

2.03

Sampling Mantle Heterogeneity through Oceanic Basalts: Isotopes and Trace Elements

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2.03.1	INTRODUCTION	61
2.03.1.1	<i>Early History of Mantle Geochemistry</i>	61
2.03.1.2	<i>The Basics</i>	62
2.03.1.2.1	<i>Major and trace elements: incompatible and compatible behavior</i>	62
2.03.1.2.2	<i>Radiogenic isotopes</i>	63
2.03.2	LOCAL AND REGIONAL EQUILIBRIUM REVISITED	64
2.03.2.1	<i>Mineral Grain Scale</i>	64
2.03.2.2	<i>Mesoscale Heterogeneities</i>	65
2.03.3	CRUST–MANTLE DIFFERENTIATION	66
2.03.3.1	<i>Enrichment and Depletion Patterns</i>	66
2.03.3.2	<i>Mass Fractions of Depleted and Primitive Mantle Reservoirs</i>	69
2.03.4	MID-OCEAN RIDGE BASALTS: SAMPLES OF THE DEPLETED MANTLE	70
2.03.4.1	<i>Isotope Ratios of Strontium, Neodymium, Hafnium, and Lead</i>	70
2.03.4.2	<i>Osmium Isotopes</i>	75
2.03.4.3	<i>Trace Elements</i>	76
2.03.4.4	<i>N-MORB, E-MORB, T-MORB, and MORB Normalizations</i>	79
2.03.4.5	<i>Summary of MORB and MORB-source Compositions</i>	80
2.03.5	OCEAN ISLAND, PLATEAU, AND SEAMOUNT BASALTS	81
2.03.5.1	<i>Isotope Ratios of Strontium, Neodymium, Hafnium, and Lead and the Species of the Mantle Zoo</i>	81
2.03.5.2	<i>Trace Elements in OIB</i>	86
2.03.5.2.1	<i>“Uniform” trace-element ratios</i>	87
2.03.5.2.2	<i>Normalized abundance diagrams (“Spidergrams”)</i>	90
2.03.6	THE LEAD PARADOX	92
2.03.6.1	<i>The First Lead Paradox</i>	92
2.03.6.2	<i>The Second Lead Paradox</i>	94
2.03.7	GEOCHEMICAL MANTLE MODELS	95
	ACKNOWLEDGMENTS	97
	REFERENCES	97

2.03.1 INTRODUCTION

2.03.1.1 Early History of Mantle Geochemistry

Until the arrival of the theories of plate tectonics and seafloor spreading in the 1960s, the Earth’s mantle was generally believed to consist

of peridotites of uniform composition. This view was shared by geophysicists, petrologists, and geochemists alike, and it served to characterize the compositions and physical properties of mantle and crust as “Sial” (silica-alumina) of low density and “Sima” (silica-magnesia) of greater

density. Thus, Hurley and his collaborators were able to distinguish crustal magma sources from those located in the mantle on the basis of their initial strontium-isotopic compositions (Hurley *et al.*, 1962; and Hurley's lectures and popular articles not recorded in the formal scientific literature). In a general way, as of early 2000s, this view is still considered valid, but literally thousands of papers have since been published on the isotopic and trace-elemental composition of oceanic basalts because they come from the mantle and they are rich sources of information about the composition of the mantle, its differentiation history and its internal structure. Through the study of oceanic basalts, it was found that the mantle is compositionally just as heterogeneous as the crust. Thus, geochemistry became a major tool to decipher the geology of the mantle, a term that seems more appropriate than the more popular "chemical geodynamics."

The pioneers of this effort were Gast, Tilton, Hedge, Tatsumoto, and Hart (Hedge and Walthall, 1963; Gast *et al.*, 1964; Tatsumoto, *et al.*, 1965; Hart, 1971). They discovered from isotope analyses of strontium and lead in young (effectively zero age) ocean island basalts (OIBs) and mid-ocean ridge basalts (MORBs) that these basalts are isotopically not uniform. The isotope ratios $^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ increase as a function of time and the respective radioactive-parent/nonradiogenic daughter ratios, $^{87}\text{Rb}/^{86}\text{Sr}$, $^{238}\text{U}/^{204}\text{Pb}$, $^{235}\text{U}/^{204}\text{Pb}$, and $^{232}\text{Th}/^{204}\text{Pb}$, in the sources of the magmas. This means that the mantle must contain geologically old reservoirs with different Rb/Sr, U/Pb, and Th/Pb ratios. The isotope story was complemented by trace-element geochemists, led primarily by Schilling and Winchester (1967, 1969) and Gast (1968) on chemical trace-element fractionation during igneous processes, and by Tatsumoto *et al.* (1965) and Hart (1971). From the trace-element abundances, particularly rare-earth element (REE) abundances, it became clear that not only some particular parent–daughter element abundance ratios but also the light-to-heavy REE ratios of the Earth's mantle are quite heterogeneous. The interpretation of these heterogeneities has occupied mantle geochemists since the 1960s.

This chapter is in part an update of a previous, more abbreviated review (Hofmann, 1997). It covers the subject in greater depth, and it reflects some significant changes in the author's views since the writing of the earlier paper. In particular, the spatial range of equilibrium attained during partial melting may be much smaller than previously thought, because of new experimental diffusion data and new results from natural settings. Also, the question of "layered" versus

"whole-mantle" convection, including the depth of subduction and of the origin of plumes, has to be reassessed in light of the recent breakthroughs achieved by seismic mantle tomography. As the spatial resolution of seismic tomography and the pressure range, accuracy, and precision of experimental data on melting relations, phase transformations, and kinetics continue to improve, the interaction between these disciplines and geochemistry *sensu stricto* will continue to improve our understanding of what is actually going on in the mantle. The established views of the mantle being engaged in simple two-layer, or simple single-layer, convection are becoming obsolete. In many ways, we are just at the beginning of this new phase of mantle geology, geophysics, and geochemistry.

2.03.1.2 The Basics

2.03.1.2.1 Major and trace elements: incompatible and compatible behavior

Mantle geochemists distinguish between major and trace elements. At first sight, this nomenclature seems rather trivial, because which particular elements should be called "major" and which "trace" depends on the composition of the system. However, this distinction actually has a deeper meaning, because it signifies fundamental differences in geochemical behavior. We define elements as "major" if they are essential constituents of the minerals making up a rock, namely, in the sense of the phase rule. Thus, on the one hand, silicon, aluminum, chromium, magnesium, iron, calcium, sodium, and oxygen are major elements because they are essential constituents of the upper-mantle minerals—olivine, pyroxene, garnet, spinel, and plagioclase. Adding or subtracting such elements can change the phase assemblage. Trace elements, on the other hand just replace a few atoms of the major elements in the crystal structures without affecting the phase assemblage significantly. They are essentially blind passengers in many mantle processes, and they are therefore immensely useful as tracers of such processes. During solid-phase transformations, they will redistribute themselves locally between the newly formed mineral phases but, during melting, they are partitioned to a greater or lesser degree into the melt. When such a melt is transported to the Earth's surface, where it can be sampled, its trace elements carry a wealth of information about the composition of the source rock and the nature of the melting processes at depth.

For convenience, the partitioning of trace elements between crystalline and liquid phases is usually described by a coefficient D , which is

just a simple ratio of two concentrations at chemical equilibrium:

$$D^i = \frac{C_s^i}{C_l^i} \quad (1)$$

where D^i is called the partition coefficient of trace element i , C_s^i and C_l^i are the concentrations (by weight) of this element in the solid and liquid phases, respectively.

Goldschmidt (1937, 1954) first recognized that the distribution of trace elements in minerals is strongly controlled by ionic radius and charge. The partition coefficient of a given trace element between solid and melt can be quantitatively described by the elastic strain this element causes by its presence in the crystal lattice. When this strain is large because of the magnitude of the misfit, the partition coefficient becomes small, and the element is partitioned into the liquid. This subject is treated in detail in Chapter 2.09.

Most trace elements have values of $D \ll 1$, simply because they differ substantially either in ionic radius or ionic charge, or both, from the atoms of the major elements they replace in the crystal lattice. Because of this, they are called *incompatible*. Exceptions are trace elements such as strontium in plagioclase, ytterbium, lutetium, and scandium in garnet, nickel in olivine, and scandium in clinopyroxene. These latter elements actually fit into their host crystal structures slightly better than the major elements they replace, and they are therefore called *compatible*. Thus, most chemical elements of the periodic table are trace elements, and most of them are incompatible; only a handful are compatible.

Major elements in melts formed from mantle rocks are by definition compatible, and most of them are well buffered by the residual minerals, so that their concentrations usually vary by factors of less than two in the melts. In contrast, trace elements, particularly those having very low partition coefficients, may vary by as many as three orders of magnitude in the melt, depending on the degree of melting. This is easily seen from the mass-balance-derived equation for the equilibrium concentration of a trace element in the melt, C_1 , given by (Shaw, 1970)

$$C_1 = \frac{C_0}{F + D(1 - F)} \quad (2)$$

where the superscript i has been dropped for clarity, C_0 is the concentration in the bulk system, and F is the melt fraction by mass. For highly incompatible elements, which are characterized by very low partition coefficients, so that $D \ll F$, this equation reduces to

$$C_1 \approx \frac{C_0}{F} \quad (3)$$

This means that the trace-element concentration is then inversely proportional to the melt fraction F ,

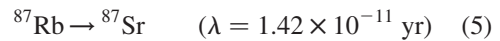
because the melt contains essentially all of the budget of this trace element. An additional consequence of highly incompatible behavior of trace elements is that their concentration ratios in the melt become constant, independent of melt fraction, and identical to the respective ratio in the mantle source. This follows directly when Equation (3) is written for two highly incompatible elements:

$$\frac{C_1^1}{C_1^2} \approx \frac{C_0^1}{C_0^2} \times \frac{F}{C_0^2} = \frac{C_0^1}{C_0^2} \quad (4)$$

In this respect, incompatible trace-element ratios resemble isotope ratios. They are therefore very useful in complementing the information obtained from isotopes.

2.03.1.2.2 Radiogenic isotopes

The decay of long-lived radioactive isotopes was initially used by geochemists exclusively for the measurement of geologic time. As noted in the introduction, their use as tracers of mantle processes was pioneered by Hurley and co-workers in the early 1960s. The decay



serves as example. The solution of the decay equation is

$$^{87}\text{Sr} = ^{87}\text{Rb} \times (e^{\lambda t} - 1) \quad (6)$$

Dividing both sides by one of the nonradiogenic isotopes, by convention ^{86}Sr , we obtain

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \frac{^{87}\text{Rb}}{^{86}\text{Sr}} \times (e^{\lambda t} - 1) \approx \frac{^{87}\text{Rb}}{^{86}\text{Sr}} \times \lambda t \quad (7)$$

The approximation in Equation (7) holds only for decay systems with sufficiently long half-lives, such as the Rb–Sr and the Sm–Nd systems, so that $\lambda t \ll 1$ and $e^{\lambda t} - 1 \approx \lambda t$. Therefore, the isotope ratio $^{87}\text{Sr}/^{86}\text{Sr}$ in a system, such as some volume of mantle rock, is a linear function of the parent/daughter chemical ratio Rb/Sr and a nearly linear function of time or geological age of the system. When this mantle volume undergoes equilibrium partial melting, the melt inherits the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the entire system. Consequently, radiogenic isotope ratios such as $^{87}\text{Sr}/^{86}\text{Sr}$ are powerful tracers of the parent–daughter ratios of mantle sources of igneous rocks. If isotope data from several decay systems are combined, a correspondingly richer picture of the source chemistry can be constructed.

Table 1 shows a list of long-lived radionuclides, their half-lives, daughter isotopes, and radiogenic-to-nonradiogenic isotope rates commonly used as tracers in mantle geochemistry. Noble-gas isotopes are not included here, because a separate chapter of this Treatise is devoted to them

Table 1 Long-lived radionuclides.

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

(see Chapter 2.06). Taken together, they cover a wide range of geochemical properties including incompatible and compatible behavior. These ratios will be used, together with some incompatible trace-element ratios, as tracers of mantle reservoirs, crust–mantle differentiation processes, and mantle melting processes in later sections of this chapter.

2.03.2 LOCAL AND REGIONAL EQUILIBRIUM REVISITED

How do we translate geochemical data from basalts into a geological model of the present-day mantle and its evolution? The question of chemical and isotopic equilibrium, and particularly its spatial dimension, has always played a fundamental role in this effort of interpretation. The basic, simple tenet of isotope geochemists and petrologists alike has generally been that partial melting at mantle temperatures, pressures, and timescales achieves essentially complete chemical equilibrium between melt and solid residue. For isotope data in particular, this means that at magmatic temperatures, the isotope ratio of the melt is identical to that of the source, and this is what made isotope ratios of volcanic rocks apparently ideal tracers of mantle composition. The question of spatial scale seemed less important, because heterogeneities in the mantle were thought to be important primarily on the 10^2 – 10^4 km scale (Hart *et al.*, 1973; Schilling, 1973; White and Schilling, 1978; Dupré and Allègre, 1983). To be sure, this simple view was never universal. Some authors invoked special isotopic effects during melting, so that the isotopic composition of the melt could in some way be “fractionated” during melting, in spite of the high temperatures prevailing, so that the isotope ratios observed in the melts would *not* reflect those of the melt sources (e.g., O’Hara, 1973; Morse, 1983). These opinions were invariably raised by authors not directly familiar with the analytical methods of isotope geochemistry, so that they did not realize that isotopic fractionation occurs in

every mass spectrometer and is routinely corrected in the reported results.

2.03.2.1 Mineral Grain Scale

Some authors invoked mineral-scale isotopic (and therefore also chemical) disequilibrium and preferential melting of phases, such as phlogopite, which have higher Rb/Sr, and therefore also higher ⁸⁷Sr/⁸⁶Sr ratios than the bulk rock, in order to explain unusually high ⁸⁷Sr/⁸⁶Sr ratios in OIBs (e.g., O’Nions and Pankhurst, 1974; Vollmer, 1976). Hofmann and Hart (1978) reviewed this subject in light of the available diffusion data in solid and molten silicates. They concluded that mineral-scale isotopic and chemical disequilibrium is exceedingly unlikely, if melting timescales are on the order of thousands of years or more. More recently, Van Orman *et al.* (2001) have measured REE diffusion coefficients in clinopyroxene and found that REE mobility in this mineral is so low at magmatic temperatures that chemical disequilibrium between grain centers and margins will persist during melting. Consequently, the melt will not be in equilibrium with the bulk residue for geologically reasonable melting times, if the equilibration occurs by volume diffusion alone. This means that the conclusions of Hofmann and Hart (1978) must be revised significantly: The slowest possible path of chemical reaction no longer guarantees attainment of equilibrium. However, it is not known whether other mechanisms such as recrystallization during partial melting might not lead to much more rapid equilibration. One possible test of this would be the examination of mantle clinopyroxenes from oceanic and ophiolitic peridotites. These rocks have undergone various extents of partial melting (Johnson *et al.*, 1990; Hellebrand *et al.*, 2001), and the residual clinopyroxenes should show compositional zoning if they had not reached equilibrium with the melt via volume diffusion. Although the above-cited studies were not specifically conducted to test this question, the clinopyroxenes were analyzed by ion microprobe,

and these analyses showed no significant signs of internal compositional gradients. It is, of course, possible in principle that the internal equilibration occurred after extraction of the melt, so this evidence is not conclusive at present. Nevertheless, these results certainly leave open the possibility that the crystals re-equilibrated continuously with the melt during melt production and extraction. There is at present no definitive case from “natural laboratories” deciding the case one way or the other, at least with respect to incompatible lithophile elements such as the REE.

Osmium isotopes currently provide the strongest case for mineral-to-mineral disequilibrium, and for mineral–melt disequilibrium available from observations on natural rocks. Thus, both osmium alloys and sulfides from ophiolites and mantle xenoliths have yielded strongly heterogeneous osmium isotope ratios (Alard *et al.*, 2002; Meibom *et al.*, 2002). The most remarkable aspect of these results is that these ophiolites were emplaced in Phanerozoic times, yet they contain osmium-bearing phases that have retained model ages in excess of 2 Ga in some cases. The melts that were extracted from these ophiolitic peridotites contained almost certainly much more radiogenic osmium and could, in any case, not have been in osmium-isotopic equilibrium with all of these isotopically diverse residual phases.

Another strong indication that melts extracted from the mantle are not in osmium-isotopic equilibrium with their source is given by the fact that osmium isotopes in MORBs are, on average, significantly more radiogenic than osmium isotopes from oceanic peridotites (see also Figure 9 further below). Although it may be argued that there is no one-to-one correspondence between basalts and source peridotites, and further, that the total number of worldwide MORB and peridotite samples analyzed is still small, these results strongly suggest that, at least with regard to osmium, MORBs are generally not in isotopic equilibrium with their sources or residues. However, osmium-isotopic disequilibrium does not automatically mean strontium, neodymium, lead, or oxygen-isotopic disequilibrium or incompatible-trace-element disequilibrium. This is because osmium is probably incompatible in all silicate phases (Snow and Reisberg, 1995; Schiano *et al.*, 1997; Burton *et al.*, 2000) but very highly compatible with nonsilicate phases such as sulfides and, possibly, metal alloys such as osmiridium “nuggets,” which may form inclusions within silicate minerals and might therefore be protected from reaction with a partial silicate melt. At the time of writing, no clear-cut answers are available, and for the time being, we will simply note that the geochemistry of osmium and rhenium is considerably less well understood than that of silicate-hosted major and trace

elements such as strontium, neodymium, lead, and their isotopic abundances.

2.03.2.2 Mesoscale Heterogeneities

By “mesoscale” I mean scales larger than about a centimeter but less than a kilometer. This intermediate scale was addressed only briefly by Hofmann and Hart, who called it a “lumpy mantle” structure. It was specifically invoked by Hanson (1977) and Wood (1979), and others subsequently, who invoked veining in the mantle to provide sources for chemically and isotopically heterogeneous melts. Other versions of mesoscale heterogeneities were invoked by Sleep (1984), who suggested that preferential melting of ubiquitous heterogeneities may explain ocean island-type volcanism, and by Allègre and Turcotte (1986), who discussed a “marble cake” structure of the mantle generated by incomplete homogenization of subducted heterogeneous lithosphere. These ideas have recently been revived in several publications discussing a mantle containing pyroxenite or eclogite layers, which may melt preferentially (Phipps Morgan *et al.*, 1995; Hirschmann and Stolper, 1996; Phipps Morgan and Morgan, 1998; Yaxley and Green, 1998; Phipps Morgan, 1999).

One of the main difficulties with these mesoscale models is that they have been difficult to test by direct geochemical and petrological field observations. Recently, however, several studies have been published which appear to support the idea of selective melting of mesoscale heterogeneities. Most important of these are probably the studies of melt inclusions showing that single basalt samples, and even single olivine grains, contain chemically and isotopically extremely heterogeneous melt inclusions. Extreme heterogeneities in REE abundances from melt inclusions had previously been explained by progressive fractional melting processes of uniform sources (Sobolev and Shimizu, 1993; Gurenko and Chaussidon, 1995). In contrast, the more recent studies have demonstrated that source heterogeneities must (also) be involved to explain the extreme variations in isotopic and chemical compositions observed (Saal *et al.*, 1998; Sobolev *et al.*, 2000). While the spatial scale of these source heterogeneities cannot be directly inferred from these melt inclusion data, it seems highly plausible that it is in the range of what is here called “mesoscale.”

