

Theory of the Earth

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Chapter 10. Isotopes

Boston: Blackwell Scientific Publications, c1989

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Recommended citation:

Anderson, Don L. Theory of the Earth. Boston: Blackwell Scientific Publications, 1989. <http://resolver.caltech.edu/CaltechBOOK:1989.001>

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Abstract:

The various chemical elements have different properties and can therefore be readily separated from each other by igneous processes. The various isotopes of a given element are not so easily separated. The abundances of the radioactive isotopes and their decay products are not constant in time. Therefore, the information conveyed by the study of isotopes is different in kind than that provided by the elements. Each isotopic system contains unique information, and the various radioactive isotopes allow dating of various processes in a planet's history. The unstable isotopes most useful in geochemistry have a wide range of decay constants, or half-lives, and can be used to infer processes occurring over the entire age of the Earth (Table 10-1). In addition, isotopes can be used as tracers and in this regard they complement the major- and trace-element chemistry of rocks and magmas.

The Earth has a spirit of growth.

—LEONARDO DA VINCI

The various chemical elements have different properties and can therefore be readily separated from each other by igneous processes. The various isotopes of a given element are not so easily separated. The abundances of the radioactive isotopes and their decay products are not constant in time. Therefore, the information conveyed by the study of isotopes is different in kind than that provided by the elements. Each isotopic system contains unique information, and the various radioactive isotopes allow dating of various processes in a planet's history. The unstable isotopes most useful in geochemistry have a wide range of decay constants, or half-lives, and can be used to infer processes occurring over the entire age of the Earth (Table 10-1). In addition, isotopes can be used as tracers and in this regard they complement the major- and trace-element chemistry of rocks and magmas.

Studies of isotope ratios have played an important role in constraining mantle and crustal evolution, convective mixing and the long-time isolation of mantle reservoirs. Isotope studies derive their power from the existence of suitable pairs of isotopes of a given element, one a "primordial" isotope present in the Earth since its formation, the other a radiogenic daughter isotope produced by radioactive decay at a known rate throughout geological time. The isotopic composition of these isotope pairs in different terrestrial reservoirs—for example, the atmosphere, the ocean, and the different parts of the crust and mantle—are a function of the transport and mixing of parent and daughter elements between the reservoirs. In some cases the parent and daughter have similar geochemical characteristics and are difficult to separate in geological processes. In other cases the parent and daughter have quite different properties, and isotopic ratios contain information that is no

longer available from studies of the elements themselves. For example the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio gives information about the time-integrated Rb/Sr ratio of the rock or its reservoirs. Since rubidium is a volatile element and separates from strontium both in preaccretional and magmatic processes, the isotopic ratios of strontium in various products of mantle differentiation, combined with mass-balance calculations, are our best guide to the rubidium content, and volatile content, of the Earth. Lead isotopes can be similarly used to constrain the U/Pb ratio, a refractory/volatile pair, of the mantle. In other cases, such as the neodymium-samarium pair, the elements in question are both refractory, have similar geochemical characteristics and are probably in the Earth in chondritic ratios. The neodymium isotopes can therefore be used to infer ages of reservoirs and to discuss whether these reservoirs are enriched or depleted, in terms of Nd/Sm, relative to chondritic or undifferentiated reservoirs. The Rb/Sr and Nd/Sm ratios of a reservoir are changed when melt is removed or added or if it is mixed with or contaminated by sediment, crust or seawater. With time, the isotopic ratios of such reservoirs diverge. The isotopic ratios of the crust and various magmas show that mantle differentiation is ancient and that remixing and homogenization is secondary in importance to separation and isolation. On the other hand we know that these isolated reservoirs can readily provide material to the surface. Although isotopes cannot tell us where these reservoirs are, or their bulk chemistry, their long-term isolation and lack of homogenization plus the temporal and spatial proximity of their products suggests that, on average, they occur at different depths. This in turn suggests that the reservoirs differ in intrinsic density and therefore in bulk chemistry and mineralogy. Melts from the reservoirs, however, are buoyant

TABLE 10-1
Radioactive Nuclides and their Decay Products

Radioactive Parent	Decay Product	Half-life (billion years)
²³⁸ U	²⁰⁶ Pb	4.468
²³² Th	²⁰⁸ Pb	14.01
¹⁷⁶ Lu	¹⁷⁶ Hf	35.7
¹⁴⁷ Sm	¹⁴³ Nd	106.0
⁸⁷ Rb	⁸⁷ Sr	48.8
²³⁵ U	²⁰⁷ Pb	0.7038
⁴⁰ K	⁴⁰ Ar, ⁴⁰ Ca	1.250
¹²⁹ I	¹²⁹ Xe	0.016
²⁶ Al	²⁶ Mg	8.8 x 10 ⁻⁴

relative to the shallow mantle. It may be that basalts originate primarily from only one of these reservoirs and that the trace-element and isotopic diversity is acquired when they traverse the shallow mantle on their way to the surface.

The crust is extremely enriched in many of the so-called incompatible elements, generally the large ionic radius or high-charge elements that do not readily fit into the lattices of the "major mantle minerals," olivine and orthopyroxene. The crust is not particularly enriched in elements of moderate charge having ionic radii between those of Ca²⁺ and Al³⁺. This suggests that the mantle has retained elements that can be accommodated in the garnet and clinopyroxene structures. The crust is also not excessively enriched in lithium, sodium, lead, bismuth and helium.

Some mantle rocks and magmas have high concentrations of the incompatible elements and isotopic ratios that reflect long-term enrichment of an appropriate incompatible-element parent. The common geochemical prejudice is that the crust is somehow involved in the evolution of these magmas, either by crustal contamination prior to or during eruption or by recycling of continent-derived sediments. Usually, however, it is impossible to distinguish this possibility from the alternative that all potential crust-forming material has not been removed from the upper mantle or that the crust formation process, efficient as it seems to be, is not 100 percent efficient in removing the incompatible elements from the mantle. Ironically, a parallel geochemical prejudice is that some magmas represent melts from "primitive" mantle, which has survived from the accretion of the Earth without any melting or melt extraction, the apparent reasoning being that part of the mantle provided the present crust, with 100 percent efficiency, and the rest of the mantle has been isolated, again with 100 percent efficiency. In this scenario, "depleted" magmas are derived from a reservoir, complementary to the continental crust, which has experienced a two-stage history (stage one involves an ancient removal of a small melt fraction, the crust; stage two involves a recent extensive melting process, which generates MORB). "Enriched" magmas (also called "primitive,"

"more primitive," "less depleted," "hotspot" or "plume" magmas) are single-stage melts from a "primitive" reservoir or depleted magmas that have experienced some type of crustal contamination.

