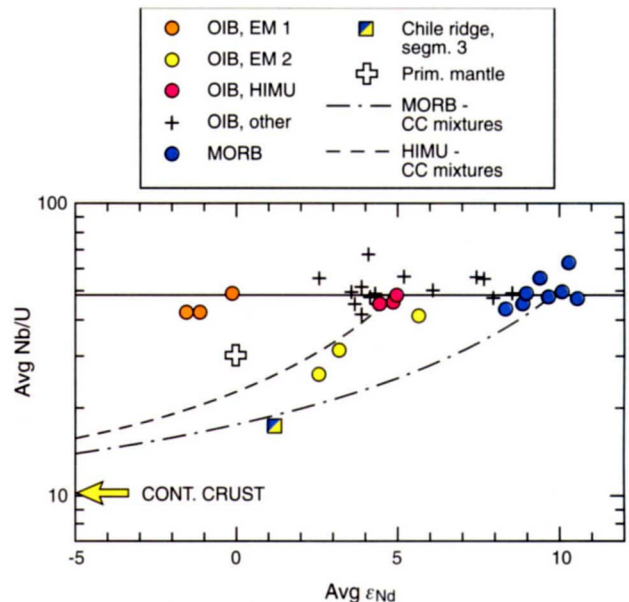


Figure 7 Nb/U plotted against ϵ_{Nd} , where ϵ_{Nd} is the deviation, in parts per 10⁴, of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of a sample from that of present-day primitive mantle (p): $\epsilon_{\text{Nd}} = 10,000[(^{143}\text{Nd}/^{144}\text{Nd}) - (^{143}\text{Nd}/^{144}\text{Nd})_p] / (^{143}\text{Nd}/^{144}\text{Nd})_p$. The points shown are average values for suites of MORB and OIB using generally different samples but the same colour coding as in Figs 3–6. EM-1: Pitcairn, Tristan-Inaccessible, Kerguelen islands; EM-2: Society, Marquesas islands; HIMU: Tubuai, St Helena; other OIB: Cameroon Line islands, Iceland, Hawaii, Reunion, Comores, MacDonal sealamount, Easter hotspot, Bouvet, Gran Canaria, Tenerife, Azores, Cape Verde, Fernando di Noronha, Trindade, Madeira, Ascension; MORB: Atlantic MORB 10°–23° N, Kolbeinsey ridge, Pacific MORB, Galapagos rift, Indian MORB, Chile ridge segment 3. All these oceanic basalt suites except EM-2 types have Nb/U averages similar to the global average of 47 ± 10 given by Hofmann *et al.*⁵⁴ using a much smaller set of data. Note that these Nb/U averages show no significant relationship to the degree of source enrichment or depletion as measured by Nd isotopes. Also, the primitive-mantle value lies completely outside the MORB–HIMU–EM-1 array. Only EM-2 type OIB and the segment 3 of the Chile ridge appear to be mixtures of MORB–HIMU type mantle with (recycled) material, probably sediments, from the continental crust. For references to this compilation, see Supplementary Information, except for unpublished data by C. H. Hémond *et al.* on Atlantic MORB 10°–23° N, and by E. Klein on the Chile ridge.

patible elements and volatiles, until it melts and generates OIB (see ref. 90). Vollmer⁹¹ has based a global mantle model on such a mechanism. The effects of metasomatism are certainly evident in many mantle xenoliths⁹², but the scale of these processes is unknown and may be small relative to the source volume of OIB⁸⁰. The viability of the plume model has largely obviated the ‘need’ for metasomatic mechanisms to generate OIB directly.

Metasomatism may also enrich substantial volumes of the mantle above a subduction zone. The oceanic crust is hydrated by ridge-crest hydrothermal and sea-floor alteration processes, and it is covered by wet sediments. During subduction, this hydrous material is heated and dehydrated. The escaping fluids migrate through the overlying mantle, thereby metasomatizing it. Island arc volcanism is likely to remove much of the effects of this metasomatism^{93,94} (as incompatible elements are partitioned into the fluid and ultimately into the melt), but some of the metasomatized mantle may be incorporated in the subcontinental lithosphere or returned to the convecting part of the mantle. In either case, the metasomatized material may ultimately be recycled through the mantle and reappear in intra-oceanic volcanism (see below).

A variant of this mechanism is metasomatism by the migration of small amounts of melt from the asthenosphere into the oceanic or

continental lithosphere^{3,59}, followed by recycling as above⁹⁵. All of these metasomatic models are difficult to test by observations, because the only tangible evidence for them is found in fist-size or smaller mantle xenoliths, which yield no clues as to the quantities of material transported or the distances travelled.