Other, more circumstantial, evidence for preferential melting of mesoscale heterogeneities has been described by Regelous and Hofmann (2002/3), who found that the Hawaiian plume delivered MORB-like magmas ~80 Ma ago, when the plume was located close to the Pacific

spreading ridge. Unless this is a fortuitous coincidence, this implies that the same plume produces “typical” OIB-like, incompatible-element-enriched melts with elevated $^{87}\text{Sr}/^{86}\text{Sr}$ and low $^{143}\text{Nd}/^{144}\text{Nd}$ ratios when the degree of melting is relatively low under a thick lithosphere, and typically MORB-like, incompatible-element-depleted melts when the degree of melting is high because of the shallow melting level near a spreading ridge. Such a dependence on the extent of melting is consistent with a marble-cake mantle containing incompatible-element-rich pyroxenite or eclogite layers having a lower melting temperature than the surrounding peridotite matrix. This melting model is further corroborated by the observation that at least three other plumes located at or near spreading ridges have produced MORB-like lavas, namely, the Iceland, the Galapagos, and the Kerguelen plume. The overall evidence is far from clear-cut, however, because the Iceland and Galapagos plumes have also delivered OIB-like tholeiites and alkali basalts more or less in parallel with the depleted MORB-like tholeiites or picrites.

To sum up, the question of grain-scale equilibration with partial melts, which had apparently been settled definitively by Hofmann and Hart (1978), has been reopened by the experimental work of Van Orman *et al.* (2001) and by recent osmium isotope data. The mesoscale equilibrium involving a veined or marble-cake mantle consisting of a mixture of lherzolite (or harzburgite) and pyroxenite (or eclogite) has also received substantial support in the recent literature. In either case, the isotopic composition of the melt is likely to change as a function of the bulk extent of melting, and the melts do not provide quantitative estimates of the isotopic composition of the bulk sources at scales of kilometers or more. It will be seen in subsequent sections that this has ramifications particularly with respect to quantitative estimates of the sizes and spatial distributions of the reservoirs hosting the geochemical mantle heterogeneities observed in basalts. While this defeats one of the important goals of mantle geochemistry, it will be seen in the course of this chapter that the geochemical data can still be used to map large-scale geochemical provinces of the mantle and to reveal much about the smaller-scale structure of the mantle heterogeneities. In addition, they remain powerful tracers of recycling and mixing processes and their history in the mantle.

2.03.3 CRUST–MANTLE DIFFERENTIATION

Before discussing the internal chemical structure of the mantle, it is necessary to have a general understanding of crust–mantle differentiation,

because this has affected the incompatible trace-element and isotope budget of the mantle rather drastically. This topic has been covered by Hofmann (1988), but the most important points will be summarized here again. The treatment here differs in detail because more recent estimates have been used for the bulk composition of the continental crust and of the bulk silicate earth (BSE), also called “primitive mantle.”

2.03.3.1 Enrichment and Depletion Patterns

The growth of the continental crust has removed major proportions of the highly incompatible elements from the mantle, and this depletion is the chief (but not the sole) cause of the specific isotope and trace-element characteristics of MORBs. The effects of ionic radius and charge, described in Section 2.03.1.2.1, on this enrichment–depletion process can be readily seen in a diagram (Figure 1) introduced by Taylor and McLennan (1985). It is obvious from this that those trace elements that have ionic properties similar to the major silicate-structure-forming elements, namely, nickel, cobalt, manganese, scandium, and chromium are not enriched in the continental crust but remain in the mantle. In contrast, elements with deviating ionic properties are more or less strongly enriched in the crust, depending on the magnitude of the deviation. Two main transfer mechanisms are available for this differentiation, both of them are ultimately driven by mantle convection. The first is partial melting and ascent of the melt to the surface or into the already existing crust. The second involves dehydration (and decarbonation) reactions during subduction, metasomatic transfer of soluble elements via hydrothermal fluid from the subducted crust-plus-sediment into the overlying

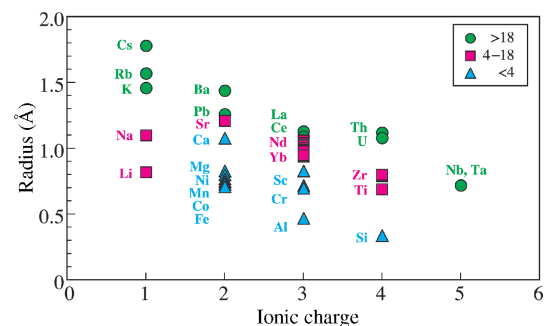


Figure 1 Ionic radius (in angstrom) versus ionic charge for lithophile major and trace elements in mantle silicates. Also shown are ranges of enrichment factors in average continental crust, using the estimate of (Rudnick and Fountain, 1995), relative to the concentrations in the primitive mantle (or “bulk silicate Earth”) (source McDonough and Sun, 1995).

mantle “wedge,” and partial melting of the metasomatized (or “fertilized”) region. This partial melt ascends and is added to the crust, carrying the geochemical signature caused by mantle metasomatic transfer into the crust. Both mechanisms may operate during subduction, and a large body of geochemical literature has been devoted to the distinction between the two (Elliott *et al.*, 1997; Class *et al.*, 2000; Johnson and Plank, 2000; see Chapter 2.11). Continental crust may also be formed by mantle plume heads, which are thought to produce large volumes of basaltic oceanic plateaus. These may be accreted to existing continental crust, or continental flood basalts, which similarly add to the total volume of crust (e.g., Abouchami *et al.*, 1990; Stein and Hofmann, 1994; Puchtel *et al.*, 1998). The quantitative importance of this latter mechanism remains a matter of some debate (Kimura *et al.*, 1993; Calvert and Ludden, 1999).

Hofmann (1988) showed that crust formation by extraction of partial melt from the mantle could well explain much of the trace-element chemistry of crust–mantle differentiation. However, a few elements, notably niobium, tantalum, and lead, do not fit into the simple pattern of enrichment and depletion due to simple partial melting (Hofmann *et al.*, 1986). The fundamentally different behavior of these elements in the MORB–OIB environment on the one hand, and in the subduction environment on the other, requires the second,

more complex, transfer mechanism via fluids (Miller *et al.*, 1994; Peucker-Ehrenbrink *et al.*, 1994; Chauvel *et al.*, 1995). Thus, local fluid transport is essential in preparing the mantle sources for production of continental crust, but the gross transport of incompatible elements from mantle to crust is still carried overwhelmingly by melting and melt ascent.

The simplest case discussed above, namely, crust–mantle differentiation by partial melting alone is illustrated in Figure 2. This shows the abundances of a large number of chemical elements in the continental crust, as estimated by (Rudnick and Fountain, 1995) and divided by their respective abundances in the primitive mantle or bulk silicate earth as estimated by (McDonough and Sun, 1995). Each element is assigned a nominal partition coefficient D as defined in Equation (1), calculated by rearranging Equation (2) and using a nominal “melt fraction” $F = 0.01$. In this highly simplified view, the continental crust is assumed to have the composition of an equilibrium partial melt derived from primitive mantle material. Also shown is the hypothetical solid mantle residue of such a partial melt and a second-stage partial melt of this depleted residue. This second-stage melt curve may then be compared with the actual element abundances of “average” ocean crust. Although this “model” of the overall crust–mantle differentiation is grossly oversimplified, it can account for the salient

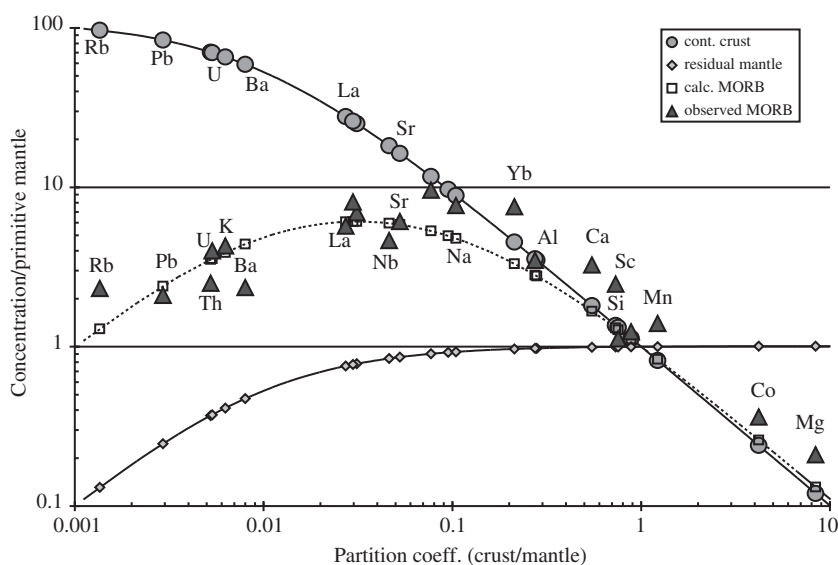


Figure 2 Comparison of the abundances of trace and (some) major elements in average continental crust and average MORB. Abundances are normalized to the primitive-mantle values (McDonough and Sun, 1995). The “partition coefficient” of each element is calculated by solving Equation (2) for D , using a melt fraction $F = 0.009$ and its abundance value in the continental crust (Rudnick and Fountain, 1995). The respective abundances in average MORB are plotted using the same value of D and using the average (“normal”) MORB values of (Su, 2002), where “normal” refers to ridge segments distant from obvious hotspots.

features of the relationship between primitive mantle, continental crust, depleted mantle, and oceanic crust quite well. This representation is remarkably successful because Equation (2) is essentially a mass-balance relationship and because these major reservoirs are in fact genetically related by enrichment and depletion processes in which partial melting plays a dominant role.

The above model of extracting continental crust and remelting the depleted residue also accounts approximately for the isotopic relationships between continental crust and residual mantle, where the isotopic composition is directly represented by MORB, using the assumption of complete local and mesoscale equilibrium discussed in Section 2.03.2. This is illustrated by Figure 3, which is analogous to Figure 2, but shows only the commonly used radioactive decay systems Rb–Sr, Sm–Nd, Lu–Hf, and Re–Os. Thus, the continental crust has a high parent–daughter ratios Rb/Sr and Re/Os, but low Sm/Nd and Lu/Hf, whereas the mantle residue has complementary opposite ratios. With time, these parent–daughter ratios will generate higher than primitive $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{187}\text{Os}/^{188}\text{Os}$, and lower than primitive $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$, ratios in the crust and complementary, opposite ratios in the mantle, and this is indeed observed for

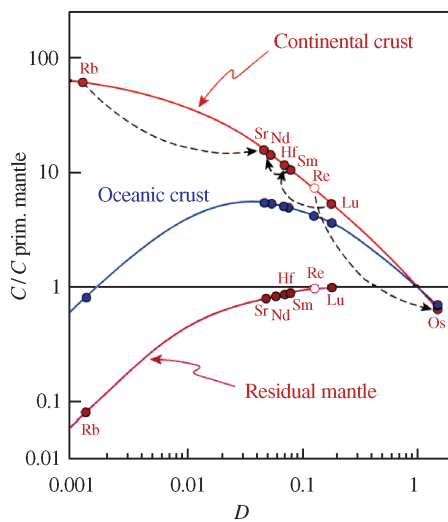


Figure 3 Crust–mantle differentiation patterns for the decay systems Rb–Sr, Sm–Nd, Lu–Hf, and Re–Os. The diagram illustrates the depletion–enrichment relationships of the parent–daughter pairs, which lead to the isotopic differences between continental crust and the residual mantle. For example, the Sm/Nd ratio is increased, whereas the Rb/Sr ratio is decreased in the residual mantle. This leads to the isotopic correlation in mantle-derived rocks plotted in Figure 4(a). The construction is similar to that used in Figure 2, but D values have been adjusted slightly for greater clarity.

strontium, neodymium, and hafnium, as will be seen in the review of the isotope data.

The case of lead isotopes is more complicated, because the estimates for the mean parent–daughter ratios of mantle and crust are similar. This similarity is not consistent with purely magmatic production of the crust, because the bulk partition coefficient of lead during partial mantle melting is expected to be only slightly lower than that of strontium (see Figure 1), but significantly higher than the coefficients for the highly incompatible elements uranium and thorium. In reality, however, the enrichment of lead in the continental crust shown in Figure 2 is slightly higher than the enrichments for thorium and uranium, and the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of continental rocks are similar to those of MORB. This famous–infamous “lead paradox,” first pointed out by Allègre (1969), will be discussed in a separate section below.

How do we know the parent–daughter ratios in crust and mantle? When both parent and daughter nuclides have refractory lithophile character, and are reasonably resistant to weathering and other forms of low-temperature alteration, as is the case for the pairs Sm–Nd and Lu–Hf, we can obtain reasonable estimates from measuring and averaging the element ratios in representative rocks of crustal or mantle heritage. But when one of the elements was volatile during terrestrial accretion, and/or is easily mobilized by low-temperature or hydrothermal processes, such as rubidium, uranium, or lead, the isotopes of the daughter elements yield more reliable information about the parent–daughter ratios of primitive mantle, depleted mantle, and crust, because the isotope ratios are not affected by recent loss (or addition) of such elements. Thus, the U/Pb and Th/Pb ratios of bulk silicate earth, depleted mantle and continental crust are essentially derived from lead isotope ratios.

Similarly, the primitive mantle Rb/Sr ratio was originally derived from the well-known negative correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in mantle-derived and crustal rocks, the so-called “mantle array” (DePaolo and Wasserburg, 1976; Richard *et al.*, 1976; O’Nions *et al.*, 1977; see also Figure 4(a)). To be sure, there is no guarantee that this correlation will automatically go through the bulk silicate earth value. However, in this case, the primitive mantle (or “bulk silicate earth”) Rb/Sr value has been approximately confirmed using element abundance ratios of barium, rubidium, and strontium. Hofmann and White (1983) found that Ba/Rb ratios in mantle-derived basalts and continental crust are sufficiently similar, so that the terrestrial value of Ba/Rb can be estimated within narrow limits. The terrestrial Ba/Sr ratio (comprising two refractory, lithophile elements)

can be assumed to be identical to the ratio in chondritic meteorites, so that the terrestrial Rb/Sr ratio can be estimated as

$$\left(\frac{\text{Rb}}{\text{Sr}}\right)_{\text{terr.}} = \left(\frac{\text{Rb}}{\text{Ba}}\right)_{\text{terr.}} \times \left(\frac{\text{Ba}}{\text{Sr}}\right)_{\text{chondr.}} \quad (8)$$

The terrestrial Rb/Sr ratio estimated in this way turned out to be indistinguishable from the ratio estimated by isotope correlations, and therefore the consistency between isotope and element abundance data is not circular. This example of internal consistency has been disturbed by the more recent crustal estimate of Ba/Rb = 6.7 (Rudnick and Fountain, 1995), which is significantly lower than the above mantle estimate Ba/Rb = 11.0 (Hofmann and White, 1983), based mostly on MORB and OIB data. This shows that, for many elements, there are greater uncertainties about the composition of the continental crust than about the mantle. The reason for this is that the continental crust has become much more heterogeneous than the mantle because of internal differentiation processes including intracrustal melting, transport of metamorphic fluids, hydrothermal transport, weathering, erosion, and sedimentation. In any case, assuming that Rudnick's crustal estimate is correct, the primitive mantle Ba/Rb should lie somewhere between 7 and 11. The lesson from this is that we must be careful when using "canonical" element ratios to make mass-balance estimates for the sizes of different mantle reservoirs.

2.03.3.2 Mass Fractions of Depleted and Primitive Mantle Reservoirs

The simple crust–mantle differentiation model shown in Figure 2 contains three "reservoirs:" continental crust, depleted residue, and oceanic crust. However, the depleted reservoir may well be smaller than the entire mantle, in which case another, possibly primitive reservoir would be needed. Thus, if one assumes that the mantle consists of two reservoirs only, one depleted and one remaining primitive, and if one neglects the oceanic crust because it is thin and relatively depleted in highly incompatible elements, one can calculate the mass fractions of these two reservoirs from their respective isotopic and/or trace-element compositions (Jacobsen and Wasserburg, 1979; O'Nions *et al.*, 1979; DePaolo, 1980; Davies, 1981; Allègre *et al.*, 1983, 1996; Hofmann *et al.*, 1986; Hofmann, 1989a). The results of these estimates have yielded mass fractions of the depleted reservoir ranging from ~30–80%. Originally, the 30% estimate was particularly popular because it

matches the mass fraction of the upper mantle above the 660 km seismic discontinuity. It was also attractive because at least some of the mineral physics data indicated that the lower mantle has a different, intrinsically denser, major-element composition. However, more recent data and their evaluations indicate that they do not require such compositional layering (Jackson and Rigden, 1998). Nevertheless, many authors argue that the 660 km boundary can isolate upper-mantle- from lower-mantle convection, either because of the endothermic nature of the phase changes at this boundary, or possibly because of extreme viscosity differences between upper and lower mantle. Although this entire subject has been debated in the literature for many years, there appeared to be good reasons to think that the 660 km seismic discontinuity is the fundamental boundary between an upper, highly depleted mantle and a lower, less depleted or nearly primitive mantle.

The most straightforward mass balance, assuming that we know the composition of the continental crust sufficiently well, can be calculated from the abundances of the most highly incompatible elements, because their abundances in the depleted mantle are so low that even relatively large relative errors do not affect the mass balance very seriously. The most highly enriched elements in the continental crust have estimated crustal abundances (normalized to the primitive mantle abundances given by McDonough and Sun (1995)) of Cs = 123, Rb = 97, and Th = 70 (Rudnick and Fountain, 1995). The estimate for Cs is rather uncertain because its distribution within the crust is particularly heterogeneous, and its primitive-mantle abundance is afflicted by special uncertainties (Hofmann and White, 1983; McDonough *et al.*, 1992). Therefore, a more conservative enrichment factor of 100 (close to the value of 97 for Rb) is chosen for elements most highly enriched in the continental crust. The simple three-reservoir mass balance then becomes

$$X_{\text{lm}} = \frac{1 - C_{\text{cc}} \times X_{\text{cc}} - C_{\text{um}} \times X_{\text{um}}}{C_{\text{lm}}} \quad (9)$$

where C refers to primitive-mantle normalized concentrations (also called "enrichment factors"), X refers to the mass fraction of a given reservoir, and the subscripts cc, lm, and um refer to continental crust, lower mantle, and upper mantle, respectively.

If the lower mantle is still primitive, so that $C_{\text{lm}} = 1$, the upper mantle is extremely depleted, so that $C_{\text{um}} = 0$, and $X_{\text{cc}} = 0.005$, the mass balance yields

$$X_{\text{lm}} = \frac{1 - 100 \times 0.005 - 0 \times X_{\text{um}}}{1} = 0.5 \quad (10)$$

Remarkably, this estimate is identical to that obtained using the amounts of radiogenic argon in the atmosphere, the continental crust and the depleted, upper mantle (Allègre *et al.*, 1996). There are reasons to think that the abundances of potassium and rubidium in BSE used in these calculations have been overestimated, perhaps by as much as 30% (Lassiter, 2002), and this would of course decrease the remaining mass fraction of primitive-mantle material. Thus, we can conclude that at least half, and perhaps 80%, of the most highly incompatible element budget now resides either in the continental crust or in the atmosphere (in the case of argon).