There is no room in these models for an ancient enriched mantle reservoir. This "box model" of the Earth contains three boxes: the continental crust, the "depleted mantle" (which is equated to the upper mantle or MORB reservoir) and "primitive mantle" (which is equated to the lower mantle) with the constraint that primitive mantle is the sum of continental crust and depleted mantle. With these simple rules many amusing games can be played with crustal recycling rates and mean age of the crust. When contradictions appear they are explained by hiding material in the lower crust, the continental lithosphere or the core, or by storing subducted material somewhere in the mantle for long periods of time. The products of mantle differentiation are viewed as readily and efficiently separable but, at the same time, storable for long periods of time in a hot, convecting mantle. Magmas having similar geochemical characteristics are given a variety of origins. "Enriched" magmas are variously attributed to continental contamination, recycling and a "lower-mantle primitive reservoir."

Isotopes are extremely useful as probes of planetary processes, and they are even more useful when used in conjunction with other petrological, geochemical and geophysical data. They are also much more interesting as tracers of the Earth's dynamics than is implied by static box models involving crust, mantle and core—the main features of the Earth acknowledged by isotope geochemists.

Isotopes make it possible to rule out conventional ideas that relate various basalts by different degrees of partial melting at different depths (the pyrolite hypothesis) or by crystal fractionation (the parent magma hypothesis). These mechanisms may still be important, but they must be combined with contamination or mixing of materials from isotopically distinct reservoirs.

LEAD ISOTOPES

Lead has a unique position among the radioactive nuclides. Two isotopes, lead-206 and lead-207, are produced from radioactive parent isotopes of the same element, uranium-238 and uranium-235. The simultaneous use of coupled parent-daughter systems allows one to avoid some of the ambiguities associated with a single parent-daughter system.

In discussing the uranium-lead system, it is convenient to normalize all isotopic abundances to that of lead-204, a stable nonradiogenic lead isotope. The total amount of lead-204 in the Earth has been constant since the Earth was formed; the uranium parents have been decreasing by radioactive decay while lead-206 and lead-207 have been increasing. The U/Pb ratio in various parts of the Earth

changes by chemical fractionation and by radioactive decay. The $^{238}\text{U}/^{204}\text{Pb}$ ratio, calculated as of the present, can be used to remove the decay effect in order to study the chemical fractionation of various reservoirs. If no chemical separation of uranium from lead occurs, the $^{238}\text{U}/^{204}\text{Pb}$ ratio for the system remains constant. This ratio is called the μ of the system.

The decay schemes are

$$\begin{aligned} (^{206}\text{Pb}/^{204}\text{Pb}) &= (^{238}\text{U}/^{204}\text{Pb})(e^{\lambda t_0} - 1) + (^{206}\text{Pb}/^{204}\text{Pb})_0 \\ (^{207}\text{Pb}/^{204}\text{Pb}) &= (^{235}\text{U}/^{204}\text{Pb})(e^{\lambda' t_0} - 1) + (^{207}\text{Pb}/^{204}\text{Pb})_0 \end{aligned}$$

where λ and λ' are the decay constants and the second terms on the right are the initial ratios (at $t = t_0$).

By combining these equations we can write an expression for t_0 in terms of isotopic ratios of lead and uranium: $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{235}\text{U}/^{238}\text{U}$. This is the basis for determining the lead-lead age of the Earth. Use of this equation does not involve measurements of the absolute concentration of either the uranium or the lead in the rock, nor does t_0 depend on the absolute concentrations of these elements. The ratio $^{235}\text{U}/^{238}\text{U}$ is very nearly constant (11137.9) in natural uranium. For uranium-rich minerals, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ are high, and the equations do not much depend on the initial ratios. These equations were used by Patterson (1956) and Houtermans (1947) to calculate the age of the Earth, using initial ratios inferred from meteoritic data.

The coupled equations can be used to calculate $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ for a given $^{238}\text{U}/^{204}\text{Pb}$ ratio, as a function of time. If the initial ratios and μ are known, or assumed from meteorite data, then the locus of points so calculated is called the *geochron*. The lead-isotopic ratios can therefore be calculated for any time, including the present, for unfractionated reservoirs. For $\mu = 8$ and $t_0 = 4.6$ Ga, values thought to be appropriate for the Earth, $^{206}\text{Pb}/^{204}\text{Pb}$ is about 17.6 and $^{207}\text{Pb}/^{204}\text{Pb}$ is about 15.45. If the Earth fractionated at any time, giving high U/Pb in the melts and low U/Pb in the residue, then present day lead-isotopic ratios will be greater and less, respectively, than present-day ratios inferred for primitive mantle.

Most lead-isotopic results can be interpreted as growth in a primitive reservoir for a certain period of time and then growth in reservoir with a different μ -value from that time to the present. By measuring the isotopic ratios of lead and uranium in a rock, the time at which the lead ratios were the same as inferred for the primitive reservoir can be determined, thus giving the lead-lead age of the rock. This dates the age of the uranium-lead fractionation event, assuming a two-stage growth model. In some cases multistage or continuous differentiation models are used.

A melt removed from the primitive reservoir at t_0 will crystallize to a rock composed of minerals with different μ values. If these minerals can be treated as closed systems, then they will have distinctive lead ratios that plot

as a straight line on a $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ plot (Figure 10-1). This line is an *isochron* because it is the locus of points all of which experienced fractionation at the same time to form minerals with differing U/Pb ratios. The residual rock will also plot on this line, on the other side of the geochron. The time at which the rock was fractionated can be calculated from the slope of the isochron. Mixing lines between genetically unrelated magmas will also be straight lines, in which case the age will be spurious unless both magmas formed at the same time.

In the uranium-lead decay system, the curve representing the growth of radiogenic lead in a closed system has marked curvature. This is because uranium-238 has a half-life (4.47 Ga) comparable to the age of the Earth, whereas uranium-235 has a much shorter half-life (0.704 Ga). In early Earth history lead-207, the daughter of uranium-235, is formed at a higher rate than lead-206. For a late fractionation event $^{207}\text{Pb}/^{204}\text{Pb}$ changes slowly with time.

For isotopic systems with very long half-lives, such as samarium-142 (106 Ga) and rubidium-87 (48.8 Ga), the analogous closed-system geochrons will be nearly straight lines. On the other hand, isochrons and mixing lines for other systems, in general, are not straight lines. They are straight in the uranium-lead system because $^{238}\text{U}/^{204}\text{Pb}$ and $^{235}\text{U}/^{204}\text{Pb}$ have identical fractionation factors, and mixing lines for ratios are linear if the ratios have the same denominator.