Recycling models. The idea that recycling crust through the mantle could explain the isotopic and chemical diversity of oceanic basalts goes back almost 30 years⁹⁶ but has found wide acceptance only in the past few years, because mantle convection was previously thought to be highly efficient at rehomogenizing the chemical and isotopic heterogeneities introduced into the mantle during subduction.

Continental crust. Armstrong^{96,97} proposed that the continental crust has maintained a constant volume through a steady-state process of growth (through accretion of island arcs) and destruction through subduction of continent-derived sediments, and suggested that this could also explain the isotopic diversity of oceanic basalts. The geochemical evidence from Pb isotopes and from Nb/U and Ce/Pb ratios now rules out large amounts of recycled continental material in OIB sources (see above), except in the cases of EM-2 OIB and Indian Ocean MORB, which have low Nb/U and Ce/Pb values correlated with high ⁸⁷Sr/⁸⁵Sr and ²⁰⁷Pb/²⁰⁴Pb ratios, and which can be explained by additions of small amounts (1–2%) of recycled sediments to the source mantle^{6,49,66,98} (see Fig. 7).

Oceanic crust. Subduction of oceanic lithosphere continuously recycles oceanic crust and thus injects about 20 km³ of enriched material per year into the mantle. This is the uniformitarian basis of the recycling model of refs 99 and 100. Soon after subduction, this crust is transformed into eclogite (and later to higher-pressure equivalents), which is about 2–4% denser than ordinary mantle (depending on pressure⁵³). The assumed segregation of the dense former oceanic crust from its lithospheric base and the main mantle mass is inhibited at normal mantle viscosities, but is enhanced in the hot boundary layer at the base of the convection system (660 or 2,900 km). Storage and isotopic evolution of some of this material for periods of 1–2 Gyr, followed ultimately by incorporation into plumes rising from this boundary layer, could generate the MORB–HIMU isotope array⁵³.

Strongly altered oceanic crust is evidently not being recycled, because alteration adds many 'mobile' elements such as Rb and U (but not Th), which would cause isotopic changes quite unlike the observed OIB isotopic arrays¹⁰¹. If such alteration has been ubiquitous in the past, it must therefore be assumed that the altered, hydrous parts of the crust were efficiently stripped from the system during subduction, so that the 'additive' effects of hydrothermal alteration were removed. Chemical and isotopic evidence from subduction-related volcanism supports this^{93,94}. In contrast, the hydrothermal subtraction of certain elements, such as lead, from the oceanic crust is probably irreversible, and this should contribute to the high U/Pb and Th/Pb ratios responsible for the extremely radiogenic lead of HIMU basalts^{49,102}.

The model of oceanic crustal recycling is supported by the still sparse isotope data for osmium. HIMU basalts in particular have elevated ¹⁸⁷Os/¹⁸⁸Os ratios, which can be explained by an ancient basaltic source component^{32–35}. Other oceanic basalt types, such as Hawaiian basalts, which have Pb isotopic compositions closer to MORB, also have high ¹⁸⁷Os/¹⁸⁸Os ratios⁵⁰ and may represent recycled, deeper oceanic crust depleted in Th and U (ref. 103).

Subcontinental lithosphere. Old subcontinental lithosphere is comparatively cold and dense, so it may be delaminated and sink into the mantle to become a plume source⁸¹. Because it has been 'pre-aged' isotopically, while it was still attached to the crust, it does not need an extended period of storage in the convecting part of the mantle before it acquires the isotopic signatures found in plumes. This is a popular source candidate for EM-1 type OIB because some xenoliths derived from the subcontinental mantle have isotopic signatures similar to that of EM-1. The lithosphere may well be

enriched as a result of fluid metasomatism during subduction^{104,105} or melt migration from the asthenosphere⁹⁵, but the scale of such processes remains largely a matter of speculation. This recycling hypothesis can now be tested using osmium isotopes, because ancient lithosphere is unique in having ¹⁸⁷Os/¹⁸⁸Os significantly lower than primitive-mantle values³⁶. So far, Os data for only two EM-1 type basalts have been published, and both of these have high, rather than low, ¹⁸⁷Os/¹⁸⁸Os (ref. 33).

Continental basalts are also commonly thought to sample the subcontinental lithosphere (see, for example, refs 104, 106) and they often resemble EM-1 type OIB. However, recent realization that continental flood basalts may sample the heads of deep-mantle plumes makes the argument somewhat circular. Thus it is not clear whether the EM-1 character is due to contamination of a plume head by the continental lithosphere or whether this signature was part of the original plume source¹⁰⁷.