Can we account for the entire silicate earth budget by just these three reservoirs (crust plus atmosphere, depleted mantle, primitive mantle), as has been assumed in all of the above estimates? Saunders *et al.* (1988) and Sun and McDonough (1989) (among others) have shown that this cannot be the case, using global systematics of a single trace-element ratio, Nb/La. Using updated, primitive-mantle normalized estimates for this ratio, namely, $(\text{Nb/La})_n = 0.66$ for the continental crust (Rudnick and Fountain, 1995), and $(\text{Nb/La})_n = 0.81$ for so-called N-type (“normal”) MORB (Su, 2002), we see that both reservoirs have lower than primitive Nb/La ratios. Using the additional constraint that niobium is slightly more incompatible than lanthanum during partial melting, we find that the sources of all these mantle-derived basalts must have sources with Nb/La ratios equal to or lower than those of the basalts themselves. This means that all the major mantle sources as well as the continental crust have $(\text{Nb/La})_n \leq 1$. By definition, the entire silicate earth has $(\text{Nb/La})_n = 1$, so there should be an additional, hidden reservoir containing the “missing” niobium. A similar case has more recently been made using Nb/Ta, rather than Nb/La. Current hypotheses to explain these observations invoke either a refractory eclogitic reservoir containing high-niobium rutiles (Rudnick *et al.*, 2000), or partitioning of niobium into the metallic core (Wade and Wood, 2001). Beyond these complications involving special elements with unexpected geochemical “behavior,” there remains the question whether ~50% portion of the mantle not needed to produce the continental crust has remained primitive, or whether it is also differentiated into depleted, MORB-source-like, and enriched, OIB-source like subreservoirs. In the past, the occurrence of noble gases with primordial isotope ratios have been used to argue that the lower part of the mantle must still be nearly primitive. However, it will be seen below that this inference is no longer as compelling as it once seemed to be.

2.03.4 MID-OCEAN RIDGE BASALTS: SAMPLES OF THE DEPLETED MANTLE

2.03.4.1 Isotope Ratios of Strontium, Neodymium, Hafnium, and Lead

The long-lived radioactive decay systems commonly used to characterize mantle compositions, their half-lives, and the isotope ratios of the respective radiogenic daughter elements are given in Table 1. The half-lives of ^{147}Sm , ^{87}Sr , ^{186}Hf , ^{187}Re , and ^{232}Th are several times greater than the age of the Earth, so that the accumulation of the radiogenic daughter nuclide is nearly linear with time. This is not the case for the shorter-lived ^{238}U and ^{235}U , and this is in part responsible for the more complex isotopic relationships displayed by lead isotopes in comparison with the systematics of strontium, neodymium, hafnium, and osmium isotopes. The mantle geochemistry of noble gases, although of course an integral part of mantle geochemistry, is treated in Chapter 2.06.

Figures 4–6 show the isotopic compositions of MORBs from spreading ridges in the three major ocean basins. Figures 4(b) and 5(a) also show isotope data for marine sediments, because these are derived from the upper continental crust and should roughly represent the isotopic composition of this crust. In general, the isotopic relationships between the continental and oceanic crust are just what is expected from the elemental parent–daughter relationships seen in Figure 3. The high Rb/Sr and low Sm/Nd and Lu/Hf ratios of continental materials relative to the residual mantle are reflected by high $^{87}\text{Sr}/^{86}\text{Sr}$ and low $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios (not shown).

In lead isotope diagrams, the differences are not nearly as clear, and they are expressed primarily by slightly elevated $^{207}\text{Pb}/^{204}\text{Pb}$ ratios for given values of $^{206}\text{Pb}/^{204}\text{Pb}$ (Figure 5(a)). This topology in lead-isotope space requires a comparatively complex evolution of the terrestrial U–Pb system. It involves an ancient period of high U/Pb ratios in continental history (with complementary, low ratios in the residual mantle). The higher $^{235}\text{U}/^{238}\text{U}$ ratios prevailing during that time led to elevated $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in the crust. This subject is treated more fully in the section on the lead paradox (Section 2.03.6) further below.

Another important observation is that, while strontium, neodymium, and hafnium isotopes all correlate with each other, they form poorer, but still significant, correlations with $^{206}\text{Pb}/^{204}\text{Pb}$ (or $^{208}\text{Pb}/^{204}\text{Pb}$, not shown) ratios in the Pacific and Atlantic, but no discernible correlation in the Indian Ocean MORB (Figure 6(a)). Nevertheless, if instead of $^{208}\text{Pb}/^{204}\text{Pb}$ or $^{206}\text{Pb}/^{204}\text{Pb}$ ratios one plots the so-called “radiogenic” $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ ratio, the lead data do correlate with neodymium

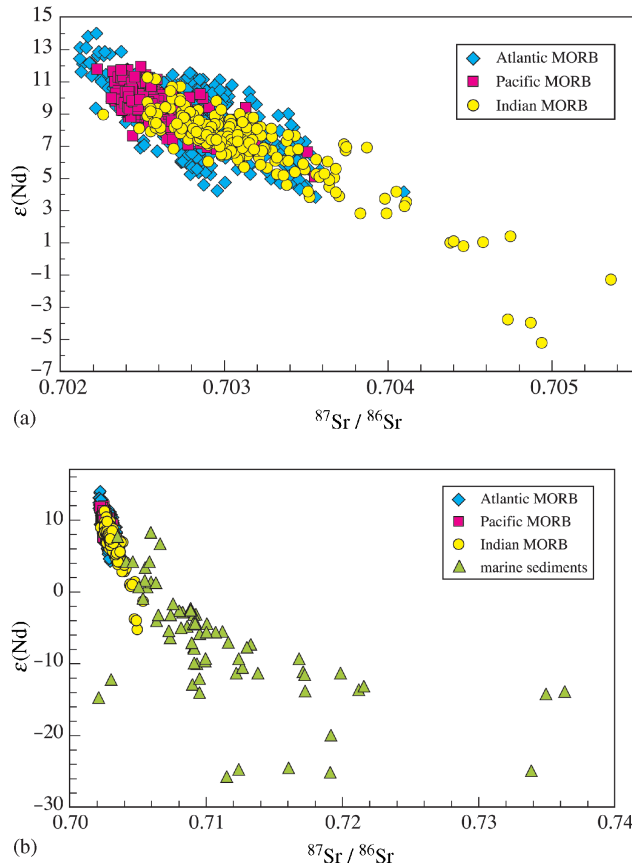


Figure 4 (a) $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\varepsilon(\text{Nd})$ for MORBs from the three major ocean basins. $\varepsilon(\text{Nd})$ is a measure of the deviation of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio from the chondritic value, assumed to be identical to the present-day value in the bulk silicate earth. It is defined as $\varepsilon(\text{Nd}) = 10^4 \times (^{143}\text{Nd}/^{144}\text{Nd}_{\text{measured}} - ^{143}\text{Nd}/^{144}\text{Nd}_{\text{Chondrite}}) / ^{143}\text{Nd}/^{144}\text{Nd}_{\text{Chondrite}}$. The chondritic value used is $^{143}\text{Nd}/^{144}\text{Nd}_{\text{Chondrite}} = 0.512638$. The data are compiled from the PETDB database (<http://petdb.ldeo.columbia.edu>). (b) $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\varepsilon(\text{Nd})$ for MORBs compared with data for turbidites and other marine sediments (Ben Othman *et al.*, 1989; Hemming and McLennan, 2001). This illustrates the complementary nature of continent-derived sediments and MORB expected from the relationships shown in Figure 3.

isotopes in all three ocean basins (Figure 6(b)). This parameter is a measure of the radiogenic additions to $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios during Earth's history; it is calculated by subtracting the primordial (initial) isotope ratios from the measured values. The primordial ratios are those found in the Th–U-free sulfide phase (troilite) of iron meteorites. Thus, the radiogenic $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ ratio is defined as

$$\frac{^{208}\text{Pb}^*}{^{206}\text{Pb}^*} = \frac{^{208}\text{Pb}/^{204}\text{Pb} - (^{208}\text{Pb}/^{204}\text{Pb})_{\text{init}}}{^{206}\text{Pb}/^{204}\text{Pb} - (^{206}\text{Pb}/^{204}\text{Pb})_{\text{init}}} \quad (11)$$

Unlike $^{208}\text{Pb}/^{204}\text{Pb}$ or $^{206}\text{Pb}/^{204}\text{Pb}$, which depend on Th/Pb and U/Pb, respectively, $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ reflects the Th/U ratio integrated over the history of the Earth. The existence of global correlations between neodymium, strontium, and hafnium isotope ratios and $^{208}\text{Pb}^*/^{206}\text{Pb}^*$, and the absence of such global correlations with $^{208}\text{Pb}/^{204}\text{Pb}$ or $^{206}\text{Pb}/^{204}\text{Pb}$, shows that the elements neodymium, strontium, hafnium, thorium, and uranium behave

in a globally coherent fashion during crust–mantle differentiation, whereas lead deviates from this cohesion.

Figures 4–6 show systematic isotopic differences between MORB from different ocean basins, reflecting some very large scale isotopic heterogeneities in the source mantle of these basalts. Also, the ranges of $\varepsilon(\text{Nd})$ values present in a single ocean basin are quite large. For example, the range of neodymium isotope ratios in Atlantic MORB ($\sim 10\varepsilon(\text{Nd})$ units) is somewhat smaller than the respective range of Atlantic OIB values of about $^{14}\varepsilon(\text{Nd})$ units (see Section 2.03.5 on OIB), but this difference does not justify calling Atlantic MORB “isotopically homogeneous.” This heterogeneity contradicts the widespread notion that the MORB-source mantle reservoir is isotopically nearly uniform, a myth that has persisted through many repetitions in the literature. One can just as easily argue that there is no such thing as a typical “normal”

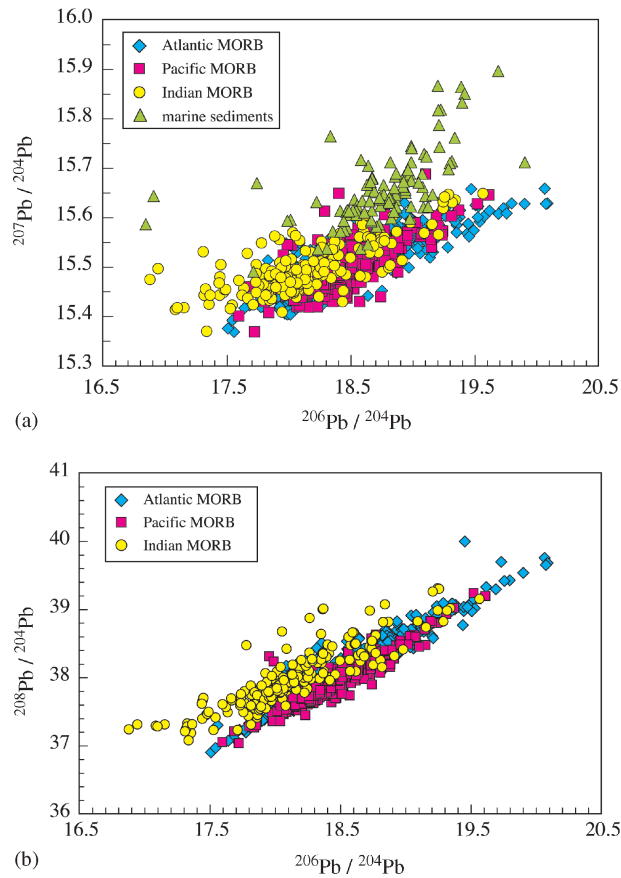


Figure 5 (a) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for MORB from three major ocean basins and marine sediments. (b) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for MORB from three major ocean basins. Sediments are not plotted because of strong overlap with the basalt data. For data sources see Figure 4.

(usually called N-type) MORB composition. In particular, the $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ ratios of Indian Ocean MORB show very little overlap with Pacific MORB (but both populations overlap strongly with Atlantic MORB). These very large scale regional “domains” were first recognized by Dupré and Allègre (1983) and named DUPAL anomaly by Hart (1984).

The boundary between the Indian Ocean and Pacific Ocean geochemical domains coincides with the Australian–Antarctic Discordance (AAD) located between Australia and Antarctica, an unusually deep ridge segment with several unusual physical and physiographic characteristics. The geochemical transition in Sr–Nd–Hf–Pb isotope space across the AAD is remarkably sharp (Klein *et al.*, 1988; Pyle *et al.*, 1992; Kempton *et al.*, 2002), and it is evident that very little mixing has occurred between these domains. The isotopic differences observed cannot be generated overnight. Rehkämper and Hofmann (1997), using lead isotopes, have estimated that the specific isotopic characteristics of the Indian Ocean MORB must be at least 1.5 Ga old. An important conclusion from this is that convective

stirring of the mantle can be remarkably *ineffective* in mixing very large scale domains in the upper mantle (see Chapter 2.12).

When we further consider the fact that the present-day ocean ridge system, though globe encircling, samples only a geographically limited portion of the total, present-day mantle, it is clear that we must abandon the notion that we can characterize the isotopic composition of the depleted mantle reservoir by a single value of any isotopic parameter. What remains is a much broader, nevertheless limited, range of compositions, which, on average, differ from other types of oceanic basalts to be discussed further below. The lessons drawn from Section 2.03.2 (local and regional equilibrium) merely add an additional cautionary note: although it is possible to map the world’s ocean ridge system using isotopic compositions of MORB, we cannot be sure how accurately these MORB compositions represent the underlying mantle. The differences between ocean basins are particularly obvious in the $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams, where Indian Ocean MORBs have consistently higher $^{208}\text{Pb}/^{204}\text{Pb}$ ratios than Pacific Ocean

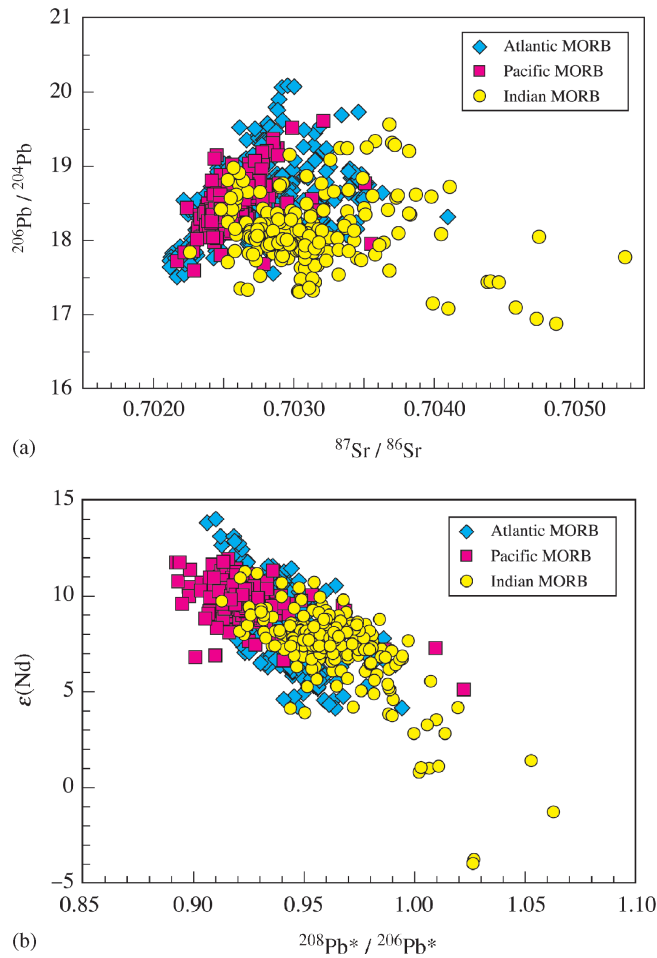


Figure 6 (a) $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for MORB from three major ocean basins. In contrast with the Sr–Nd and the Pb–Pb diagrams (Figures 4 and 5), the $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ data correlate well only for Pacific MORB and not at all for Indian MORB. This indicates some anomalous behavior of the U–Pb decay system during global differentiation. For data sources see Figure 4. (b) $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ versus $\epsilon(\text{Nd})$ for MORB from three major ocean basins. The overall correlation is similar to the Sr–Nd correlation shown in Figure 4(a). This indicates that the Th/U ratios, which control $^{208}\text{Pb}^*/^{206}\text{Pb}^*$, do correlate with Sm/Nd (and Rb/Sr) ratios during mantle differentiation. Taken together, (a) and (b) identify Pb as the element displaying anomalous behavior.

MORBs. Diagrams involving neodymium isotopes show more overlap, but Indian Ocean MORBs have many $\epsilon(\text{Nd})$ values lower than any sample from the Pacific Ocean.

An intermediate scale of isotopic variations is shown in Figures 7 and 8, using basalts from the Mid-Atlantic Ridge (MAR). The isotope ratios of strontium and neodymium (averaged over 1° intervals for clarity) vary along the ridge with obvious maxima and minima near the oceanic islands of Iceland, the Azores, and the Bouvet triple junction, and with large scale, relatively smooth gradients in the isotope ratios, e.g., between 20°S and 38°S . In general, the equatorial region between 30°S and 30°N is characterized by much lower strontium isotope ratios than the ridge segments to the north and the south. Some of this variation may be related to the vicinity of the mantle hotspots of

Iceland, the Azores, or Bouvet, and the literature contains a continuing debate over the subject of “plume–asthenosphere interaction.” Some authors argue the case where excess, enriched plume material spreads into the asthenosphere and mixes with depleted asthenospheric material to produce the geochemical gradients observed (e.g., Hart *et al.*, 1973; Schilling, 1973). Others argue that the hotspot or plume is internally heterogeneous and contains depleted, MORB-like material, which remains behind during normal plume-generated volcanism, spreads out in the asthenosphere, and becomes part of the asthenospheric mantle (Phipps Morgan and Morgan, 1998; Phipps Morgan, 1999). Irrespective of the specific process of plume–ridge interaction, the existence of compositional gradients up to $\sim 2,000$ km long implies some rather large-scale mixing processes,

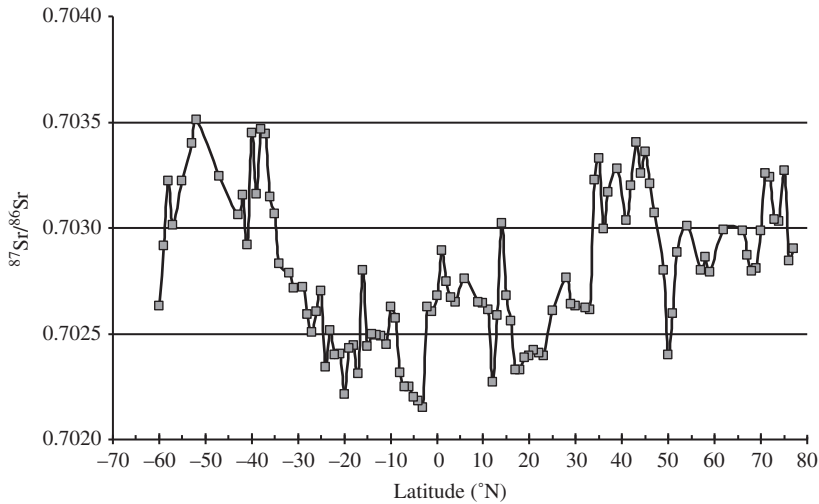


Figure 7 $^{87}\text{Sr}/^{86}\text{Sr}$ versus latitude variations in MORB along the Mid-Atlantic Ridge. The isotope data have been averaged by 1° intervals. For data sources see Figure 4.

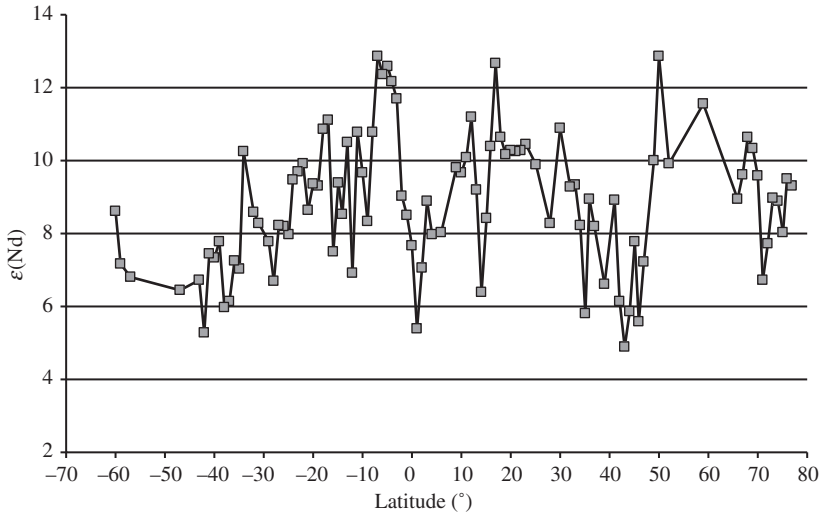


Figure 8 $\epsilon(\text{Nd})$ versus latitude variations in MORB along the MAR. The isotope data have been averaged by 1° intervals. For data sources see Figure 4.

quite distinct from the sharpness of the compositional boundary seen at the AAD.