The initial lead-isotopic composition in iron meteorites can be obtained since these bodies are essentially free of uranium. Galenas are also high in lead and low in uranium and therefore nearly preserve the lead-isotopic ratios of their parent at the time of their birth. Galenas of various ages fall close to a unique single-stage growth curve. The small departures can be interpreted as further fractionation events.

The equations describing the evolution of a given set of lead-isotope compositions from a single common composition in systems that may lose lead or gain or lose uranium are

$$^{206}\text{Pb}/^{204}\text{Pb} = (^{206}\text{Pb}/^{204}\text{Pb})_0 + \int_0^{t_0} \mu(t) e^{\lambda t} \lambda dt$$

$$^{207}\text{Pb}/^{204}\text{Pb} = (^{207}\text{Pb}/^{204}\text{Pb})_0 + (^{235}\text{U}/^{238}\text{U}) \int_0^{t_0} \mu(t) e^{\lambda' t} dt$$

If μ changes discontinuously at various times, then the above equations can be written as the appropriate sums.

The μ values for basaltic magmas are usually quite high, 15–45, compared to primitive mantle. Their lead-isotopic ratios will therefore grow more rapidly with time than the primitive mantle, and the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of such magmas are high. Oceanic islands have such high lead-isotopic ratios that they must have come from ancient enriched reservoirs or contain, as a component, ancient enriched material. MORB thought to come from an ancient depleted reservoir, also have ratios in excess of the geochron. This suggests either the mantle (or

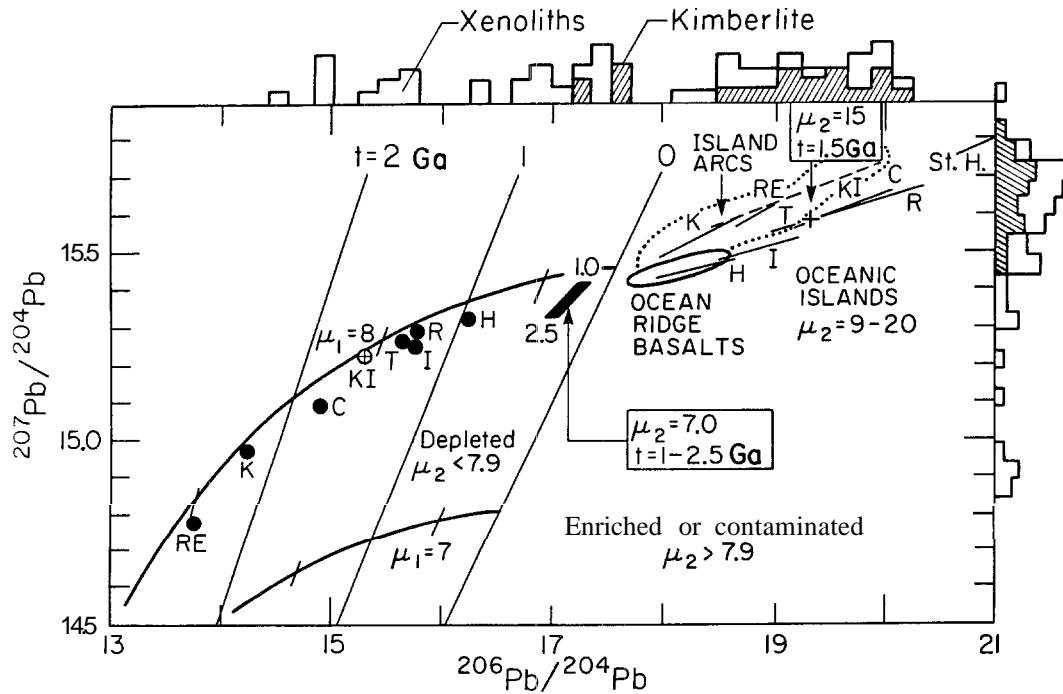


FIGURE 10-1

Lead isotope diagram. Age of Earth is taken as 4.57 Ga. Straight lines labeled with letters are values for oceanic islands. Black dots are the inferred primary isotopic ratios if the island data are interpreted as secondary isochrons. Growth curves for $^{238}\text{U}/^{204}\text{Pb}$ (μ_1) values of 7.0 and 8.0 and primary isochrons at 1 Ga intervals are shown. The primary mantle reservoir appears to have a μ_1 of 7.9. Oceanic-island basalts appear to have evolved in enriched reservoirs ranging in age from 1 to 2.5 Ga with μ_2 (the second-stage μ value) values ranging from 9 to 20. A point is shown for a two-stage model with $\mu_1 = 7.9$ before 1.5 Ga and $\mu_2 = 15$ subsequently. The black bar represents the range of values for depleted reservoirs with $\mu_2 = 7.0$ and a range of depletion ages from 1 to 2.5 Ga. The range for mid-ocean-ridge basalts could be due to growth in an enriched reservoir or due to contamination by enriched magmas. Isotopic ratios for xenoliths and kimberlites are shown along the axes. Xenoliths are primarily from the shallow mantle and many are enriched. KI is kimberlite. Diagram is modified from Chase (1981).

upper mantle) has continuously lost lead, relative to uranium, to the lower crust or core (or lower mantle), or that MORB basalts have been contaminated by material with high isotopic ratios, prior to eruption.

Oldenberg (1984) performed a detailed analysis of lead-isotopic data from conformable ore deposits to obtain information about the movement of uranium, thorium and lead into or out of the mantle source region. He showed that $\mu(t) = ^{238}\text{U}(t)/^{204}\text{Pb}$ increased from 8.03 ± 0.3 in the first billion years after Earth formation to 9.8 ± 0.3 between 2.0 and 3.0 Ga ago. The ratio μ apparently decreased in the time interval 2 to 1 Ga ago, perhaps representing removal of uranium and lead from the mantle to the continental crust or the preferential sampling of a relatively depleted reservoir during that period of time. The ratio $\xi = ^{232}\text{Th}/^{204}\text{Pb}$ also increased with time from about 35 to 38, also with a

dip at 2–1 Ga ago. The ratio $k(t) = \xi(t)/\mu(t)$ thus maintained a value near 4.0 since the Earth formed.

In a cooling, crystallizing mantle the μ of the residual melt will increase with time, assuming that solid silicates and sulfides retain lead more effectively than uranium. Modeling shows that most of the mantle had solidified prior to 3.8 Ga, close to the age of the oldest known rock. Oldenberg estimated that the residual, depleted solid mantle might have μ of about 6.0. Basalts from oceanic islands have apparently experienced secondary growth in reservoirs with μ from about 10 to 20, after a long period of growth in a more "primitive" reservoir ($\mu \approx 7.9$).