Towards a unified model for mantle evolution

My preferred model for the evolution of the mantle is based on a simple-minded, uniformitarian approach that uses known geological processes and avoids exotic processes whenever possible. Thus, I assume that much of the chemical diversity of the isotopic mantle 'species' is caused by subduction, which introduces oceanic crust and small amounts of sediments of variable composition into the mantle.

Timescales of crust–mantle evolution. Continental crust formation extracts incompatible elements very efficiently from the mantle and enriches them in the crust roughly 100-fold. Continental crust may be returned to the mantle by subduction of sediments, but its lifetime is at least 20 times that of the oceanic crust, which has a mean life of only about 100 Myr. The present-day production rate of continental crust (1 km³ yr^{−1}; ref. 108) is also about 20 times lower than that of oceanic crust (20 km³ yr^{−1}). Because of the grossly different timescales, global differentiation may be approximated roughly by a two-stage process⁵⁴:

(1) The 'continental stage' or 'primary differentiation' of primitive mantle into continental crust with high Rb/Sr and Th/U, and low Sm/Nd, Nb/U and Ce/Pb ratios, and a residual mantle with complementary low Rb/Sr and Th/U, and high Sm/Nd, Nb/U and Ce/Pb. The mean age of the crust thus produced is 2–2.5 Gyr (ref. 58). The trace-element patterns of MORB (Fig. 2) reflect the residual nature of their source mantle. (2) The 'oceanic stage' continuously differentiates the residual mantle by ridge and subduction processes and rehomogenizes it by convection. This differentiation–homogenization process has time constants averaging 1–1.3 Gyr^{53,72} (see discussion on ages of mantle heterogeneities), and it creates most of the chemical and isotopic diversity seen in Figs 3–6.

The complementary Nb(Ta) and Pb anomalies in the oceanic and continental crusts (Fig. 2) are caused by special processes during continent production. Niobium and tantalum are retained in the mantle by Ti minerals¹⁰⁹ or amphibole¹¹⁰ during subduction-related volatile transfer¹¹¹ and/or magmatism. The continental crust grows, in part, by accretion of subduction-related, Nb–Ta depleted island-arc magmas and thus acquires the large negative Nb–Ta and smaller Ti anomalies seen in Fig. 2. The mantle therefore becomes relatively enriched in Nb and Ta, and this positive anomaly is homogenized through relatively rapid (see above) convective stirring. This explains the relatively uniform Nb/U ratios seen in Fig. 7. Oceanic (MORB and OIB) magmatism does not create new Nb–Ta anomalies because the minerals or volatiles that could fractionate Nb/U are absent in the MORB–OIB melting region.

'Lead paradox'. The positive lead anomaly in the continental crust and the complementary negative anomalies in oceanic basalts (Fig. 2) are created by hydrothermal processes in two stages. First, lead is extracted from the basaltic crust and redeposited in metalliferous sediments by hydrothermal ridge processes¹⁰². When the crust is subducted, additional lead is extracted from the crust and

the sediments by dehydration. This lead is ultimately transferred to the continental crust via island arc magmatism (see above).

This transfer process provides the key to the solution of the 'lead isotope paradox' and the absence of a global correlation of $^{206}\text{Pb}/^{204}\text{Pb}$ with Sr and Nd isotopes (Fig. 5). The hydrothermal processes have enriched the continental crust in lead to a similar degree as in uranium (see Fig. 2). Consequently, the continental crust has, on average, similar U/Pb and therefore $^{206}\text{Pb}/^{204}\text{Pb}$ ratios as the (residual) mantle. Similarly, most of the MORB data also lie close to the 'geochron' in Fig. 4a, rather than falling to the 'depleted', low- $^{206}\text{Pb}/^{204}\text{Pb}$ side (caused by low U/Pb) that would be expected if the sources were produced by purely magmatic depletion processes. (For a detailed discussion of the 'best' position of the geochron, see ref. 27.) Continent-derived ocean-floor sediments have $^{206}\text{Pb}/^{204}\text{Pb}$ ratios similar to average upper oceanic crust (Fig. 4), but possess an extremely large range of U/Pb ratios¹¹², which will, in time, generate a large range of Pb-isotopic compositions. When such sediments are recycled through the mantle, they will destroy the correlations between the U/Pb, Rb/Sr and Sm/Nd ratios that are produced by purely magmatic differentiation processes. This appears to have happened in EM-2 (and possibly also in EM-1) type OIB, as well as in Indian Ocean MORB, which show no correlations between Sr (or Nd) and Pb isotopes (Fig. 5). In contrast, Pacific and Atlantic MORB show good correlations and appear to be nearly free of recycled continental material.