Isotopic heterogeneities are also observed on much smaller scales than so far discussed. For example, the region around 14°N on the MAR shows a sharp “spike” in neodymium and strontium isotope ratios (see Figures 7 and 8) with an amplitude in $\epsilon(\text{Nd})$ nearly as large as that of the entire Atlantic MORB variation, even though there is no obvious depth anomaly or other physiographic evidence for the possible presence of a mantle plume.

Finally, work on melt inclusions from phenocrysts has recently shown that sometimes extreme isotopic and trace-element heterogeneities exist

within single hand specimens from mid-ocean ridges. Initially, the extreme chemical heterogeneities found in such samples were ascribed to the effects of progressive fractional melting of initially uniform source rocks (Sobolev and Shimizu, 1993), but recent Pb-isotope analyses of melt inclusions from a single MORB sample have shown a large range of isotopic compositions that require a locally heterogeneous source (Shimizu *et al.*, 2003). This phenomenon had previously also been observed in some OIBs (Saal *et al.*, 1998; Sobolev *et al.*, 2000), and future work must determine whether this is the exception rather than the rule. In any case, the normally observed local homogeneity of bulk basalt

samples may turn out to be the result of homogenization in magma chambers rather than melting of homogeneous sources.

In summary, it should be clear that the mantle that produces MORB is isotopically heterogeneous on all spatial scales ranging from the size of ocean basins down to kilometers or possibly meters. The often-invoked homogeneity of MORB and MORB sources is largely a myth, and the definition of “normal” or N-type MORB actually applies to the depleted end of the spectrum rather than average MORB. It would be best to abandon these obsolete concepts, but they are likely to persist for years to come. Any unbiased evaluation of the actual MORB isotope data shows unambiguously, e.g., that Indian Ocean MORBs differ substantially from Pacific Ocean MORBs, and that only about half of Atlantic MORB conform to what is commonly referred to as “N-type” with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios lower than 0.7028 and $\varepsilon(\text{Nd})$ values higher than +9. Many geochemists think that MORB samples with higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and lower $\varepsilon(\text{Nd})$ values do not represent normal upper mantle but are generated by contamination of the normally very depleted, and isotopically extreme, upper mantle with plume material derived from the deeper mantle. Perhaps this interpretation is correct, especially in the Atlantic Ocean, where there are several hotspots/plumes occurring near the MAR, but its automatic application to all enriched samples (such as those near 14° N on the MAR) invites circular reasoning and it can get in the way of an unbiased consideration of the actual data.

2.03.4.2 Osmium Isotopes

The Re–Os decay system is discussed separately, in part because there are far fewer osmium isotope data than Sr–Nd–Pb data. This is true because, until ~10 years ago, osmium isotopes in silicate rocks were extraordinarily difficult to measure. The advent of negative-ion thermal ionization mass spectrometry has decisively changed this (Creaser *et al.*, 1991; Völkening *et al.*, 1991), and subsequently the number of publications providing osmium isotope data has increased dramatically.

Osmium is of great interest to mantle geochemists because, in contrast with the geochemical properties of strontium, neodymium, hafnium, and lead, all of which are incompatible elements, osmium is a compatible element in most mantle melting processes, so that it generally remains in the mantle, whereas the much more incompatible rhenium is extracted and enriched in the melt and ultimately in the crust. This system therefore provides information that is different from, and complementary to, what we can learn from

strontium, neodymium, hafnium, and lead isotopes. However, at present there are still significant obstacles to the full use and understanding of osmium geochemistry. There are primarily three reasons for this:

(i) Osmium is present in oceanic basalts usually at sub-ppb concentration levels. Especially, in low-magnesium basalts, the concentrations can approach low ppt levels. The problem posed by this is that crustal rocks and seawater can have $^{187}\text{Os}/^{188}\text{Os}$ ratios 10 times higher than the (initial) ratios in mantle-derived melts. Thus, incorporation of small amounts of seawater-altered material in a submarine magma chamber may significantly increase the $^{187}\text{Os}/^{188}\text{Os}$ ratio of the magma. Indeed, many low-magnesium, moderately to highly differentiated oceanic basalts have highly radiogenic osmium, and it is not easy to know which basalts are unaffected by this contamination.

(ii) The geochemistry of osmium is less well understood than other decay systems, because much of the osmium resides in non-silicate phases such as sulfides, chromite and (possibly) metallic phases, and these phases can be very heterogeneously distributed in mantle rocks. This frequently leads to a “nugget” effect, meaning that a given sample powder is not necessarily representative of the system. Quite often, the reproducibility of concentration measurements of osmium and rhenium is quite poor by normal geochemical standards, with differences of several percent between duplicate analyses, and this may be caused either by intrinsic sample heterogeneity (“nugget effect”) or by incomplete equilibration of sample and spike during dissolution and osmium separation.

(iii) There are legitimate doubts whether the osmium-isotopic composition of oceanic basalts are ever identical to those of their mantle source rocks (Section 2.03.2.1).

The point (iii) above is illustrated in Figure 9, which shows osmium isotope ratios and osmium concentrations in abyssal peridotites and in MORB. This diagram shows two remarkable features: (i) The osmium isotope ratios of MORB and abyssal peridotites have very little overlap, the peridotites being systematically lower than those of seafloor basalts. (ii) The MORB data show a strong negative correlation between isotope ratios and osmium concentrations. These results suggest that the basalts may not be in isotopic equilibrium with their source rocks, but we have no proof of this, because we have no samples of specific source rocks for specific basalt samples. Also, the total number of samples represented in Figure 9 is rather small. Nevertheless, the apparently systematically higher $^{187}\text{Os}/^{188}\text{Os}$ ratios of the basalts compared with the peridotites seem to indicate that unradiogenic

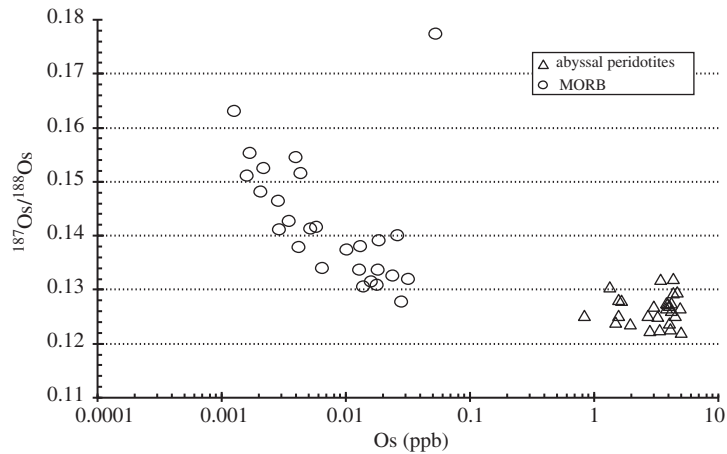


Figure 9 Osmium isotope ratios in MORB and abyssal peridotites. This diagram shows that osmium is generally compatible in peridotites during MORB melting. The systematic differences in $^{187}\text{Os}/^{188}\text{Os}$ ratios between MORB and peridotites suggest that the melts may not be in isotopic equilibrium with their residual peridotite (sources Martin, 1991; Roy-Barman and Allègre, 1994; Snow and Reisberg, 1995; Schiano *et al.*, 1997; Brandon *et al.*, 2000).

portions of the source peridotites did not contribute to, or react with, the melt. The negative correlation displayed by the MORB data may mean that essentially *all* the melts are contaminated by seawater-derived osmium and that the relative contribution of the contaminating osmium to the measured isotopic compositions is inversely correlated with the osmium concentration of the sample. However, the MORB samples also show a strong positive correlation between $^{187}\text{Os}/^{188}\text{Os}$ and Re/Os (not shown). Therefore, it is also possible that MORB osmium is derived from heterogeneous sources in such a way that low-osmium, high- Re/Os samples are derived from high- Re/Os portions of the sources (such as pyroxenitic veins), whereas high-osmium, low- Re/Os samples are derived from the peridotitic or even harzburgitic matrix.

To avoid the risk of contamination by seawater, either through direct contamination of the samples or contamination of the magma by assimilation of contaminated material, many authors disregard samples with very low osmium concentrations. Unfortunately, this approach does not remove the inherent ambiguity of interpretation, and it may simply bias the sampling. What is clearly needed are independent measures of very low levels of magma chamber and sample contamination.

2.03.4.3 Trace Elements

The general model of crust–mantle differentiation predicts that, after crust formation, the residual mantle should be depleted in incompatible elements. Melts from this depleted mantle may be absolutely enriched but should still show a

relative depletion of highly incompatible elements relative to moderately incompatible elements, as illustrated in Figure 2. Here I examine actual trace-element data of real MORB and their variability. An inherent difficulty is that trace-element abundances in a basalt depend on several factors, namely, the source composition, the degree, and mechanism of melting and melt extraction, the subsequent degree of magmatic fractionation by crystallization, and finally, on possible contamination of the magma during this fractionation process by a process called AFC (assimilation with fractional crystallization). This inherent ambiguity resulted in a long-standing debate about the relative importance of these two aspects. O'Hara, in particular, championed the case of fractional crystallization and AFC processes in producing enrichment and variability of oceanic basalts (e.g., O'Hara, 1977; O'Hara and Mathews, 1981). In contrast, Schilling and co-workers argued that variations in trace-element abundances, and in particular ratios of such abundances, are strongly controlled by source compositions. They documented several cases where REE patterns vary systematically along mid-ocean ridge segments, and they mapped such variations specifically in the vicinity of hotspots, which they interpreted as the products of mantle plumes relatively enriched in incompatible elements. As was the case for the isotopic variations, they interpreted the trace-element variations in terms of mixing of relatively enriched plume material with relatively depleted upper mantle, the asthenospheric mantle (Schilling, 1973; White and Schilling, 1978). Figure 10 shows a compilation of La/Sm ratios (normalized to primitive mantle values) of basalts

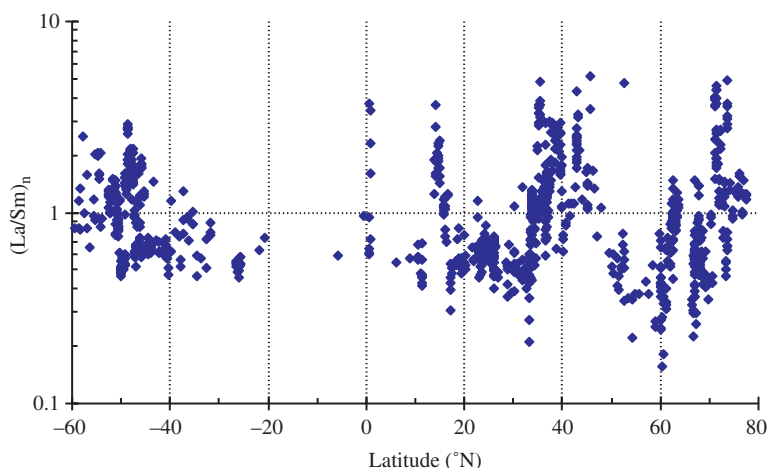


Figure 10 La/Sm ratios in MORB (not smoothed), normalized to primitive-mantle values, as a function of latitude along the MAR.

dredged from the MAR. This parameter has been used extensively by Schilling and co-workers as a measure of source depletion or enrichment, where they considered samples with $(\text{La}/\text{Sm})_n < 1.0$ as normal or “N-type” MORB derived from depleted sources with similar or even lower La/Sm ratios. As was found for the isotope ratios, only two-thirds of the MAR shows “typical” or “normal” La/Sm ratios lower than unity. In general, the pattern resembles that of the isotope variations, especially in the North Atlantic, where the coverage for both parameters is extensive. Thus, high La/Sm and $^{87}\text{Sr}/^{86}\text{Sr}$ values are found near the hotspots of Iceland and the Azores, between 45°S and 50°S , 14°N , and 43°N . Because of these correlations, the interpretation that the trace-element variations are primarily caused by source variations has been widely accepted. Important confirmation for this has come from the study of Johnson *et al.* (1990). They showed that peridotites dredged from near-hotspot locations along the ridge are more depleted in incompatible elements than peridotites from normal ridge segments. This implies that they have been subjected to higher degrees of melting (and loss of that melt). In spite of this higher degree of melting, the near-hotspot lavas are more enriched in incompatible elements, and therefore their initial sources must also have been more enriched.

Trace-element abundance patterns, often called “spidergrams,” of MORB are shown in Figure 11 (“spidergram” is a somewhat inappropriate but a convenient term coined by R. N. Thompson (Thompson *et al.*, 1984), presumably because of a perceived resemblance of these patterns to spider webs, although the resemblance is tenuous at best). The data chosen for this plot are taken from le Roux *et al.* (2002) for MORB glasses from the MAR (40 – 55°S), which encompasses

both depleted regions and enriched regions resulting from ridge–hotspot interactions. The patterns are highly divergent for the most incompatible elements, but they converge and become more parallel for the more compatible elements. This phenomenon is caused by the fact that variations in melt fractions produce the largest concentration variations in the most highly incompatible elements in both melts and their residues. This is a simple consequence of Equation (3), which states that for elements with very small values of D the concentration in the melt is inversely proportional to the melt fraction. At the other end of the spectrum, compatible elements, those with D values close to unity or greater, become effectively buffered by the melting assemblage. For an element having $D \gg F$, Equation (2) reduces to

$$C_1 \approx \frac{C_0}{D} \quad (12)$$

and for $D = 1$, it reduces to

$$C_1 = C_0 \quad (13)$$

In both cases, the concentration in the melt becomes effectively buffered by the residual mineral assemblage until the degree of melting is large enough, so that the specific mineral responsible for the high value of D is exhausted. This buffering effect is displayed by the relatively low and uniform concentrations of scandium (Figure 11). It is caused by the persistence of residual clinopyroxene during MORB melting.

These relationships lead to the simple consequence that the variability of element concentrations in large data sets of basalt analyses are related to the bulk partition coefficients of these elements (Hofmann, 1988; Dupré *et al.*, 1994). This can be verified by considering a set of trace

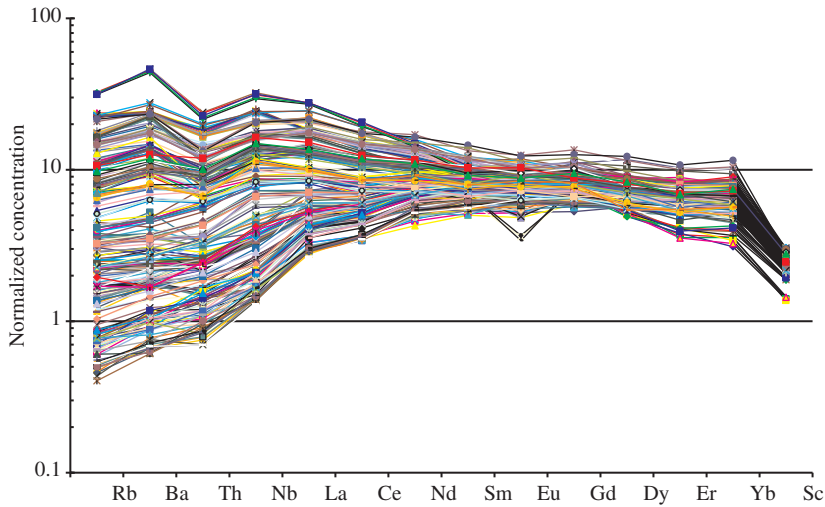


Figure 11 Trace element abundances of 250 MORB between 40° S and 55° S along the Mid-Atlantic Ridge. Each sample is represented by one line. The data are normalized to primitive-mantle abundances of (McDonough and Sun, 1995) and shown in the order of mantle compatibility. This type of diagram is popularly known as “spidergram.” The data have been filtered to remove the most highly fractionated samples containing less than 5% MgO (source le Roux *et al.*, 2002).

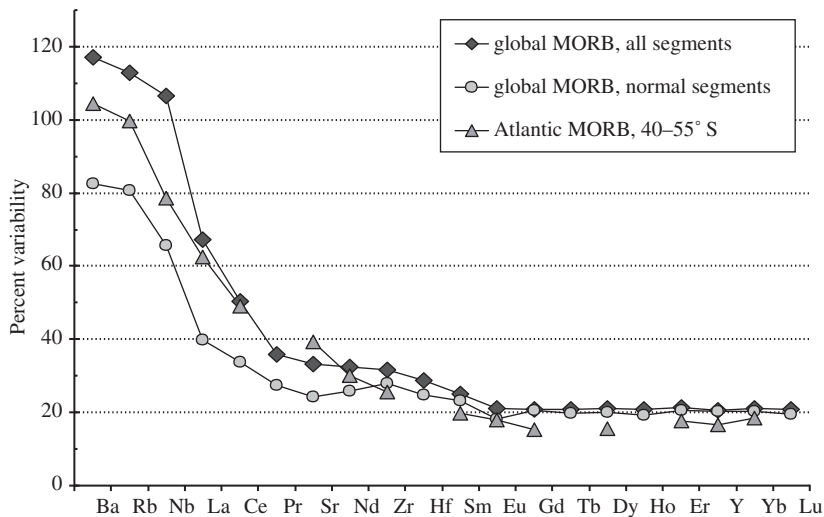


Figure 12 Variability of trace element concentrations in MORB, expressed as $100 \times \text{standard deviation}/\text{mean concentration}$. The data for “Global MORB” are from the PETDB compilation of (Su, 2002). “All segments” refers to ~ 250 ridge segments from all oceans. “Normal segments” refers to ~ 62 ridge segments that are considered not to represent any sort of “anomalous” ridges, because those might be affected by such factors as vicinity to mantle plumes or subduction of sediments (e.g., back-arc basins and the Southern Chile Ridge). The Atlantic MORB, 40–55° S, from which samples with less than 5% MgO have been removed (source le Roux *et al.*, 2002).

elements for which enough experimental data are available to be confident of the relative solid–melt partition coefficients, namely, the REE. These coefficients decrease monotonically from the heavy to light REEs, essentially because the ionic radii increase monotonically from heavy to light REEs (with the possible exception of europium, which has special properties because of its variable valence). Figure 12 shows three

plots of variability of REEs and other trace elements in MORB as a function of mantle compatibility of the elements listed. Variability is defined as the standard deviation of the measured concentrations divided by the respective mean value. Compatibilities of elements other than the REEs are estimated from global correlations of trace-element ratios with absolute abundances as derived from simple partial melting

theory (Hofmann *et al.*, 1986; Hofmann, 1988) (see also Figures 17 and 18). Two sets of data are from a new, ridge segment-by-segment compilation made by Su (2002) using the MORB database <http://petdb.ldeo.columbia.edu>. The third represents data for 270 MORB glasses from the South Atlantic ridge (40–55° S) (le Roux *et al.*, 2002). The qualitative similarity of the three plots is striking. It indicates that the order of variabilities is a robust feature. For example, the variabilities of the heavy REEs (europium to lutetium) are all essentially identical at 20% in all three plots. For the light REEs, the variability increases monotonically from europium to lanthanum, consistent with their decreasing partition coefficients in all mantle minerals. As expected, variabilities are greatest for the very highly incompatible elements (VICES) niobium, rubidium, and barium. The same is true for thorium and uranium in South Atlantic MORBs (le Roux *et al.*, 2002), which are not shown here because their averages and standard deviations were not compiled by Su (2002). All of this is consistent with the enrichment pattern in the continental crust (Figure 2), which shows the greatest enrichments for barium, rubidium, thorium, and uranium in the continental crust, as well as monotonically decreasing crustal abundances for the REEs from lanthanum to lutetium, with a characteristic flattening from europium to lutetium. Obvious exceptions to this general consistency are the elements niobium and lead. These will be discussed separately below.