Leads from basaltic suites in many oceanic islands form linear areas on $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ diagrams (Figure 10-1). These could represent either mixing lines or secondary isochrons. Two-stage histories indicate that the

leads from each island were derived from a common primary reservoir ($\mu = 7.9$) at different times from 2.5 to 1.0 Ga ago. Alternatively, the magmas from each island could represent mixtures between an enriched end-member and a less enriched or depleted end-member. In either case the ocean-island basalts involve a source region with ancient U/Pb enrichment. One mechanism for such enrichment is removal of a melt from a primitive reservoir to another part of the mantle that subsequently provides melts to the oceanic islands or contaminates MORB. The most logical storage place for such a melt is the shallow mantle. The enrichment event must have been ancient, older than 1 Ga. To explain the various trends of the individual islands by mixing, the enriched end-member must come from parts of the mantle that were enriched at different times or that have different time-integrated U/Pb ratios. In a crystallizing cumulate or magma ocean, the U/Pb ratio of the remaining fluid probably increases with time, and regions of the mantle that were enriched by this melt would have variable μ depending on when and how often they were enriched. If the enriched reservoir is global, as indicated by the global distribution of enriched magmas, it is plausible that different parts of it were enriched at different times.

STRONTIUM AND NEODYMIUM ISOTOPES

Strontium-isotope measurements are now almost as routine as trace-element measurements and are used in similar ways in petrological investigations. Magmas that are genetically related have the same isotopic ratios. Midocean-ridge basalts have $^{87}\text{Sr}/^{86}\text{Sr}$ less than 0.703, and "pure" MORB may have values of 0.702 or less. Ocean-island, island-arc and continental flood basalts are generally much higher than 0.703, commonly higher than 0.71. Primitive mantle values of $^{87}\text{Sr}/^{86}\text{Sr}$ are unknown because the mantle Rb/Sr is unknown, but it probably falls between 0.704 and 0.705. Basalts with high $^{87}\text{Sr}/^{86}\text{Sr}$ are often considered to be contaminated by crust or recycled material or seawater. They may also come from ancient enriched mantle reservoirs, but other isotope and trace-element data are required to remove the ambiguities. Attributing the properties of MORB to "normal mantle" and, more recently, to the whole upper mantle, leaves crustal contamination, recycling or the lower mantle as the only alternatives to explain ocean-island and other "plume" or "hotspot" basalts. However, the upper mantle itself is probably inhomogeneous. In some cases continental, sediment or seawater contamination can be ruled out. There is no evidence that any magma comes from a primordial reservoir or from the lower mantle.

The radioactive isotope samarium-147 decays to neodymium-143 with a half-life of 106 Ga. $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are expressed in terms of deviations, in parts per 10^4 , from

the value in a reservoir that has had chondritic ratios of Sm/Nd for all time,

$$\varepsilon_{\text{Nd}} = \left[\frac{(^{143}\text{Nd}/^{144}\text{Nd})}{(^{143}\text{Nd}/^{144}\text{Nd})_c} - 1 \right] \times 10^4$$

Clearly, a chondritic unfractionated reservoir has $\varepsilon_{\text{Nd}} = 0$ at all times. Samarium and neodymium are both refractory rare-earth elements and should be in the Earth in chondritic ratios. However, they are separated by magmatic process and thus record the magmatic or fractionation history of the Earth. Samarium has a higher crystal-melt partition coefficient than neodymium, and thus the Sm/Nd ratio is smaller in melts than in the original rock. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio, normalized as above, will therefore be positive in reservoirs from which a melt has been extracted and negative in the melts or regions of the mantle that have been infiltrated by melts. The Sm/Nd ratio depends on the extent of melting and the nature of the residual phases, and ε_{Nd} depends on the Sm/Nd and the age of the fractionation event.

Since neodymium and samarium are geochemically similar and are both refractory elements, the neodymium-isotope system has certain advantages over the strontium and lead systems:

1. Rocks are less sensitive to alteration, in particular seawater alteration.
2. The Sm/Nd ratio of the Earth is probably well known (chondritic).
3. There is probably little separation of samarium and neodymium once a rock has been formed.

Nevertheless, there is generally good correlation between neodymium and strontium isotopes. Positive ε_{Nd} correlates with low $^{87}\text{Sr}/^{86}\text{Sr}$ and vice versa. Midocean-ridge basalts have high ε_{Nd} and low $^{87}\text{Sr}/^{86}\text{Sr}$, indicating time-integrated depletions of Nd/Sm and Rb/Sr. The isotopic ratios are so extreme that the depletion must have occurred in the MORB reservoir more than 1 Ga ago, probably more than 2 Ga ago. The depletion may have occurred at the time the continental crust formed or even during the accretion of the Earth. The measured Sm/Nd and Rb/Sr ratios in MORB generally would not support such ancient ages, but the depletion may have been progressive and MORB may be mixtures of a more depleted and an enriched material.

Incompatible-element ratios such as Rb/Sr and Nd/Sm are increased in partial melts. However, for large fractions of partial melting the ratios are similar to the original rock. Since elements with D much less than 1 (such as Rb, Sr, Nd and Sm) are not retained effectively by residual crystals, it is difficult to change their ratio in melts, but the residual crystals, although low in these elements, have highly fractionated ratios. Partial melts representing large degrees of partial melting from primitive mantle will also have near-primitive ratios, as will regions of the mantle invaded by

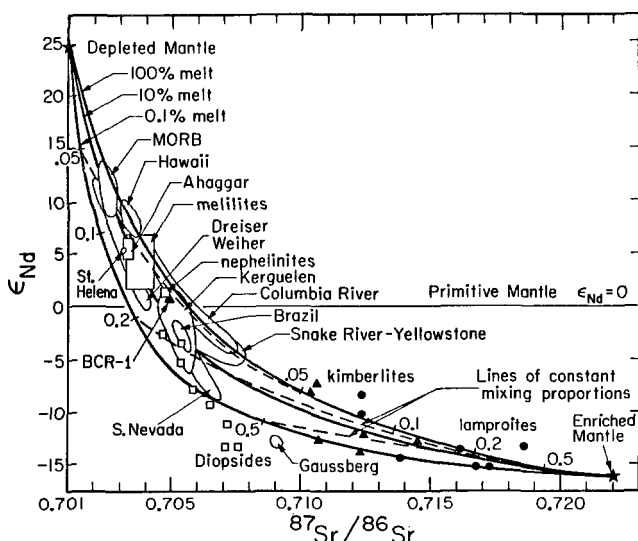


FIGURE 10-2
 ϵ_{Nd} versus $^{87}Sr/^{86}Sr$ for mixtures involving a depleted magma or residual fluids from such a magma after crystal fractionation, and an enriched component (EM) (after Anderson, 1985).

these melts. If the melt cools and crystallizes, with refractory crystals being removed and isolated, the Sm/Nd ratio changes. Thus, it is dangerous to infer that a melt came from a primitive reservoir simply because the $^{143}Nd/^{144}Nd$ ratio appears primitive. Similarly, magmas with ϵ_{Nd} near 0 can result from mixtures of melts, with positive and negative ϵ_{Nd} .