Role of plumes and mantle layering. Geochemical evidence, especially that derived from noble gases, favours some type of layered mantle convection, but one in which the layers are not completely isolated. I therefore suggest that plumes may come from both the 660-km discontinuity and the core-mantle boundary. Small, short-lived plumes and those carrying no enrichment in primordial ^3He are most likely to have a shallow origin. Large, long-lived, ^3He -rich plumes, and especially those that have generated enormous volumes of oceanic or continental flood basalts, are more likely to have come from the base of the lower mantle⁸⁹.

This history of deep-plume activity may well have been episodic and linked to times of high rates of continent formation^{18,108}. Several of the large oceanic plateaux were created in the Cretaceous period, and this may constitute an unusual event in Earth history¹¹³. These plateaux may represent the heads of deep-mantle plumes⁸⁹ that will ultimately be accreted to the continental crust. The relatively large number of ^3He -rich plumes may therefore be mostly remnants of deep-mantle plumes that started in Cretaceous time and are still active today. Similarly, deep subduction of oceanic lithosphere into the lower mantle, for which there is mounting seismological evidence⁸⁷, may be a sporadic event that balances the occasional deep-mantle plume flux¹⁷.

In geologically 'normal' times, both plate-tectonic convection and plume generation may be confined to the upper mantle. This implies further that at present we are seeing both the remnants of a deep-plume and deep-subduction event (in the form of the remaining plume trails) and the resumption of isolated upper-mantle convection dominated by plate tectonics and upper-mantle plumes¹⁸.

Depletion, replenishment, recycling. The uppermost mantle, the source of MORB, is depleted in incompatible elements by two processes. (1) Devolatilization and melting during subduction transfer incompatible elements to long-time (or permanent) storage in the continental crust and lithosphere; and (2) a portion of the subducted oceanic crust is stored at the base of the convecting system and thus sequesters incompatible elements temporarily. The remainder of this crust is mixed back into the MORB reservoir. Consequently, the MORB mantle has a 'marble cake' structure²⁴ containing schlieren of enriched, recycled material. In addition, plume injection creates 'regional' (100–1,000 km) scale chemical and isotopic gradients in MORB mantle (see, for example, ref. 12). The Indian Ocean MORB source region differs from Pacific and

Atlantic regions in that it has been 'polluted' by ancient sediments⁹⁸ or subcontinental lithosphere¹¹⁴ (see section on the lead paradox).

The former oceanic crust stored as potential plume sources at 660 and 2,900 km depth contains a wide variety of 'enriched' material. HIMU plume sources are enriched in former MORB, in which hydrothermal ridge processes had caused loss of lead and therefore an increase in (U, Th)/Pb (refs 6, 49). EM-2 sources represent recycled oceanic crust containing a few per cent of continent-derived sediment^{49,66,115}. This is consistent with their high $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ and low Nb/U and Ce/Pb ratios (see Fig. 7). EM-1 sources are the most enigmatic members of the mantle zoo. Their slightly subnormal Nb/U, low $^{206}\text{Pb}/^{204}\text{Pb}$ and high $^{208}\text{Pb}/^{206}\text{Pb}$ ratios are consistent with a contribution from either recycled, ancient pelagic sediment^{6,49} or recycled ancient subcontinental lithosphere^{81,107,116}. Osmium isotopes (see above) should resolve the issue.

Conclusion and outlook

Although many parts of the story remain controversial and difficult to decipher, I regard the following conclusions to be reasonably robust. Recycling of oceanic crust and lithosphere plays an important role in generating mantle heterogeneities. Available geochemical mass balances favour compositional layering, which is maintained by partial or intermittent convective isolation between upper and lower mantle.

The controversy over the issue of convective layering and depth of plume sources is likely to be resolved when the so far rather fuzzy seismic imaging of the Earth's interior becomes comparable in resolution to that achieved by geochemical mapping, so that geophysical and geochemical data can be more specifically correlated. The origin of the geochemical 'mantle species' will be clarified by a rapidly expanding data base of osmium isotopes and high-quality data for well-established tracer elements such as Nb and Pb, as well as relatively 'new' tracers such as B and Sb, and by high-precision oxygen isotope microanalysis of igneous minerals¹¹⁷, capable of recognizing a sedimentary or hydrothermal prehistory of the magma. □

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