Some additional lessons can be learned from Figure 12:

(i) The flattening of the heavy-REE variabilities in MORB are consistent with the flat heavy-REE patterns almost universally observed in MORB, and these are consistent with the flat pattern of HREE partition coefficients in clinopyroxene (see Chapter 2.09). This does not rule out some role of garnet during MORB melting, but it does probably rule out a major role of garnet.

(ii) Strontium, zirconium, and hafnium have very similar variabilities as the REEs neodymium and samarium. Again, this is consistent with the abundance patterns of MORB and with experimental data (Chapter 2.09). Overall, the somewhat tentative suggestion made by Hofmann (1988) regarding the relationship between concentration variability and degree of incompatibility, based on a very small set of MORB data, is strongly confirmed by the very large data sets now available. A note of caution is in order for strontium, which has a high partition coefficient in plagioclase. Thus, when oceanic basalts crystallize plagioclase, the REEs tend to increase in the residual melt, but strontium is removed from the melt by the plagioclase. The net effect of this is

that the overall variability of strontium is reduced in data sets incorporating plagioclase-fractionated samples. Such samples have been partly filtered out from the South Atlantic data set. This is the likely reason why strontium shows the greatest inconsistencies between the three plots shown in Figure 12.

2.03.4.4 N-MORB, E-MORB, T-MORB, and MORB Normalizations

It has become a widely used practice to define standard or average compositions of N-MORB, E-MORB, and T-MORB (for normal, enriched, and transitional MORB), and to use these as standards of comparison for ancient rocks found on land. In addition, many authors use “N-MORB” compositions as a normalization standard in trace-element abundance plots (“spidergrams”) instead of chondritic or primitive mantle. This practice should be discouraged, because trace-element abundances in MORB form a complete continuum of compositions ranging from very depleted to quite enriched and OIB-like. A plot of global La/Sm ratios (Figure 13) demonstrates this: there is no obvious typical value but a range of lanthanum concentrations covering two orders of magnitude and a range of La/Sm ratios covering about one-and-a-half orders of magnitude. Although the term N-MORB was intended to describe “normal” MORB, it actually refers to depleted MORB, often defined by $(La/Sm)_n < 1$. Thus, while these terms do serve some purpose for characterizing MORB compositions, there is no sound basis for using any of them as normalizing values to compare other rocks with “typical” MORB.

The strong positive correlation seen in Figure 13 is primarily the result of the fact that lanthanum is much more variable than samarium. Still, the overall coherence of this relationship is remarkable. It demonstrates that the variations of the REE abundances are not strongly controlled by variations in the degree of crystal fractionation of MORB magmas, because these would cause similar variability of lanthanum and samarium. Although this reasoning is partly circular because highly fractionated samples containing less than 6% MgO have been eliminated, the total number of such samples in this population of ~2,000 is less than 100. Thus, it is clear that the relationship is primarily controlled either by source or by partial melting effects. Figure 14 shows that the La/Sm ratios are also negatively correlated with $^{143}\text{Nd}/^{144}\text{Nd}$. Because this isotope ratio is a function of source Sm/Nd (and time), and neodymium is intermediate in bulk partition coefficient between lanthanum and samarium, such a negative correlation is expected if the

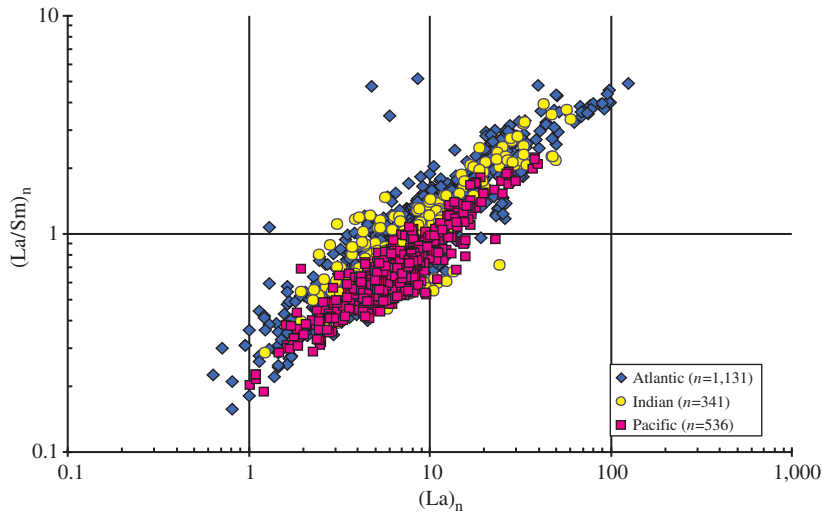


Figure 13 Primitive-mantle normalized La/Sm versus La for MORB from three Ocean basins. Numbers in parentheses refer to the number of samples from each ocean basin. Lanthanum concentrations vary by about two orders of magnitude; La/Sm varies by more than one order of magnitude. Data were extracted from PETDB.

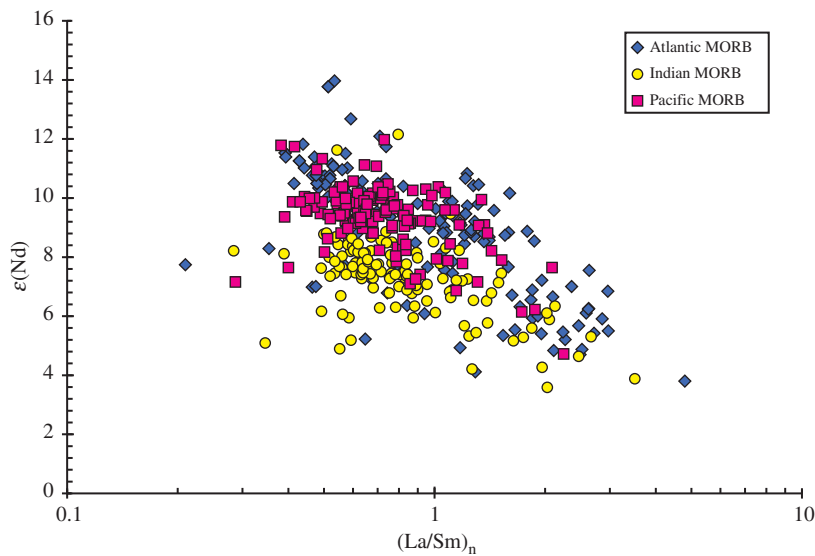


Figure 14 Primitive-mantle normalized La/Sm versus $^{143}\text{Nd}/^{144}\text{Nd}$ for MORB from three ocean basins. The (weak but significant) negative correlation is consistent with the inference that the variations in La/Sm in the basalts are to a significant part inherited from their mantle sources.

variability of the REE abundances is (at least in part) inherited from the source. Thus, while it would be perfectly possible to generate the relationship seen in Figure 13 purely by variations in partial melting, we can be confident that La/Sm ratios (and other highly incompatible element ratios) do track mantle source variations, as was shown by Schilling many years ago. It is important to realize, however, that such differences in source compositions were originally also produced by melting. These sources

are simply the residues of earlier melting events during previous episodes of (continental or oceanic) crust formation.

2.03.4.5 Summary of MORB and MORB-source Compositions

Klein and Langmuir (1987), in a classic paper, have shown that the element sodium is almost uniquely suited for estimating the degree of melting required to produce MORBs from their

respective sources. This element is only slightly incompatible at low melt fractions produced at relatively high pressures. As a result, the extraction of the continental crust has reduced the sodium concentration of the residual mantle by no more than ~10% relative to the primitive-mantle value. We therefore know the approximate sodium concentration of all MORB sources. In contrast, this element behaves much more incompatibly during production of oceanic crust, where relatively high melt fractions at relatively low pressures produce ocean floor basalts. This allowed Klein and Langmuir to estimate effective melt fractions ranging from 8% to 20%, with an average of ~10%, from sodium concentrations in MORB. Once the melt fraction is known, the more highly incompatible-element concentrations of the MORB-source mantle can be estimated from the measured concentrations in MORB. For the highly incompatible elements, the source concentrations are therefore estimated at ~10% of their respective values in the basalts. This constitutes a significant revision of earlier thinking, which was derived from melting experiments and the assumption that essentially clinopyroxene-free harzburgites represent the typical MORB residue, and which led to melt fraction estimates of 20% and higher.

The compilation of extensive MORB data from all major ocean basins has shown that they comprise wide variations of trace-element and isotopic compositions and the widespread notion of great compositional uniformity of MORB is largely a myth. An exception to this may exist in helium-isotopic compositions; see Chapter 2.06. From the state of heterogeneity of the more refractory elements it is clear, however, that the apparently greater uniformity of helium compositions is not the result of mechanical mixing and stirring, because this process should homogenize all elements to a similar extent. Moreover, the isotope data of MORB from different ocean basins show that different regions of the upper mantle have not been effectively mixed in the recent geological past, where “recent” probably means approximately the last 10^9 yr.

The general, incompatible-element depleted nature of the majority of MORBs and their sources is well explained by the extraction of the continental crust. Nevertheless, the bulk continental crust and the bulk of the MORB sources are not *exact* chemical complements. Rather, the residual mantle has undergone additional differentiation, most likely involving the generation of OIBs and their subducted equivalents. In addition, there may be more subtle differentiation processes involving smaller-scale melt migration occurring in the upper mantle (Donnelly *et al.*, 2003). It is these additional differentiation processes that have

generated much of the heterogeneity observed in MORBs and their sources.

2.03.5 OCEAN ISLAND, PLATEAU, AND SEAMOUNT BASALTS

These basalts represent the oceanic subclass of so-called intraplate basalts, which also include continental varieties of flood and rift basalts. They will be collectively referred to as “OIB,” even though many of them are not found on actual oceanic islands either because they never rose above sea level or because they were formed on islands that have sunk below sea level. Continental and island arc basalts will not be discussed here, because at least some of them have clearly been contaminated by continental crust. Others may or may not originate in, or have been “contaminated” by, the subcontinental lithosphere. For this reason, they are not considered in the present chapter, which is concerned primarily with the chemistry of the sublithospheric mantle.

Geochemists have been particularly interested in OIB because their isotopic compositions tend to be systematically different from MORB, and this suggests that they come from systematically different places in the mantle (e.g., Hofmann *et al.*, 1978; Hofmann and Hart, 1978). Morgan’s mantle plume theory (Morgan, 1971) thus provided an attractive framework for interpreting these differences, though not quite in the manner originally envisioned by Morgan. He viewed the entire mantle as a single reservoir, in which plumes rise from a lower boundary layer that is not fundamentally different in composition from the upper mantle. Geochemists, on the other hand, saw plumes being formed in a fundamentally different, more primitive, less depleted, or enriched, deeper part of the mantle than MORB sources (e.g., Wasserburg and Depaolo, 1979). The debate about these issues continues to the present day, and some of the mantle models based on isotopic and trace-element characteristics will be discussed below.

2.03.5.1 Isotope Ratios of Strontium, Neodymium, Hafnium, and Lead and the Species of the Mantle Zoo

Radiogenic isotope ratios of OIB are shown on Figure 15. These diagrams display remarkably similar topologies as the respective MORB data shown in Figures 4–6. Strontium isotope ratios are negatively correlated with neodymium and hafnium isotopes, and correlations between strontium, neodymium, and hafnium isotopes and lead

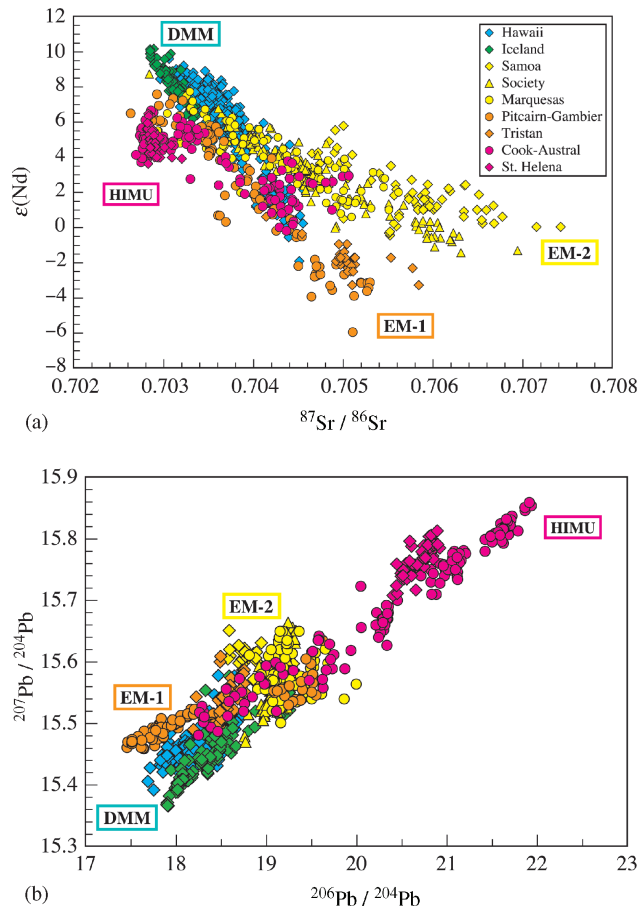


Figure 15 (a) $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\epsilon(\text{Nd})$ for OIB (excluding island arcs). The islands or island groups selected are chosen to represent extreme isotopic compositions in isotope diagrams. They are the “type localities” for HIMU (Cook-Austral Islands and St. Helena), EM-1 (Pitcairn-Gambier and Tristan), EM-2 (Society Islands, Samoa, Marquesas), and PREMA (Hawaiian Islands and Iceland). See text for explanations of the acronyms. (b) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for the same OIB as plotted in (a). Note that the $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of St. Helena and Cook-Australs are similar but not identical, whereas they overlap completely in the other isotope diagrams. (c) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for the same OIB as plotted in (a). (d) $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for the same OIB as plotted in (a). Note that correlations are either absent (e.g., for the EM-2 basalts from Samoa, the Society Islands and Marquesas) or point in rather different directions, a situation that is similar to the MORB data (Figure 6(a)). (e) $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ versus $\epsilon(\text{Nd})$ for the same OIB as plotted in (a). Essentially all island groups display significant negative correlations, again roughly analogous to the MORB data. Data were assembled from the GEOROC database (<http://georoc.mpch-mainz.gwdg.de>).

isotopes are confined to $^{208}\text{Pb}^*/^{206}\text{Pb}^*$, and the ranges of isotope ratios are even greater (although not dramatically so) for OIBs than MORBs. There is one important difference, however, namely, a significant shift in all of these ratios between MORBs and OIBs. To be sure, there is extensive overlap between the two populations, but OIBs are systematically more radiogenic in strontium and less radiogenic in neodymium and hafnium isotopes. In lead isotopes, OIBs overlap the MORB field completely but extend to more extreme values in $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$. As was true for MORBs, OIB isotopic composition can be “mapped,” and certain oceanic islands or island groups can be

characterized by specific isotopic characteristics. Recognition of this feature has led to the well-known concept of end-member compositions or “mantle components” initially identified by White (1985) and subsequently labeled HIMU, PREMA, EM-1, and EM-2 by Zindler and Hart (1986). These acronyms refer to mantle sources characterized by high μ values (HIMU; $\mu = (^{238}\text{U}/^{204}\text{Pb})_{t=0}$), “prevalent mantle” (PREMA), “enriched mantle-1” (EM-1), and “enriched mantle-2” (EM-2). “PREMA” has, in recent years, fallen into disuse. It has been replaced by three new terms, namely, “FOZO” (for “focal zone,” Hart *et al.* (1992)), “C” (for “common” component, Hanan and Graham (1996)), or “PHEM”

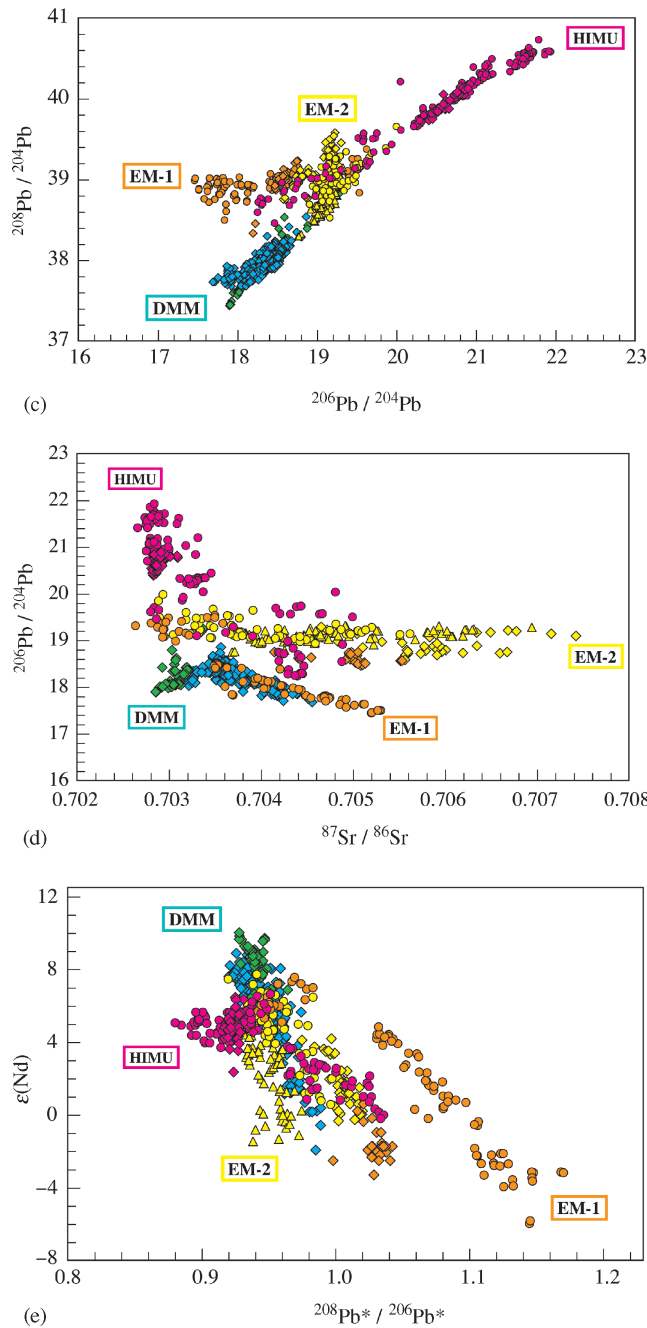


Figure 15 (continued).

(for “primitive helium mantle,” Farley *et al.* (1992)), which differ from each other only in detail, if at all. In contrast with the illustration chosen by Hofmann (1997), which used color coding to illustrate how the isotopic characteristics of, e.g., extreme HIMU samples appear in different isotope diagrams, irrespective of their geographic location, here I use the more conventional representation of identifying “type localities” of the various “species” of this mantle isotope zoo.

Two extreme notions about the meaning of these components or end members (sometimes also called “flavors”) can be found in the literature. One holds that the extreme isotopic end members of these exist as identifiable “species,” which may occupy separate volumes or “reservoirs” in the mantle. In this view, the intermediate compositions found in most oceanic basalts are generated by instantaneous mixing of these species during melting and emplacement of OIBs. The other notion considers them to be merely extremes of a

continuum of isotopic compositions existing in mantle rocks.