Figure 10-2 shows the ϵ_{Nd} versus strontium isotope correlation for a variety of materials.

THE LEAD PARADOX

Both uranium and lead are incompatible elements in silicates, and uranium apparently enters the melt more readily than lead. The U/Pb ratio should therefore increase in melts and decrease in the solid residue. One would expect, therefore, that the MORB reservoir should be depleted in U/Pb as well as Rb/Sr and Nd/Sm. A time-average depletion would give $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios that fall to the left of the primary geochron and below the mantle growth curve. Figure 10-1 shows, however, that both MORB and ocean-island tholeiites appear enriched relative to the primary growth curve. This implies that MORB has been contaminated by high-uranium or high-U/Pb material before being sampled, or that lead has been lost from the MORB reservoir. Early lead loss to the core, in sulfides, is possible, but the isotopic results, if interpreted in terms of lead removal, also require lead extraction over the period 3–1 Ga. Contamination of MORB is a possible explanation, particu-

larly if the depleted reservoir is deeper than the enriched reservoir.

The lead reservoirs for oceanic islands are heterogeneous but may have been derived from a fairly uniform reservoir with $\mu = 7.9$ at times ranging from 2.5 to 10 Ga ago (Chase, 1981). There is some indication that the more recently formed reservoirs are more enriched in U/Pb. This is consistent with progressive enrichment of the ocean-island basalt (OIB) reservoir over time. Kimberlites from South Africa appear to have evolved in a similar reservoir prior to 1.5 Ga and in an enriched reservoir subsequent to that time (Kramers, 1977). The uniform mantle reservoir would have $^{206}Pb/^{204}Pb$ of about 17.5 if sampled today. After depletion, this reservoir would evolve in a low- μ environment ($\mu < 7.9$) and would generate magmas with $^{206}Pb/^{204}Pb$ values less than 17.5. If midocean-ridge basalts originate in the depleted reservoir and are contaminated by magmas from the complementary enriched reservoirs, then the field of MORB on a lead-lead plot should fall on a mixing line between OIB and the uncontaminated magmas. This constrains the field of these magmas on a lead-lead evolution diagram. Assuming that the depleted and enriched reservoirs have the same range, 1.0–2.5 Ga, one can calculate that μ of the depleted reservoir should be about 7 or less. Magmas from depleted reservoirs that formed over the above time interval would have $^{206}Pb/^{204}Pb$ ratios of 17.0 to 17.4. In the MORB system itself variations of U/Pb, Rb/Sr and Nd/Sm are correlated.

TABLE 10-2
 Parameters Adopted for Uncontaminated Ocean Ridge Basalts (1) and Contaminant (2)

Parameter	Pure MORB (1)	Enriched Contaminant (2)	
Pb	0.08 ppm	2 ppm	
U	0.0085 ppm	0.9 ppm	
U/Pb	0.10	0.45	
$^{238}U/^{204}Pb$	7.0	30.0	
$^{206}Pb/^{204}Pb$	17.2	19.3, 21	
Rb	0.15 ppm	28 ppm	
Sr	50 ppm	350 ppm	
$^{87}Sr/^{86}Sr$	0.7020	0.7060	
Sm	2 ppm	7.2 ppm	
Nd	5 ppm	30 ppm	
$^{143}Nd/^{144}Nd$	0.5134	0.5124	
Enrichment Factors *			
Pb	24.6	U/Pb	4.5
Sr	7.0	Rb/Sr	26.7
Nd	6.0	Sm/Nd	0.60

(1) Assumed composition of uncontaminated midocean-ridge basalts.

(2) Assumed composition of contaminant. This is usually near the extreme end of the range of oceanic-island basalts.

*Ratio of concentration in two end-members.

In order to test if contamination is a viable explanation for the location of the field of MORB on lead-lead isotopic diagrams, we must estimate the lead content of uncontaminated depleted magmas and the lead and lead-isotopic ratios of the contaminant. Table 10-2 lists the parameters we shall use.

The lead content appropriate for a $^{206}\text{Pb}/^{204}\text{Pb}$ range of 17.0 to 17.2 is 0.07 to 0.09 ppm (Sun and others, 1975). Let us adopt 0.08 ppm. The U/Pb ratio for basalt glasses is about 0.08 to 0.19. Adopting 0.11, we derive a uranium content for pure MORB basalts of 0.0085 ppm. For the contaminant, we adopt the values in Table 8-4. These are close to the extreme values measured on ocean-island tholeiites. For the contaminant $^{206}\text{Pb}/^{204}\text{Pb}$ ratio we adopt 19.3, corresponding to 1.5 Ga of secondary growth in a reservoir with $\mu = 15$. This is a conservative value since ratios as high as 21 are observed on oceanic islands. The effect of a contaminant with this value is also shown in Figure 10-3.

The results of mixing calculations are shown in Figure 10-3 for the $^{143}\text{Nd}/^{144}\text{Nd}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ systems. The differences between the lead and other systems is striking. A small amount of contamination, less than 0.5 percent, pushes MORB compositions into the enriched field for lead but not for neodymium or strontium. In terms of single-stage evolution, both observed (contaminated) MORB and oceanic-island basalt will appear to have future ages on a lead-lead geochron diagram. The neodymium and strontium isotopic ratios are not affected as much, and contaminated MORB will appear to come from depleted reservoirs.

The large increase of $^{206}\text{Pb}/^{204}\text{Pb}$ caused by a small amount of contamination is mainly a function of the choice of the ratios $\text{Pb}(\text{contaminant})/\text{Pb}(\text{MORB})$ and $^{206}\text{Pb}/^{204}\text{Pb}$ of the contaminant. The lowest measured lead concentration in MORB is about 0.2 ppm, a factor of 2.5 times greater than the value adopted for uncontaminated MORB on the basis of uranium-lead systematics. On the other hand, the value adopted for the contaminant, 2 ppm, is five to eight times less than values commonly observed for oceanic-island basalts. The lead enrichment adopted for the mixing calculation, 24.6, therefore is conservative. The enrichment factors for strontium and neodymium are much less, and this is the main reason for the greater sensitivity of MORB to lead contamination. If the enriched and depleted reservoirs are chemically distinct layers in the mantle, they will experience convection with scale lengths of the order of one of the layer thicknesses. The individual cells may experience enrichment/depletion events at different times. Thus, the reservoirs, even if global in extent, need not be homogeneous in trace-element geochemistry. In the mantle differentiation scheme I present here, the depleted source region is below the enriched source region. It seems likely that MORB evolves in shallow mantle magma chambers prior to eruption. Therefore, contamination of MORB is probably unavoidable, at least at the low levels discussed here. The isotopes alone, of course, do not con-