Apparent support for the “species” hypothesis is provided by the observation that the isotopically extreme compositions can be found in more than a single ocean island or island group, namely, Austral Islands and St. Helena for HIMU, Pitcairn Island and Walvis-Ridge-Tristan Island for EM-1, and Society Islands and Samoa for EM-2 (Hofmann, 1997). Nevertheless, it seems to be geologically implausible that mantle differentiation, by whatever mechanism, would consistently produce just four (or five, when the “depleted MORB mantle” DMM (Zindler and Hart, 1986) is included) species of essentially identical ages, which would then be remixed in variable proportions. It is more consistent with current understanding of mantle dynamics to assume that the mantle is differentiated and remixed continuously through time. Moreover, we can be reasonably certain that a great many rock types with differing chemistries are continuously introduced into the mantle by subduction and are thereafter subjected to variable degrees of mechanical stirring and mixing. These rock types include ordinary peridotites, harzburgites, gabbros, tholeiitic and alkali basalts, terrigenous sediments, and pelagic sediments. Most of these rock types have been affected by seafloor hydrothermal and low-temperature alteration, submarine “weathering,” and subduction-related alteration and metasomatism. Finally, it is obvious that, overall, the OIB isotopic data constitute a continuously heterogeneous spectrum of compositions, just as is the case for MORB compositions.

In spite of the above uncertainties about the meaning of mantle components and reservoirs, it is clear that the extreme isotopic compositions represent melting products of sources subjected to some sort of ancient and comparatively extreme chemical differentiation. Because of this, they probably offer the best opportunity to identify the specific character of the types of mantle differentiation also found in other OIBs of less extreme isotopic composition. For example, the highly radiogenic lead isotope ratios of HIMU samples require mantle sources with exceptionally high U/Pb and Th/Pb ratios. At the same time, HIMU samples are among those OIBs with the least radiogenic strontium, requiring source-Rb/Sr ratios nearly as low as those of the more depleted MORBs. Following the currently popular hypothesis of Hofmann and White (1980, 1982); Chase, 1981, it is widely thought that such rocks are examples of recycled oceanic crust, which has lost alkalis and lead during alteration and subduction (Chauvel *et al.*, 1992). However, there are other possibilities. For example, the characteristics of HIMU sources might also be explained by

enriching oceanic lithosphere “metasomatically” by the infiltration of low-degree partial melts, which have high U/Pb and Th/Pb ratios because of magmatic enrichment of uranium and thorium over lead (Sun and McDonough, 1989). The Rb/Sr ratios of these sources should then also be elevated over those of ordinary MORB sources, but this enrichment would be insufficient to significantly raise $^{87}\text{Sr}/^{86}\text{Sr}$ ratios because the initial Rb/Sr of these sources was well below the level where any significant growth of radiogenic ^{87}Sr could occur. Thus, instead of recycling more or less ordinary oceanic crust the enrichment mechanism would involve recycling of magmatically enriched oceanic lithosphere.

The origin of EM-type OIBs is also controversial. Hawkesworth *et al.* (1979) had postulated a sedimentary component in the source of the island of Sao Miguel (Azores), and White and Hofmann (1982) argued that EM-2 basalt sources from Samoa and the Society Islands are formed by recycled ocean crust with an addition of the small amount of subducted sediment. This interpretation was based on the high $^{87}\text{Sr}/^{86}\text{Sr}$ and high $^{207}\text{Pb}/^{204}\text{Pb}$ (for given $^{206}\text{Pb}/^{204}\text{Pb}$) ratios of EM-2 basalts, which resemble the isotopic signatures of terrigenous sediments. However, this interpretation continues to be questioned on the grounds that there are isotopic or trace-element parameters that appear inconsistent with this interpretation (e.g., Widom and Shirey, 1996). Workman *et al.* (2003) argue that the geochemistry of Samoa is best explained by recycling of melt-impregnated oceanic lithosphere, because their Samoa samples do not show the trace-element fingerprints characteristic of other EM-2 suites (see discussion of neodymium below). In addition, it has been argued that the sedimentary signature is present, but it is not part of a deep-seated mantle plume but is introduced as a sedimentary contaminant into plume-derived magmas during their passage through the shallow mantle or crust (Bohrson and Reid, 1995).

The origin of the EM-1 flavor is similarly controversial. Its distinctive features include very low $^{143}\text{Nd}/^{144}\text{Nd}$ coupled with relatively low $^{87}\text{Sr}/^{86}\text{Sr}$, and very low $^{206}\text{Pb}/^{204}\text{Pb}$ coupled with relatively high $^{208}\text{Pb}/^{204}\text{Pb}$ (leading to high $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ values). The two leading contenders for the origin of this are (i) recycling of delaminated subcontinental lithosphere and (ii) recycling of subducted ancient pelagic sediment. The first hypothesis follows a model originally proposed by McKenzie and O’Nions (1983) to explain the origin of OIBs in general. The more specific model for deriving EM-1 type basalts from such a source was developed by Hawkesworth *et al.* (1986), Mahoney *et al.* (1991), and Milner and le Roex (1996). It is based on the observation that mantle xenoliths

from Precambrian shields display similar isotopic characteristics. The second hypothesis is based on the observation that many pelagic sediments are characterized by high Th/U and low (U,Th)/Pb ratios (Ben Othman *et al.*, 1989; Plank and Langmuir, 1998), and this will lead to relatively unradiogenic lead with high $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ ratios after passage of 1–2 Ga (Weaver, 1991; Chauvel *et al.*, 1992; Rehkämper and Hofmann, 1997; Eisele *et al.*, 2002). Additional support for this hypothesis has come from hafnium isotopes. Many (though not all) pelagic sediments have high Lu/Hf ratios (along with low Sm/Nd ratios), because they are depleted in detrital zircons, the major carrier of hafnium in sediments (Patchett *et al.*, 1984; Plank and Langmuir, 1998). This is expected to lead to relatively high $^{176}\text{Hf}/^{177}\text{Hf}$ ratios combined with low $^{143}\text{Nd}/^{144}\text{Nd}$ values, and these relationships have indeed been observed in lavas from Koolau volcano, Oahu (Hawaiian Islands) (Blichert-Toft *et al.*, 1999) and from Pitcairn (Eisele *et al.*, 2002). Gasperini *et al.* (2000) have proposed still another origin for EM-1 basalts from Sardinia, namely, recycling of gabbros derived from a subducted, ancient plume head.

Recycling of subducted ocean islands and oceanic plateaus was suggested by Hofmann (1989b) to explain not the extreme end-member compositions of the OIB source zoo, but the enrichments seen in the basalts forming the main “mantle array” of negatively correlated $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The $^{143}\text{Nd}/^{144}\text{Nd}$ values of many of these basalts (e.g., many Hawaiian basalts) are too low, and their $^{87}\text{Sr}/^{86}\text{Sr}$ values too high, for these OIBs to be explained by recycling of depleted oceanic crust. However, if the recycled material consists of either enriched MORB, tholeiitic or alkaline OIB, or basaltic oceanic plateau material, such a source will have the pre-enriched Rb/Sr and Nd/Sm ratios capable of producing the observed range of strontium- and neodymium-isotopic compositions of the main OIB isotope array.

Melt inclusions in olivine phenocrysts have been shown to preserve primary melt compositions, and these have revealed a startling degree of chemical and isotopic heterogeneity occurring in single-hand specimens and even in single olivine crystals (Sobolev and Shimizu, 1993; Sobolev, 1996; Saal *et al.*, 1998; Sobolev *et al.*, 2000; Hauri, 2002). These studies have demonstrated that rather extreme isotopic and chemical heterogeneities exist in the mantle on scales considerably smaller than the melting region of a single volcano, as discussed in Section 2.03.2.2 on “mesoscale” heterogeneities. One of these studies, in particular, demonstrated the geochemical fingerprint of recycled oceanic gabbros in melt inclusions from Mauna Loa Volcano, Hawaii

(Sobolev *et al.*, 2000). These rare melt inclusions have trace-element patterns that are very similar to those of oceanic and ophiolitic gabbros. They are characterized by very high Sr/Nd and low Th/Ba ratios that can be ascribed to cumulus plagioclase, which dominates the modes of many of these gabbros. Chemical and isotopic studies of melt inclusions therefore have great potential for unraveling the specific source materials found in oceanic basalts. These inclusions can preserve primary heterogeneities of the melts much better than the bulk melts do, because the latter go through magma chamber mixing processes that attenuate most of the primary melt features.

The origin of FOZO-C-PHEM-PREMA, simply referred to as “FOZO” hereafter, may be of farther-reaching consequence than any of the other isotope flavors, if the inference of (Hart *et al.*, 1992) is correct, namely, that it represents material from the lower mantle that is present as a mixing component in all deep-mantle plumes. The evidence for this is that samples from many individual OIB associations appear to form binary mixing arrays that radiate from this “focal zone” composition in various directions toward HIMU, EM-1, or EM-2. These relationships are shown in Figure 16. The FOZO composition is similar, but not identical, to DMM represented by MORB. It is

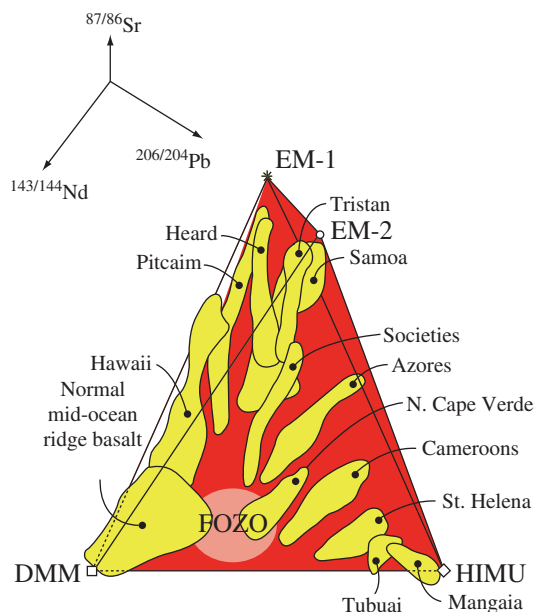


Figure 16 Three-dimensional projection of $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{206}\text{Pb}/^{204}\text{Pb}$ isotope arrays of a large number of OIB groups (after Hart *et al.*, 1992). Most of the individual arrays appear to radiate from a common region labeled “FOZO” (for focal zone) thought to represent the composition of the deep mantle. The diagram was kindly made available by S. R. Hart.

only moderately more radiogenic in strontium, less radiogenic in neodymium and hafnium, but significantly more radiogenic in lead isotopes than DMM. If plumes originate in the very deep mantle and rise from the core–mantle boundary, rather than from the 660 km seismic discontinuity, they are likely to entrain far more deep-mantle material than upper-mantle material (Griffiths and Campbell, 1990; Hart *et al.*, 1992). It should be noted, however, that the amount of entrained material in plumes is controversial, with some authors insisting that plumes contain very little entrained material (e.g., Farnetani *et al.*, 2002).

2.03.5.2 Trace Elements in OIB

Most OIBs are much more enriched in incompatible trace elements than most MORB, and there are two possible reasons for this: (i) their sources may be more enriched than MORB sources, and (ii) OIBs may be produced by generally lower degrees of partial melting than MORBs. Most likely, both factors contribute to this enrichment. Source enrichment (relative to MORB sources) is required because the isotopic compositions require relative enrichment of the more incompatible of the parent–daughter element ratios. Low degrees of melting are caused by the circumstance that most OIB are also within-plate basalts, so a rising mantle diapir undergoing partial melting encounters a relatively cold lithospheric lid, and melting is confined to low degrees and relatively deep levels. This is also the reason why most OIBs are alkali basalts rather than tholeiites, the predominant rock type in MORBs. Important exceptions to this rule are found primarily in OIBs erupted on or near-ocean ridges (such as on Iceland and the Galapagos Islands) and on hotspots created by especially strong plume flux, which generates tholeiites at relatively high melt fractions, such as in Hawaii.

The high incompatible-element enrichments found in most OIBs are coupled with comparatively low abundances of aluminum, ytterbium, and scandium. This effect is almost certainly caused by the persistence of garnet in the melt residue, which has high partition coefficients for these elements, and keeps them buffered at relatively low abundances. Haase (1996) has shown that Ce/Yb and Tb/Yb increase systematically with increasing age of the lithosphere through which OIBs are erupting. This effect is clearly related to the increasing influence of residual garnet, which is stable in peridotites at depths greater than ~80 km. Allègre *et al.* (1995) analyzed the trace-element abundances of oceanic basalts statistically and concluded that OIBs are more variable in isotopic compositions, but less variable in incompatible element abundances than

MORBs. However, their sampling was almost certainly too limited to properly evaluate the effect of lithospheric thickness on the abundances and their variability. In particular, their near-ridge sampling was confined to 11 samples from Iceland and 4 samples from Bouvet. The actual range of abundances of highly incompatible elements, such as thorium and uranium, from Iceland spans nearly three orders of magnitude. In contrast, ytterbium varies by only a factor of 10. This means that either the source of Iceland basalts is internally extremely heterogeneous, or the melt fractions are highly variable, or both. Because of this ambiguity, the REE abundance patterns and most of the moderately incompatible elements, sometimes called “MICE,” are actually not very useful to unravel the relative effects of partial melting and source heterogeneity.

The very highly incompatible elements, sometimes called “VICE,” are much less fractionated from each other in melts (through normal petrogenetic processes), but they are more severely fractionated in melt residues. This is the reason why their relative abundances vary in the mantle and why these variations can be traced by VICE ratios in basalts, which are in this respect similar to, though not as precise as, isotope ratios. VICE ratios thus enlarge the geochemical arsenal for determining mantle chemical heterogeneities and their origins. These differences are conventionally illustrated either by the “spidergrams” (primitive-mantle normalized element abundance diagrams), or by plotting trace-element abundance ratios.

Spidergrams have the advantage of representing a large number of trace element abundances of a given sample by a single line. However, they can be confusing because there are no standard rules about the specific sequence in which the elements are shown or about the normalizing abundances used. The (mis)use of N-MORB or E-MORBs as reference values for normalizations has already been discussed and discouraged in Section 2.03.4.4. However, there are other pitfalls to be aware of: One of the most widely used normalizations is that given by Sun and McDonough (1989), which uses primitive-mantle estimates for all elements *except* lead, the abundance of which is adjusted by a factor of 2.5, presumably in order to generate smoother abundance patterns in oceanic basalts. The great majority of authors using this normalization simply call this “primitive mantle” without any awareness of the fudge factor applied. Such *ad hoc* adjustments for esthetic reasons should be strongly discouraged. Spidergrams communicate their message most effectively if they are standardized as much as possible, i.e., if they use only one standard for normalization, namely primitive-mantle abundances, and if the sequence of elements used is

in the order of increasing compatibility (see also Hofmann, 1988). The methods for determining this order of incompatibility are addressed in the subsequent Section 2.03.5.2.1.

Spidergrams tend to carry a significant amount of redundant information, most of which is useful for determining the general level of incompatible-element enrichment, rather than specific information about the sources. Therefore, diagrams of critical trace-element (abundance) ratios can be very effective in focusing on specific source differences. Care should be taken to use ratios of elements with similar bulk partition coefficients during partial melting (or, more loosely speaking, similar incompatibilities). Otherwise, it may be difficult or impossible to separate source effects from melting effects. Some rather popular element pairs of mixed incompatibility, such as Zr/Nb, which are almost certainly fractionated at the relatively low melt fractions prevailing during intraplate melting, are often used in a particularly confusing manner. For example, in the popular plot of Zr/Nb versus La/Sm, the more incompatible element is placed in the numerator of one ratio (La/Sm) and in the denominator of the other (Zr/Nb). The result is a hyperbolic relationship that looks impressive, but carries little if any useful information other than showing that the more enriched rocks have high La/Sm and low Zr/Nb, and the more depleted rocks have low La/Sm and high Zr/Nb.

Trace-element ratios of similarly incompatible pairs, such as Th/U, Nb/U, Nb/La, Ba/Th, Sr/Nd, or Pb/Nd, tend to be more useful in identifying source differences, because they are fractionated relatively little during partial melting. Elements that appear to be diagnostic of distinctive source types in the mantle are niobium, tantalum, lead, and to a lesser extent strontium, barium, potassium, and rubidium. These will be discussed in connection with the presentation of specific "spidergrams in Section 2.03.5.2.2.

2.03.5.2.1 "Uniform" trace-element ratios

In order to use geochemical anomalies for tracing particular source compositions, it is necessary to establish "normal" behavior first. Throughout the 1980s, Hofmann, Jochum, and co-workers noticed a series of trace-element ratios that are globally more or less uniform in both MORBs and OIBs. For example, the elements barium, rubidium, and caesium, which vary by about three orders of magnitude in absolute abundances, have remarkably uniform relative abundances in many MORBs and OIBs (Hofmann and White, 1983). This became clear only when sufficiently high analytical precision (isotope dilution at the time) was applied to fresh

glassy samples. Hofmann and White (1983) argued that this uniformity must mean that the Ba/Rb and Rb/Cs ratios found in the basalts reflect the respective ratios in the source rocks. And because these ratios were so similar in highly depleted MORBs and in enriched OIBs, these authors concluded that these element ratios have not been affected by processes of global differentiation, and they therefore also reflect the composition of the primitive mantle. Similarly, Jochum *et al.* (1983) estimated the K/U ratio of the primitive mantle to be 1.27×10^4 , a value that became virtually canonical for 20 years, even though it was based on remarkably few measurements. Other such apparently uniform ratios were Sn/Sm and Sb/Pr (Jochum *et al.*, 1993; Jochum and Hofmann, 1994) and Sr/Nd (Sun and McDonough, 1989). Zr/Hf and Nb/Ta were also thought to be uniform (Jochum *et al.*, 1986), but recent analyses carried out at higher precision and on a greater variety of rock types have shown systematic variations of these ratios.

The above approach of determining primitive-mantle abundances from apparently globally unfractionated trace-element ratios was up-ended by the discovery that Nb/U and Ce/Pb are also rather uniform in MORBs and OIBs the world over, but these ratios are higher by factors of ~5–10 than the respective ratios in the continental crust (Hofmann *et al.*, 1986). This invalidated the assumption that primitive-mantle abundances could be obtained simply from MORB and OIB relations, because the continental crust contains such a large portion of the total terrestrial budget of highly incompatible elements. However, these new observations meant that niobium and lead could potentially be used as tracers for recycled continental material in oceanic basalts. In other words, while ratios such as Nb/U show only limited variation when comparing oceanic basalts as a function of enrichment or depletion on a global or local scale, this uniformity can be interpreted to mean that such a specific ratio is not significantly fractionated during partial melting. If this is true, then the variations that do exist may be used to identify differences in source composition.