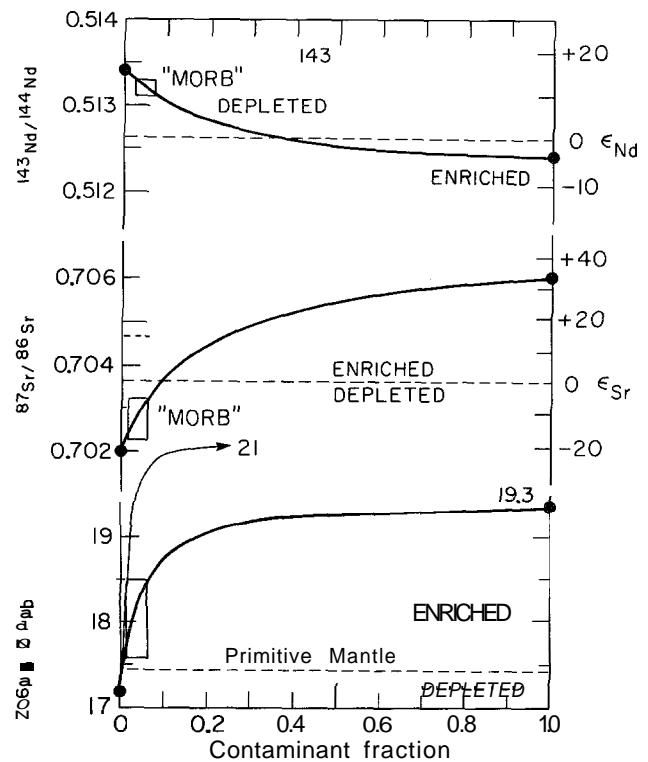


FIGURE 10-3

Isotopic ratios versus contamination. Note that a small amount of contamination has a large effect on the lead system. Enriched magmas and slightly contaminated depleted magmas will both fall in the "enriched" field relative to primitive mantle and will both give "future" ages on a single-stage Pb-Pb evolution diagram. Slight contamination has less effect on ϵ_{Nd} and ϵ_{Sr} , and MORB will still appear depleted. Curves for two values for $^{206}\text{Pb}/^{204}\text{Pb}$ for the contaminant are shown. The correlation line cannot be used to estimate the primitive value for $^{87}\text{Sr}/^{86}\text{Sr}$ if basalts are mixtures (e.g. Fig. 10-2).

strain the locations of the depleted and enriched reservoirs. It is the time sequence of eruption of enriched and depleted basalts, the seismic data for the depth of the MORB reservoir, the tendency of melts to migrate upward and the vulnerability of the shallow mantle to contamination by subduction and trapped melts that suggest the stratification favored here.

ISOTOPIC EVOLUTION OF THE MANTLE

Neodymium-isotope results were initially interpreted in terms of simple one- and two-stage differentiation schemes, with a primary stage characterized by growth in a primitive reservoir followed by secondary growth in a reservoir with constant Sm/Nd ratio. In this scheme the change in Sm/Nd

ratio of the mantle source of MORB was attributed to extraction of the continental crust. Continental tholeiites were regarded as coming from a primitive unfractionated reservoir and MORB from the depleted reservoir. Enriched magmas were considered to be contaminated by the continental crust or to have come from a mantle reservoir that had been metasomatized prior to being sampled.

Lead isotopes, on the other hand, indicate the presence of ancient enriched reservoirs in the mantle and, in many cases, require episodic or continuous differentiation rather than simple two-stage growth. If the U/Pb ratios of the mantle reservoirs have changed with time, it is likely that the Rb/Sr and Sm/Nd ratios have changed as well. Lead isotopes also show that MORB are enriched in U/Pb relative to primitive mantle. Accretional calculations suggest that extensive melting and differentiation were processes that were occurring during most of the accretion of the Earth. Geochemical models for the evolution of the mantle, however, usually assume the survival of a large primitive unfractionated reservoir and that ancient fractionation events involved only very small degrees (1–2 percent) of partial melting, based on the assumption that the continental crust is the only enriched reservoir and that it forms by partial melting of primitive mantle and 100 percent efficient extraction of the crustal melt.

The present levels of Rb/Sr and Nd/Sm in oceanic-island and continental basalts are often too high to explain their strontium and neodymium isotopic ratios by one- or two-stage differentiation schemes. Episodic, multistage or continuous differentiation models are required to interpret lead-isotopic data, and similar models should be applicable to the strontium and neodymium systems. Lead-isotope data identify a single relatively homogeneous reservoir from about 4.5 to 3.8 Ga ago. This reservoir is not necessarily the whole mantle, nor need it have chondritic or terrestrial ratios of the key elements used in isotopic studies, such as U/Th, U/Pb, Rb/Sr and Sm/Nd. It may itself represent the product of early core-mantle or upper mantle–lower mantle separation. The latter may be a result of partial melting during accretion and concentration of aluminum, calcium, and the incompatible trace elements into the upper mantle. If the partial melt fraction, F , is appreciable, say 15–25 percent, then the incompatible elements will be more or less uniformly enriched by a factor of $1/F$ into the upper mantle, and such ratios as Rb/Sr and Sm/Nd will be nearly unfractionated but slightly higher and lower, respectively, than primitive mantle values because of the differences in partition coefficients.

The existence of complementary depleted and enriched (relative to each other) reservoirs is evident in most isotopic systems by about 2 Ga ago or earlier. The process depleting one is presumably enriching the other. For example, transfer of fluids (such as terrestrial KREEP) from one level in the primary reservoir to a different level will generate complementary depleted and enriched reservoirs. The present

levels of enrichment (such as high values of Rb/Sr and U/Pb) inferred for the present source region of many alkali basalts, continental tholeiites and other enriched magmas are so high that these reservoirs must have been enriched very recently, or they have reached their present level of enrichment gradually over time, or they are mixtures of enriched and depleted magmas. The depletion/enrichment process could have started as early as 3.8 Ga ago, but the fractionation may have been gradual. It is useful to calculate the isotopic evolution of a continuously differentiating mantle.

The trend of oceanic-island leads on lead-lead diagrams supports a model of episodic and heterogeneous secondary enrichment in uranium relative to lead of the mantle source regions for oceanic-island basalt (Oldenburg, 1984; Chase, 1981). At the same time, episodic or continuous enrichment of rubidium relative to strontium and neodymium relative to samarium may explain the trace-element and isotopic data for these systems.