Figure 17 shows updated versions of the Nb/U variation diagram introduced by Hofmann *et al.* (1986). It represents an attempt to determine which other highly incompatible trace element is globally most similar to niobium in terms bulk partition coefficient during partial melting. The form of the diagram was chosen because an element ratio will systematically increase as the melt fractions decrease and the absolute concentration of the elements increase. It is obvious that Nb/Th and Nb/La ratios vary systematically with niobium concentration, but Nb/U does not. Extending the comparison to other elements, such as the heavier REEs (not shown), simply increases the slopes of

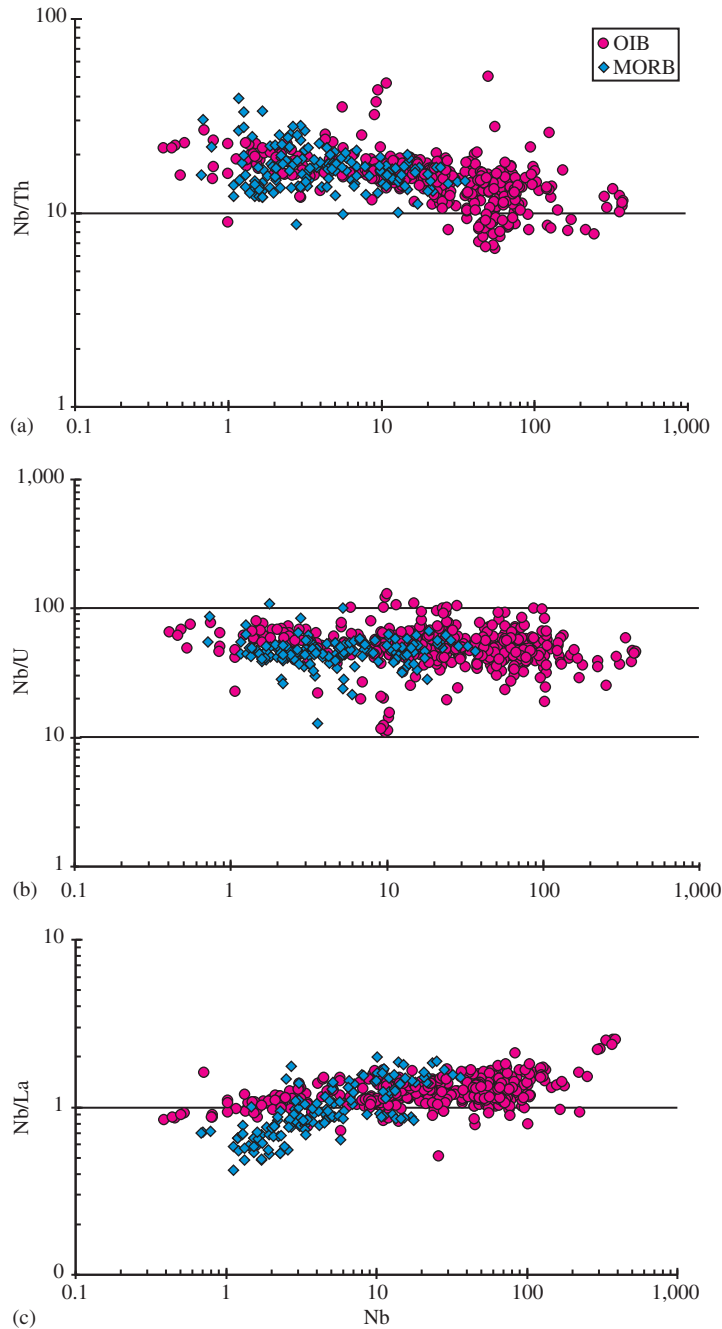


Figure 17 Nb/Th, Nb/U, and Nb/La ratios versus Nb concentrations of global MORB and (non-EM-2-type) OIBs (Hawaiian Isl., Iceland, Australs, Pitcairn, St. Helena, Canary, Bouvet, Gough Tristan, Ascension, Madeira, Fernando de Noronha, Cameroon Line Isl., Comores, Cape Verdes, Azores, Galapagos, Easter, Juan Fernandez, San Felix). The diagram shows a systematic increase of Nb/Th, approximately constant Nb/U, and systematic decrease of La/Nb as Nb concentrations increase over three orders of magnitude.

such plots. Thus, while Nb/U is certainly *not constant* in oceanic basalts, its variations are the lowest and the least systematic. To be sure, there is possible circularity in this argument, because it is possible, in principle, that enriched sources have systematically lower Nb/U ratios, which are systematically (and relatively precisely)

compensated by partition coefficients that are lower for niobium than uranium, thus systematically compensating the lower source ratio during partial melting. Such a compensating mechanism has been advocated by Sims and DePaolo (1997), who criticized the entire approach of Hofmann *et al.* (1986) on this basis. Such fortuitously

compensating circumstances, as postulated in the model of Sims and DePaolo (1997), may be *ad hoc* assumptions, but they are not *a priori* impossible.

The model of Hofmann *et al.* (1986) can be tested by examining more local associations of oceanic basalts characterized by large variations in melt fraction. Figure 18 shows Nb–Th–U–La–Nd relationships on Iceland, for volcanic rocks ranging from picrites to alkali basalts, as compiled from the recent literature. The representation differs from Figure 17, which has the advantage of showing the element ratios directly, but the disadvantage pointed out by Sims and DePaolo (1997) that the two variables used are not independent. The simple log–log plot of Figure 18 is less intuitively obvious but in this sense more rigorous. In this plot, a constant concentration ratio yields a slope of unity. The Th–Nb, U–Nb, La–Nb, and Nd–Nb plots show progressively increasing slopes, with the log U–log Nb and the log La–log Nb plots being closest to unity. The data from Iceland shown in Figure 18 are therefore consistent with the global data set shown in Figure 17. This confirms that uranium and niobium have nearly identical bulk partition coefficients during mantle melting in most oceanic environments.

The point of these arguments is not that an element ratio such as Nb/U in a melt will *always* reflect the source ratio very precisely. Rather, because of varying melting conditions, the specific partition coefficients of two such chemically different elements must vary *in detail*, as expected from the partitioning theory of Blundy and Wood (1994). The nephelinites and nepheline melilitites of the Honolulu Volcanic Series, which represent the post-erosional, highly alkalic phase

of Koolau Volcano, Oahu, Hawaii, may be an example where the partition coefficients of niobium and uranium are significantly different. These melts are highly enriched in trace elements and must have been formed by very small melt fractions from relatively depleted sources, as indicated by their nearly MORB-like strontium and neodymium isotopic compositions. Their Nb/U ratios average 27, whereas the alkali basalts average Nb/U = 44 (Yang *et al.*, 2003). This may indicate that under melting conditions of very low melt fractions, Nb is significantly more compatible than uranium, and the relationships that are valid for basalts cannot necessarily be extended to more exotic rock types such as nephelinite.

In general, the contrast between Nb/U in most OIBs and MORBs and those in sediments, island arcs and continental rocks is so large that it appears to provide an excellent tracer of recycled continental material in oceanic basalts. A significant obstacle in applying this tracer is the lack of high-quality Nb–U data, partly because of analytical limitations and partly because of sample alteration. The latter can, however, often be overcome by “interpolating” the uranium concentration between thorium and lanthanum (the nearest neighbors in terms of compatibility) and replacing Nb/U by the primitive-mantle normalized Nb/(Th + La) ratio (e.g., Weaver, 1991; Eisele *et al.*, 2002).

Having established that Nb/U or Nb/(Th + La) ratios can be used to trace-mantle source compositions of basalts, this parameter can be turned into a tool to trace recycled continental material in the mantle. The mean Nb/U of 166 MORBs is Nb/U = 47 ± 11 , and mean of nearly 500 “non-EM-type” OIBs is Nb/U = 52 ± 15 . This contrasts with a mean value of the continental

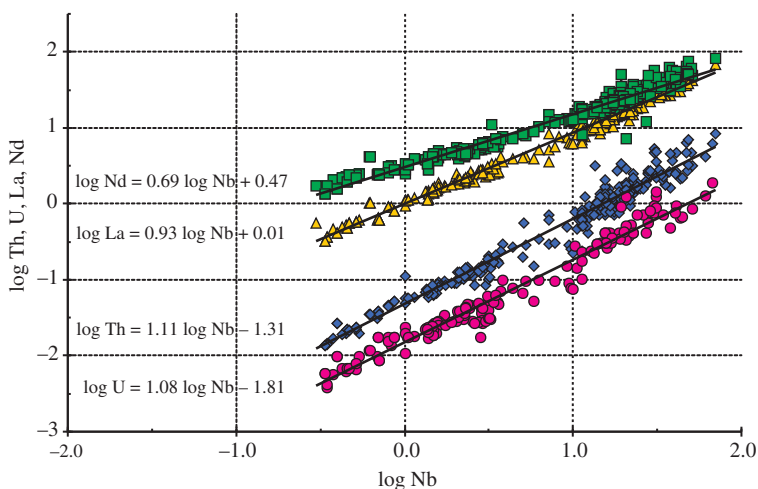


Figure 18 Concentrations of Th, U, La, and Nd versus Nb for basalts and picrites from Iceland. On this logarithmic plot, a regression line of slope 1 represents a constant element concentration ratio (corresponding to a horizontal line in Figure 17). Slopes greater than 1 correspond to positive slopes, and slopes lower than 1 correspond to negative slopes in Figure 17. The correlations of U and La versus Nb yields the slope closest to unity ($=1.08$ and 0.93).

crust of $Nb/U = 8$ (Rudnick and Fountain, 1995). As is evident from Figure 4(b), continent-derived sediments also have consistently higher $^{87}Sr/^{86}Sr$ ratios than ordinary mantle rocks; therefore, any OIB containing significant amounts of recycled sediments should be distinguished by high $^{87}Sr/^{86}Sr$ and low Nb/U ratios. Figure 19 shows that this is indeed observed for EM-2 type OIBs and, to a lesser extent, for EM-1 OIBs as well. Of course, this does not “prove” that EM-type OIBs contain recycled sediments. However, there is little doubt that sediments have been subducted in geological history. Much of their trace-element budget is likely to have been short-circuited back into island arcs during subduction. But if any of this material has entered the general mantle circulation and is recycled at all, then EM-type OIBs are the best candidates to show it. Perhaps the greater surprise is that there are so few EM-type ocean islands.

Finding the “constant-ratio partner” for lead has proved to be more difficult. Originally, Hofmann *et al.* (1986) chose cerium because, on average, the Ce/Pb ratio of their MORB data was most similar to their OIB average. However, Sims and DePaolo (1997) pointed out one rather problematic aspect, namely, that even in the original, very limited data set, each separate population showed a distinctly positive slope. In addition, they showed that Ce/Pb ratios appear to correlate with europium anomalies in the MORB population, and this is a strong indication that both parameters are affected by plagioclase fractionation. Recognizing these problems, Rehkämper and Hofmann (1997) argued on the basis of more extensive and more recent data that Nd/Pb is a better indicator of source chemistry than Ce/Pb .

Unfortunately, lead concentrations are not often analyzed in oceanic basalts, partly because lead is subject to alteration and partly because it is difficult to analyze, so a literature search tends to yield highly scattered data. Nevertheless, the average MORB value of $Pb/Nd = 0.04$ is lower than the average continental value of 0.63 by a factor of 15. Because of this great contrast, this ratio is potentially an even more sensitive tracer of continental contamination or continental recycling in oceanic basalts.

But why are Pb/Nd ratios so different in continental and oceanic crust in the first place? An answer to that question will be attempted in the following section.

2.03.5.2.2. Normalized abundance diagrams (“Spidergrams”)

The techniques illustrated in Figures 17 and 18 can be used to establish an approximate compatibility sequence of trace elements for mantle-derived melts. In general, this sequence corresponds to the sequence of decreasing (normalized) abundances in the continental crust shown in Figure 2, but this does not apply to niobium, tantalum, and lead for which the results discussed in the previous section demand rather different positions (see also Hofmann, 1988). Here I adopt a sequence similar to that used by Hofmann (1997), but with slightly modified positions for lead and strontium.

Figure 20 shows examples of “spidergrams” for representative samples of HIMU, EM-1, EM-2, and Hawaiian basalts, in addition to average MORB and average “normal” MORB, average

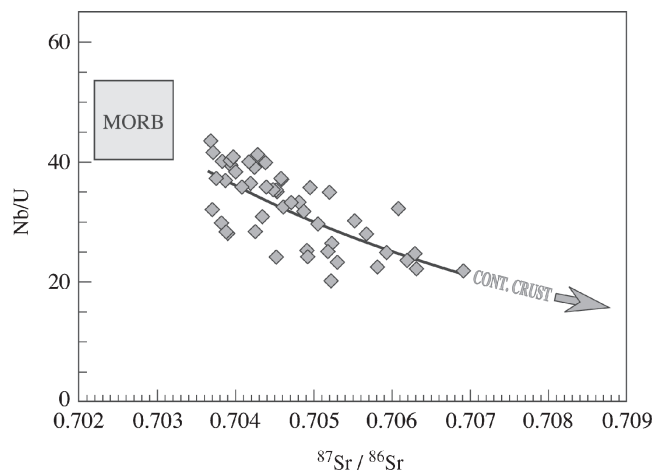


Figure 19 Nb/U versus $^{87}Sr/^{86}Sr$ for basalts from the Society Islands using data of White and Duncan (1996). Two samples with $Th/U > 6.0$ have been removed because they form outliers on an Nb/Th versus Nb/U correlation and are therefore suspected of alteration or analytical effects on the U concentration. One strongly fractionated trachyte sample has also been removed. This correlation and a similar one of Nd/Pb versus $^{87}Sr/^{86}Sr$ (not shown) is consistent with the addition of a sedimentary or other continental component to the source of the Society Island (EM-2) basalts.

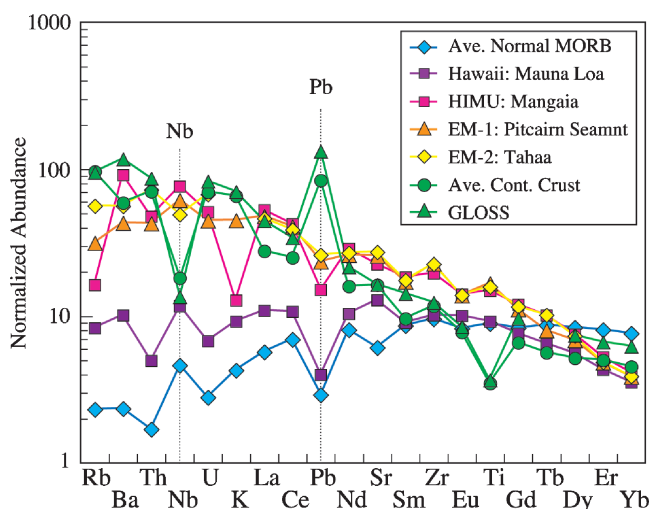


Figure 20 Examples of primitive-mantle normalized trace element abundance diagrams (“spidergrams”) for representative samples of HIMU (Mangaia, Austral Islands, sample M-11; Woodhead (1996)), EM-1 (Pitcairn Seamount sample 49DS1; Eisele *et al.* (2002)), EM-2 (Tahaa, Society Islands, sample 73-190; White and Duncan (1996)); Average Mauna Loa (Hawaii) tholeiite (Hofmann, unpublished data), average continental crust (Rudnick and Fountain, 1995), average subducting sediment, GLOSS (Plank and Langmuir, 1998), and Average Normal MORB (Su, 2002). Th, U, and Pb values for MORB were calculated from average Nb/U = 47, and Nd/Pb = 26. All abundances are normalized to primitive/mantle values of McDonough and Sun (1995).

subducting sediment, and average continental crust. Prominent features of these plots are negative spikes for niobium in average continental crust and in sediment, and corresponding positive anomalies in most oceanic basalts except EM-type basalts. Similarly, the positive spikes for lead in average continental crust and in sediments is roughly balanced by negative anomalies in most oceanic basalts. More subtle features distinguishing the isotopically different OIB types are relative deficits for potassium and rubidium in HIMU basalts and high Ba/Th ratios coupled with elevated Sr/Nd ratios in Mauna Loa basalts.

The prominent niobium and lead spikes of continental materials are not matched by any of the OIBs and MORBs reviewed here. They are, however, common features of subduction-related volcanic rocks found on island arcs and continental margins. It is therefore likely that the distinctive geochemical features of the continental crust are produced during subduction, where volatiles can play a major role in the element transfer from mantle to crust. The net effect of these processes is to transfer large amounts of lead (in addition to mobile elements like potassium and rubidium) into the crust. At the same time, niobium and tantalum are retained in the mantle, either because of their low solubility in hydrothermal solutions, or because they are partitioned into residual mineral phases such as Ti-minerals or certain amphiboles. These processes are the subject of much ongoing research, but are beyond the scope of this chapter.

For the study of mantle circulation, these chemical anomalies can help trace the origin of different types of OIBs and some MORBs. Niobium and lead anomalies, coupled with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, seem to be the best tracers for material of continental origin circulating in the mantle. They have been found not only in EM-2-type OIBs but also in some MORBs found on the Chile Ridge (Klein and Karsten, 1995). Other trace-element studies, such as the study of the chemistry of melt inclusions, have already identified a specific recycled rock type, namely, a gabbro, which could be recognized by its highly specific trace-element “fingerprint” (Sobolev *et al.*, 2000).

Until quite recently, the scarceness of high-quality data for the diagnostic elements has been a serious impediment to progress in gaining a full interpretation of the origins of oceanic basalts using complete trace-element data together with complete isotope data. All data compilations aimed at detecting global geochemical patterns are currently seriously hampered by spotty literature data of uncertain quality on samples of unknown freshness. This is now changing, because of the advent of new instrumentation capable of producing large quantities of high-quality data of trace elements at low abundances. The greater ease of obtaining large quantities of data also poses significant risks from lack of quality control. Nevertheless, we are currently experiencing a dramatic improvement in the general quantity and quality of geochemical

data, and we can expect significant further improvements in the very near future. These developments offer a bright outlook for the future of deciphering the chemistry and history of mantle differentiation processes.

2.03.6 THE LEAD PARADOX

2.03.6.1 The First Lead Paradox

One of the earliest difficulties in understanding terrestrial lead isotopes arose from the observation that almost all oceanic basalts (i.e., both MORBs and OIBs) have more highly radiogenic lead than does the primitive mantle (Allègre, 1969). In effect, most of these basalts lie to the right-hand side of the so-called “geochron” on a diagram of $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ ratios (Figure 21). The Earth was assumed to have the same age as meteorites, so that the “geochron” is identical to the meteorite isochron of 4.56 Ga. If the total silicate portion of the Earth remained a closed system involved only in internal (crust–mantle) differentiation, the sum of the parts of this system must lie on the geochron. The reader is referred to textbooks (e.g., Faure, 1986) on isotope geology for fuller explanations of the construction and meaning of the geochron and the construction of common-lead isochrons.

The radiogenic nature of MORB lead was surprising because uranium is expected to be considerably more incompatible than lead during mantle melting. The MORB source, being depleted in highly incompatible elements, is therefore expected to have had a long-term history of U/Pb ratios lower than primitive ones, just as was found to be the case for Rb/Sr and Nd/Sm. Thus, the lead paradox (sometimes also called the “first paradox”) is given by the observation that, although one would expect most MORBs to plot well to the left of the geochron, they actually do plot mostly to the right of the geochron. This expectation is reinforced by a plot of U/Pb versus U, as first used by White (1993), an updated version of which is shown in Figure 22. This shows that the U/Pb ratio is strongly correlated with the uranium concentration, thus confirming the much greater incompatibility of uranium during mantle melting.