It is natural to assume that an enriched reservoir in the mantle, along with the continental crust, is the complement to the depleted reservoir and that both formed over the same time interval. Because of the upward migration of fluids and subduction of sediments and hydrothermally altered oceanic crust, it is also natural to assume that the enriched layer is in the uppermost mantle. Because of the various contributions to enrichment (metasomatism, subduction), it is difficult to determine an appropriate functional form for the time history of enrichment. Because of the isotopic evidence for slow enrichment in the first 1 Ga after continental formation and rapid enrichment in the last billion years, an enrichment of the form $\exp(t/\tau)$ may be appropriate for the early stages of the process, where t is measured from the start of the enrichment/depletion process and τ is a time constant. The time constant of differentiation appears to be several billion years. We therefore adopt

$$f(t) = (\text{Rb/Sr})_N - 1 = ae^{t/\tau} = ae^{t/2}$$

where $(\text{Rb/Sr})_N$ is the mantle-normalized ratio, and similar equations for $f(t)_{\text{Sm/Nd}}$ and U/Pb. Results are shown in Figure 10-4.

If we assume that the fractionation factors $(\text{Rb/Sr})_N - 1$ and $(\text{Sm/Nd})_N - 1$ have grown exponentially with time, with $\tau = 2$ Ga, from 3.8 Ga ago, the magnitude and spread of the ε values are much reduced compared to simple two-stage models. Also the ages of the more enriched reservoirs agree with the ages of the more depleted reservoirs and with the age spread of the continental crust. Although the depleted reservoir may also deplete progressively, successive depletion is difficult, because a large fraction of the incompatible elements is removed with the first melt increment. These results are shown in Figure 10-4. Progressive enrichment and magma mixing are two of the ways that apparently contradictory isotopic and parent/daughter ratios in a magma can be reconciled. It is not necessary, with these

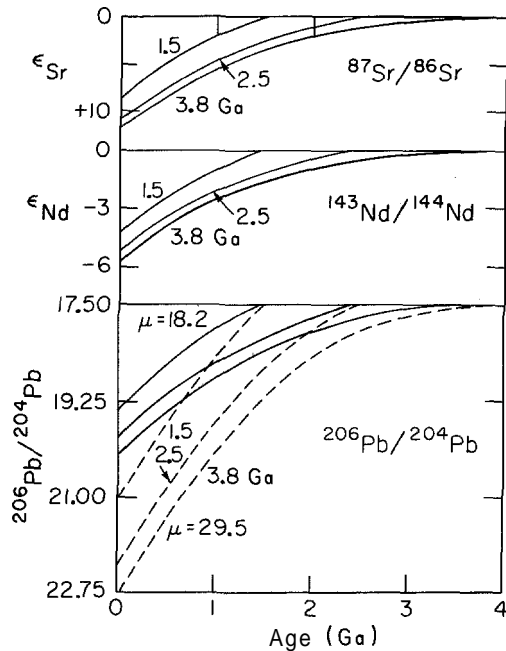


FIGURE 10-4 Evolution of ϵ_{Sr} , ϵ_{Nd} and $^{206}\text{Pb}/^{204}\text{Pb}$ in enriched reservoirs ranging in age from 3.8 to 1.5 Ga. The fractionation factor is assumed to vary as $f(t) = a(e^{t/\tau} - 1)$ where t is measured to the left from the start of differentiation, τ is the characteristic time associated with the fractionation and a is calculated from the present enrichment. Adopted values are $f_{\text{Rb/Sr}} = 0.67$, $f_{\text{Sm/Nd}} = -0.17$ and $^{238}\text{U}/^{204}\text{Pb}$ (μ) = 29.5 (dashed lines) and 18.2 (solid lines). These are determined from the inferred present composition of the source region for oceanic-island and continental flood basalts. τ is assumed to be 2 Ga. Upper curve in each series is for a differentiation initiation age of 1.5 Ga; central and lower curves are for 2.5 and 3.8 Ga respectively. This type of progressive enrichment can result from, for example, progressive crystallization of the donor reservoir, giving more enriched late-stage fluids. Islands showing positive ϵ_{Nd} values may represent mixtures of depleted MORB magmas and enriched (hotspot) magmas. On this basis Tristan and Kerguelen magmas appear to be the most enriched, or least diluted by MORB.

mechanisms, that the Rb/Sr, Sm/Nd and U/Pb ratios, for example, of magmas represent the time-integrated values in the reservoir.

OXYGEN ISOTOPES

The analysis of $^{18}\text{O}/^{16}\text{O}$ ratios is a powerful geochemical tool because of the large difference between crustal and mantle rocks. It has recently become evident that various mantle basalts also exhibit differences in this ratio. Rocks that have reacted with the atmosphere or hydrosphere are typically richer in oxygen-18, through mass fractionation, than those from the mantle. Crustal contamination and re-

flux of crustal material into the mantle serve to increase the $^{18}\text{O}/^{16}\text{O}$ ratio of basalts affected by these processes.

Oxygen is not a trace element; it comprises about 50 weight percent of most common rocks. There are three stable isotopes of oxygen, of mass 16, 17 and 18, which occur roughly in the proportions of 99.76 percent, 0.038 percent and 0.20 percent. Variations in $^{18}\text{O}/^{16}\text{O}$ are expressed as

$$\delta^{18}\text{O}(\text{‰}) = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{m}} - (^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} \right] \times 1000$$

where SMOW is Standard Mean Ocean Water, a convenient standard.

Oxygen isotopic variations in rocks are chiefly the result of fractionation between water and minerals. The fractionation between minerals is small. $\delta^{18}\text{O}$ generally decreases in the order quartz–feldspar–pyroxene–garnet–ilmenite, with olivine and spinel showing large variations. Metasomatism increases $\delta^{18}\text{O}$ as well as the LIL elements (McCulloch and others, 1981). Appropriate fluids can be derived from subducted oceanic crust.

Most unaltered MORB has $\delta^{18}\text{O}$ near 5.7 per mil whereas alkali basalts tend to be more ^{18}O -rich. Carbonatites, potassic lavas and andesites have $\delta^{18}\text{O}$ of 6.0 to 8.5 per mil (Kyser and others, 1982). The maximum $\delta^{18}\text{O}$ variations in rocks known to be derived from the mantle are those recorded in eclogite, 1.5 to 9.0 per mil (Garlich, 1971). Peridotites are generally 5.2 to 7.0, but the olivines in the same rocks range from 4.4 to 7.5. The $\delta^{18}\text{O}$ range in pyroxenes are very much smaller, +5.3 to 6.5 per mil. The upper parts of the subducted slab are extremely ^{18}O -rich ($\delta^{18}\text{O} = 10\text{--}25$ per mil; Gregory and Taylor, 1981), and subduction is a plausible way of increasing $\delta^{18}\text{O}$ of the shallow mantle. Gregory and Taylor (1981) proposed that oxygen-18 and LIL enrichment go hand in hand and suggested that both subducted material and kimberlitic magmas have the appropriate characteristics.