Numerous explanations have been advanced for this paradox. The most recent treatment of the subject has been given by Murphy *et al.* (2003), who have also reviewed the most important solutions to the paradox. These include delayed uptake of lead by the core (“core pumping,” Allègre *et al.* (1982)) and storage of unradiogenic lead (to balance the excess

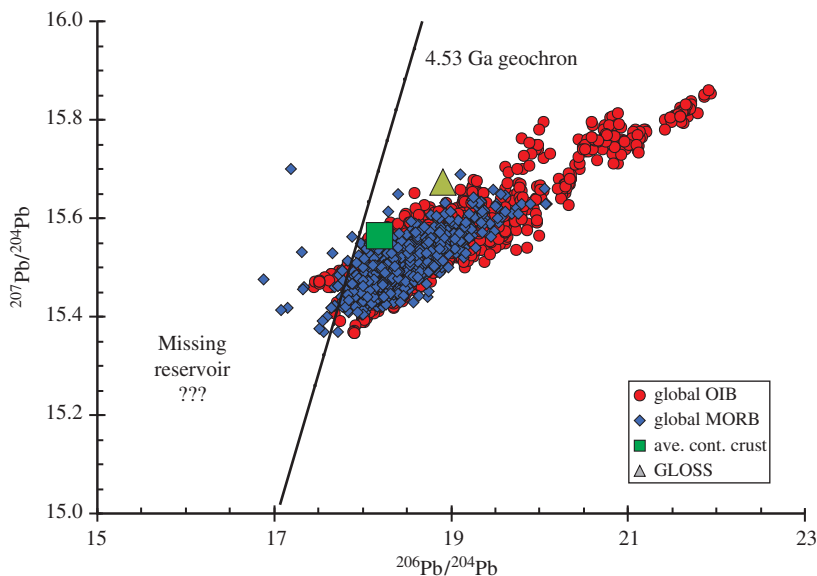


Figure 21 Illustration of the first lead paradox. Estimates of the average composition of the continental crust (Rudnick and Goldstein, 1990), of average “global subducted sediments” (GLOSS, Plank and Langmuir, 1998) mostly derived from the upper continental crust, and a global compilation of MORB and OIB data (from GEOROC and PETDB databases) lie overwhelmingly on the right-hand side of the 4.53 Ga geochron. One part of the paradox is that these data require a hidden reservoir with lead isotopes to the left of the geochron in order to balance the reservoirs represented by the data from the continental and oceanic crust. The other part of the paradox is that both continental and oceanic crustal rocks lie rather close to the geochron, implying that there is surprisingly little net fractionation of the U/Pb ratio during crust–mantle differentiation, even though U is significantly more incompatible than Pb (see Figure 22).

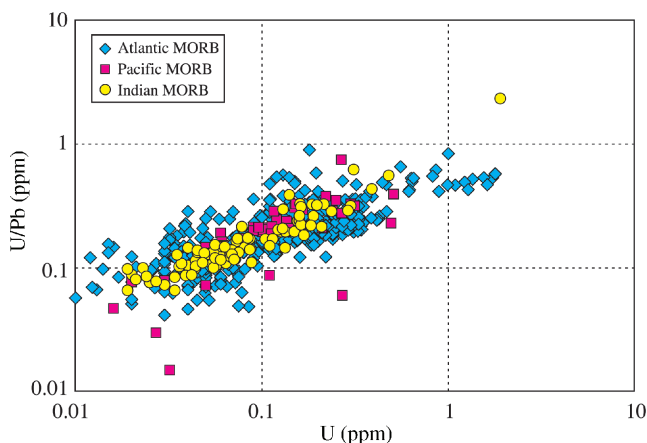


Figure 22 U/Pb versus U concentrations for MORB from three ocean basins. The positive slope of the correlation indicates that U is much more incompatible than Pb during mantle melting. This means that the similarity of Pb isotopes in continental and oceanic crust (see Figure 21) is probably caused by a nonmagmatic transport of lead from mantle to the continental crust.

radiogenic lead seen in MORBs, OIBs, and upper crustal rocks) in the lower continental crust or the subcontinental lithosphere (e.g., Zartman and Haines, 1988; Kramers and Tolstikhin, 1997).

An important aspect not addressed by Murphy *et al.* is the actual position of the geochron. This is the locus of any isotopic mass balance of a closed-system silicate earth. This is not the meteorite isochron of 4.56 Ga, because later core formation and giant impact(s) are likely to have prevented closure of the bulk silicate earth with regard to uranium and lead until lead loss by volatilization and/or loss to the core effectively ended. Therefore, the reference line (geochron) that is relevant to balancing the lead isotopes from the various silicate reservoirs is younger than, and it lies to the right of, the meteorite isochron. The analysis of the effect of slow accretion on the systematics of terrestrial lead isotopes (Galer and Goldstein, 1996) left reasonably wide latitude as to where the relevant geochron should actually be located. This was further reinforced by publication of early tungsten isotope data (daughter product of the short-lived ^{182}Hf), which appeared to require terrestrial core formation to have been delayed by at least 50 Myr (Lee and Halliday, 1995). This would have moved the possible locus of bulk silicate lead compositions closer to the actual positions of oceanic basalts, thus diminishing the magnitude of the paradox, or possibly eliminating it altogether. However, the most recent redeterminations of tungsten isotopes in chondrites by Kleine *et al.* (2002) and Yin *et al.* (2002) have shown the early tungsten data to be in error, so that core and moon formation now appear to be constrained at ~ 4.53 Ga. This value is not

sufficiently lower than the meteorite isochron of 4.56 Ga to resolve the problem.

This means that the lead paradox is alive and well, and the search for the unradiogenic, hidden reservoir continues. The lower continental crust remains (in the author's opinion) a viable candidate, even though crustal xenolith data appear to be, on the whole, not sufficiently unradiogenic (see review of these data by Murphy *et al.* (2003)). It is not clear how representative the xenoliths are, particularly of the least radiogenic, Precambrian lower crust. Another hypothetical candidate is a garnetite reservoir proposed by Murphy *et al.* (2003).

The above discussion, and most of the relevant literature, does not address the perhaps geochemically larger and more interesting question, namely, why are the continental crust and the oceanic basalts so similar in lead isotopes in the first place? It is quite remarkable that most MORBs and most continent-derived sediments cover the same range of $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, namely, ~ 17.5 – 19.5 . This means that MORB sources and upper continental crust, from which these sediments are derived, have very similar U/Pb ratios, when integrated over the entire Earth history. The main offset between lead isotope data for oceanic sediments and MORBs is in terms of $^{207}\text{Pb}/^{204}\text{Pb}$, and even this offset is only marginally outside the statistical scatter of the data. In the previous section we have seen that lead behaves as a moderately incompatible element such as neodymium or cerium, but both uranium and thorium are highly incompatible elements. So the important question remains why lead and uranium are nearly equally enriched in the continental crust, whereas they are very significantly fractionated during the formation of the oceanic crust

and ocean islands. Therefore, the unradiogenic reservoir (lower crust or hidden mantle reservoir) needed to balance the existing, slightly radiogenic reservoirs in order to obtain full, bulk-silicate-earth lead isotope values represents only a relatively minor aspect of additional adjustment to this major discrepancy. The answer is, in my opinion, that lead behaves relatively compatibly during MORB–OIB production because it is partially retained in the mantle by a residual phase(s), most likely sulfide(s). This would account for the relationships seen in Figure 22. However, when lead is transferred from mantle to the continental crust, two predominantly nonigneous processes become important: (i) hydrothermal transfer from oceanic crust to metalliferous sediment (Peucker-Ehrenbrink *et al.*, 1994), and (ii) transfer from subducted oceanic crust-plus-sediment into arc magma sources (Miller *et al.*, 1994). This additional, nonigneous transfer enriches the crust to a similar extent as uranium and thorium, and this explains why the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of crustal and mantle rocks are so similar to each other and so close to the geochron. Thus, the anomalous geochemical behavior of lead is the main cause of the “lead paradox,” the high Pd/Nd ratios of island arc and continental rocks, and the lead “spikes” seen in Figure 20.

The above explanation does not account for the elevated $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of continental rocks and their sedimentary derivatives relative to mantle-derived basalts (Figures 5(a) and 21). This special feature can be explained by a more complex evolution of continents subsequent to their formation. New continental crust formed during Archean time by subduction and accretion processes must have initially possessed a U/Pb ratio slightly higher than that of the mantle. At that time, the terrestrial $^{235}\text{U}/^{238}\text{U}$ ratio was significantly higher than today, and this produced elevated $^{207}\text{Pb}/^{204}\text{Pb}$ relative to $^{206}\text{Pb}/^{204}\text{Pb}$. Some of this crust was later subjected to high-grade metamorphism, causing loss of uranium relative to lead in the lower crust, and transporting the excess uranium into the upper crust. From there, uranium was lost by the combined action of oxidation, weathering, dissolution, and transport into the oceans. This uranium loss retarded the growth of $^{206}\text{Pb}/^{204}\text{Pb}$ while preserving the relatively elevated $^{207}\text{Pb}/^{204}\text{Pb}$ of the upper crust. The net result of this two-stage process is the present position of sediments directly above the mantle-derived basalts in $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ space. Another consequence of this complex behavior of uranium will be further discussed in the following section. Here it is important to reiterate that lead, not uranium or thorium, is the *major* player in generating the main part of the lead paradox.

2.03.6.2 The Second Lead Paradox

Galer and O’Nions (1985) made the important observation that measured $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ ratios (see Equation (11)) in most MORBs are higher than can be accounted for by the relatively low Th/U ratios actually observed in MORBs, if the MORB source reservoir had maintained similarly low Th/U ratios over much of Earth’s history. A simple two-stage Th/U depletion model with a primitive, first-stage value of $\kappa = (^{232}\text{Th}/^{238}\text{U})_{\text{today}} = 3.9$ changing abruptly to a second stage value of $\kappa = 2.5$ yields a model age for the MORB source of only ~ 600 Ma. Because much of the continental mass is much older than this, and because the development of the depleted MORB source is believed to be linked to this, this result presented a dilemma. Galer and O’Nions (1985) and Galer *et al.* (1989) resolved this with a two-layer model of the mantle, in which the upper, depleted layer is in a steady state of incompatible-element depletion by production of continental crust and replenishment by leakage of less depleted material from the lower layer. This keeps the $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ ratio of the upper mantle at a relatively high value in spite of the low chemical Th/U ratio. However, such two-layer convection models have fallen from grace in recent years, mostly because of the results of seismic mantle tomography (see below). Therefore, other solutions to this second lead paradox have been sought.

A fundamentally different mechanism for lowering the Th/U ratio of the mantle has been suggested by Hofmann and White (1982), namely, preferential recycling of uranium through dissolution of oxidized (hexavalent) uranium at the continental surface, riverine transport into the oceans, and fixation by ridge-crest hydrothermal circulation and reduction to the tetravalent state. The same mechanism was invoked in the quantitative “plumbotectonic” model of Zartman and Haines (1988). Staudigel *et al.* (1995) introduced the idea that this preferential recycling of uranium into the mantle may be connected to a change toward oxidizing conditions at the Earth’s surface relatively late in Earth’s history. Geological evidence for a rapid atmospheric change toward oxidizing conditions during Early Proterozoic time (i.e., relatively late in Earth’s history) has been presented by Holland (1994), and this has been confirmed by new geochemical evidence showing that sulfides and sulfates older than ~ 2.4 Ga contain non-mass-dependent sulfur isotope fractionations, which can be explained by high-intensity UV radiation in an oxygen-absent atmosphere (Farquhar *et al.*, 2000). Kramers and Tolstikhin (1997) and Elliott *et al.* (1999) have developed quantitative models to resolve the second lead paradox by starting to recycle

uranium into the mantle ~2.5 Ga ago. This uranium cycle is an excellent example how mantle geochemistry, surface and atmospheric chemistry, and the evolution of life are intimately interconnected.

2.03.7 GEOCHEMICAL MANTLE MODELS

The major aim of mantle geochemistry has been, from the beginning, to elucidate the structure and evolution of the Earth's interior, and it was clear that this can only be done in concert with observations and ideas derived from conventional field geology and from geophysics. The discussion here will concentrate on the chemical structure of the recent mantle, because the early mantle evolution and dynamics and history of convective mixing are treated in Chapters 2.12 and 2.13.

The isotopic and chemical heterogeneities found in mantle-derived basalts, reviewed on the previous pages, mandate the existence of similar or even greater heterogeneities in the mantle. The questions are: how are they spatially arranged in the mantle? When and how did they originate? Because these heterogeneities have their primary expression in trace elements, they cannot be translated into physical parameters such as density differences. Rather, they must be viewed as passive tracers of mantle processes. These tracers are separated by melting and melt migration, as well as fluid transport, and they are stirred and remixed by convection. Complete homogenization appears to be increasingly unlikely. Diffusion distances in the solid state have ranges of centimeters at best (Hofmann and Hart, 1978), and possibly very much less (Van Orman *et al.*, 2001), and homogenization of a melt source region, even via the movement and diffusion through a partial melt, becomes increasingly unlikely. This is attested by the remarkable chemical and isotopic heterogeneity observed in melt inclusions preserved in magmatic crystals from single basalt samples (Saal *et al.*, 1998; Sobolev *et al.*, 2000). The models developed for interpreting mantle heterogeneities have, with some exceptions, largely ignored the possibly extremely small scale of these heterogeneities. Instead, they have usually relied on the assumption that mantle-derived basalts are, on the whole, representative of some chemical and isotopic average for a given volcanic province or source volume.

In the early days of mantle geochemistry, the composition of the bulk silicate earth, also called "primitive mantle" (i.e., mantle prior to the formation of any crust; see Chapter 2.01) was not known for strontium isotopes because of the obvious depletion of rubidium of the Earth relative to chondritic meteorites (Gast, 1960).

The locus of primitive-mantle lead was assumed to be on the meteorite isochron (which was thought to be identical to the geochron until the more recent realization of delayed accretion and core formation; see above), but the interpretation of the lead data was confounded by the lead paradox discussed above. This situation changed in the 1970s with the first measurements of neodymium isotopes in oceanic basalts (DePaolo and Wasserburg, 1976; Richard *et al.*, 1976; O'Nions *et al.*, 1977) and the discovery that $^{143}\text{Nd}/^{144}\text{Nd}$ was negatively correlated with $^{87}\text{Sr}/^{86}\text{Sr}$ (see Figures 6 and 15). Because both samarium and neodymium are refractory lithophile elements, the Sm/Nd and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the primitive mantle can be safely assumed to be chondritic. With this information, a primitive-mantle value for the Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ was inferred, and it became possible to estimate the size of the MORB source reservoir primarily from isotopic abundances. The evolution of a silicate Earth consisting of three boxes—primitive mantle, depleted mantle, and continental crust—were subsequently modeled by Jacobsen and Wasserburg (1979), O'Nions *et al.* (1979), DePaolo (1980), Allègre *et al.* (1983), and Davies (1981) cast this in terms of a simple mass balance similar to that given above in Equation (11) but using isotope ratios:

$$X_{\text{dm}} = \frac{X_{\text{cc}}C_{\text{cc}}(R_{\text{dm}} - R_{\text{cc}})}{C_{\text{pm}}(R_{\text{dm}} - R_{\text{pm}})} \quad (13)$$

where X are mass fractions, R are isotope or trace-element ratios, C are the concentrations of the denominator element of R , and the subscripts cc, dm, and pm refer to continental crust, depleted mantle, and primitive mantle reservoirs, respectively.

With the exception of Davies, who favored whole-mantle convection all along, the above authors concluded that it was only the upper mantle above the 660 km seismic discontinuity that was needed to balance the continental crust. The corollary conclusion was that the deeper mantle must be in an essentially primitive, nearly undepleted state, and consequently convection in the mantle had to occur in two layers with only little exchange between these layers. These conclusions were strongly reinforced by noble gas data, especially $^3\text{He}/^4\text{He}$ ratios and, more recently, neon isotope data. These indicated that hotspots such as Hawaii are derived from a deep-mantle source with a more primordial, high $^3\text{He}/^4\text{He}$ ratio, whereas MORBs are derived from a more degassed, upper-mantle reservoir with lower $^3\text{He}/^4\text{He}$ ratios. The noble-gas aspects are treated in Chapter 2.06. In the present context, two points must be mentioned. Essentially all quantitative evolution models dealing with the noble gas evidence concluded that, although plumes carry

the primordial gas signature from the deep mantle to the surface, the plumes themselves do not originate in the deep mantle. Instead they rise from the base of the upper mantle, where they entrain very small quantities of lower-mantle, noble-gas-rich material. However, all of these models have been constrained by the present-day very low flux of helium from the mantle into the oceans. This flux does not allow the lower mantle to be significantly degassed over the Earth's history. Other authors, who do not consider this constraint on the evolution models to be binding, have interpreted the noble gas data quite differently: they argue that the entire plume comes from a nearly primitive deep-mantle source and rises through the upper, depleted mantle. The former view is consistent with the geochemistry of the refractory elements, which strongly favors some type of recycled, not primitive mantle material to supply the bulk of the plume source. The latter interpretation can be reconciled with the refractory-element geochemistry, if the deep-mantle reservoir is not actually primitive (or close to primitive), but consists of significantly processed mantle with the geochemical characteristics of the FOZO (C, PHEM, etc.) composition, which is characterized by low $^{87}\text{Sr}/^{86}\text{Sr}$ but relatively high $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, together with high $^3\text{He}/^4\text{He}$ and solar-like neon isotope ratios. The processed nature of this hypothetical deep-mantle reservoir is also evident from its trace-element chemistry, which shows the same nonprimitive (high) Nb/U and (low) Pb/Nd ratios as MORBs and other OIBs. It is not clear how and why the near-primordial noble gas compositions would have survived this processing. So far, except for the two-layer models, no internally consistent mantle evolution model has been published that accounts for all of these observations (see also Chapter 2.12).

The two-layer models have been dealt a rather decisive blow by recent results of seismic mantle tomography. The images of the mantle produced by this discipline appear to show clear evidence for subduction reaching far into the lower mantle (Grand, 1994; van der Hilst *et al.*, 1997). If this is correct, then there must be a counterflow from the lower mantle across the 660 km boundary, which in the long run would surely destroy the chemical isolation between upper- and lower-mantle reservoirs. Most recently, mantle tomography appears to be able to track some of the major mantle plumes (Hawaii, Easter Island, Cape Verdes, Reunion) into the lowermost mantle (Montelli *et al.*, 2003). If these results are confirmed, there is, at least in recent mantle history, no convective isolation, and mantle evolution models reconciling all of the geochemical aspects with the geophysical evidence clearly require new ideas.

As of early 2000s, the existing literature and scientific conferences all show clear signs of a

period preceding a significant or even major paradigm shift as described by Thomas Kuhn in his classic work *The Structure of Scientific Revolutions* (Kuhn, 1996): The established paradigm is severely challenged by new observations. While some scientists attempt to reconcile the observations with the paradigm by increasingly complex adjustments of the paradigm, others throw the established conventions overboard and engage in increasingly free speculation. This process continues until a new paradigm evolves or is discovered, which is consistent with all the observations. Examples of the effort of reconciliation are the papers by Stein and Hofmann (1994) and Allègre (1997). These authors point out that the current state of whole-mantle circulation may be episodic or recent, so that whole-mantle chemical mixing has not been achieved.

Examples of the more speculative thinking are the papers by Albarède and van der Hilst (1999) and Kellogg *et al.* (1999), who essentially invent new primitive reservoirs within the deep mantle, which are stabilized by higher chemical density, and may be very irregularly shaped. In the same vein, Porcelli and Halliday (2001) have proposed that the storage reservoir of primordial noble gases may be the core, whereas Tolstikhin and Hofmann (2002) speculate that the lowermost layer of the mantle, called D'' by seismologists, contains the "missing" budget of heat production and primordial noble gases. Finally, an increasing number of convection and mantle evolution modelers are throwing the entire concept of geochemical reservoirs overboard. For example, Phipps Morgan and Morgan (1998) and Phipps Morgan (1999) suggest that the specific geochemical characteristics of plume-type mantle are randomly distributed in the deeper mantle. Plumes rising from the core–mantle boundary constitute the main upward flux balancing the subduction flux. They preferentially lose their enriched components during partial melting, leaving a depleted residue that replenishes the depleted upper mantle.

Starting with the contribution of Christensen and Hofmann (1994), a steadily increasing number of models have recently been published, in which geochemical heterogeneities are specifically incorporated in mantle convection models (e.g., van Keken and Ballentine, 1998; Tackley, 2000; van Keken *et al.*, 2001; Davies, 2002; Farnetani *et al.*, 2002; Tackley, 2002). Thus, while the current state of understanding of the geochemical heterogeneity of the mantle is unsatisfactory, to say the least, the formerly quite separate disciplines of geophysics and geochemistry have begun to interact intensely. This process surely offers the best approach to reach a new paradigm and an understanding of how the mantle really works.

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