Although $\delta^{18}\text{O}$ values are generally used to investigate crustal contamination, the recognition that mantle magmas also vary in $\delta^{18}\text{O}$ provides an additional tool for characterizing the various mantle reservoirs, and for unraveling the nature of the enrichment process. Whether $\delta^{18}\text{O}$ enrichment is caused by upward migration of kimberlitic fluids or subduction of oceanic crust, it is probable that the enriched layer is shallow. Most islands are high in $^3\text{He}/^4\text{He}$ (that is, "primitive"), suggesting that subducted material, or crustal recycling, is not the sole source of enrichment.

Continental rocks are generally enriched in $\delta^{18}\text{O}$ (6 to 9 per mil) relative to MORB. It is usually stated that the continental crust is enriched relative to the mantle, but some crustal rocks are low, due to interaction with rain water, and some mantle magmas have high $\delta^{18}\text{O}$, as previously mentioned.

Contamination of mantle-derived magmas by the shallow mantle, lithosphere or crust may be caused by bulk as-

sinilation of solid rock, by isotopic and trace-element exchange between magma and wallrock, or by magma mixing between the original melt and melts from the wallrock. Isotopic and trace-element exchange between magma and solid rock are likely to be too inefficient to be important because of the very low diffusivities. Diffusion distances, and therefore equilibration distances, are only a few centimeters per million years. Bulk assimilation or isotope exchange during partial melting are probably the most efficient means of magma contamination, and Taylor (1980) discussed these processes in detail. This is not a simple two-component mixing process. It involves three end-members, the magma, the contaminant and a cumulate phase, which crystallizes to provide the heat required to partially melt the wallrock or dissolve the assimilated material.

Most ocean-ridge tholeiites have $\delta^{18}\text{O}$ near 5.7 per mil. Potassic lavas have $\delta^{18}\text{O}$ values of 6.0 to 8.5, and continental tholeiites range up to 7.0. Oceanic alkalic basalts go as high as 10.7. Kimberlites and carbonatites have values up to 26. Alkalic basalts apparently form in a region of the mantle that is more ^{18}O -rich than the MORB source region. At high temperature clinopyroxene and garnet have lower $\delta^{18}\text{O}$ values than olivine. It is possible, therefore, from the ^{18}O evidence that tholeiites originate in a garnet-clinopyroxene-rich reservoir and alkalic basalts have more olivine in their source regions. In addition, olivine fractionation at low temperature increases the $\delta^{18}\text{O}$ of residual melts.

A sample mixing calculation is shown in Figure 10-5. In order to match the higher $\delta^{18}\text{O}$ values found for oceanic islands and have reasonable amounts of fractionation and contamination, a $\delta^{18}\text{O}$ of about 17 per mil is implied for the enriched component. Oxygen fractionation is ignored in this calculation.

Pillow lavas in the upper parts of ophiolites have $\delta^{18}\text{O}$ values of over 12 per mil (Gregory and Taylor, 1981). Sub-

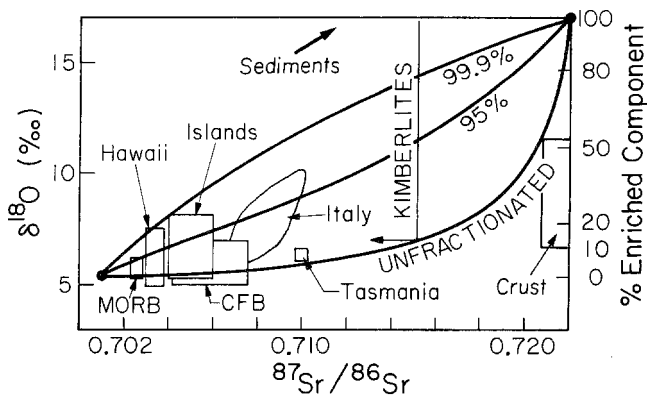


FIGURE 10-5
 $\delta^{18}\text{O}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for magmas, oceanic sediments, kimberlites and continental crust. Mixing curves are shown for various degrees of crystal removal from the depleted end-member.

duction of this material may contribute to the high $\delta^{18}\text{O}$ of the enriched reservoir. Regardless of the origin of the distinct $\delta^{18}\text{O}$ reservoirs, mixing of magmas from these reservoirs can explain the spread of values over the $^{87}\text{Sr}/^{86}\text{Sr}$ - $\delta^{18}\text{O}$ plane.

RARE GASES

Rare-gas isotope pairs place constraints both on the evolution of the atmosphere and on transport processes in the mantle. The rare-gas radiogenic/primordial isotope pairs are ^4He - ^3He , ^{40}Ar - ^{36}Ar , ^{129}Xe - ^{130}Xe and ^{136}Xe - ^{130}Xe . The radiogenic isotopes are produced from α -decay of uranium and thorium, β -decay of potassium-40, β -decay of iodine-129 and spontaneous fission of plutonium-244 and uranium-238. Iodine-129 and plutonium-244 are referred to as extinct since they have respective half-lives of 17 and 76 Ma; they therefore provide constraints on the earliest stages of outgassing of the atmosphere. Due to the volatility of the noble gases and the involatility of the parent isotopes (^{40}K , ^{238}U , ^{235}U , ^{232}Th , ^{244}Pu), the isotope evolution is strongly affected by degassing. This is not the case for the samarium-neodymium and rubidium-strontium systems. Results to date show that the depleted MORB reservoir was outgassed in earliest Earth history. Midocean-ridge basalts, which are low in potassium, uranium, thorium and rubidium compared to ocean-island basalts, are high in $^{40}\text{Ar}/^{36}\text{Ar}$, $^3\text{He}/^4\text{He}$ and $^{129}\text{Xe}/^{130}\text{Xe}$. Ocean-island basalts are higher in the "primordial" components. This does not necessarily mean that they come from a primordial or undegassed reservoir. The presence of primordial gases in the mantle shows that outgassing of the mantle has not been 100 percent efficient. This in turn implies that the crust extraction process has left "crustal elements" behind in the mantle. These are important points since the assumptions that the upper mantle was totally and efficiently depleted by extraction of the continental crust and that the presence of primitive gases implies primitive, undegassed mantle have led to hypotheses about lower-mantle reservoirs and deep-mantle plumes.

Helium Isotopes

Helium has two stable isotopes of mass 3 and mass 4, which vary in their ratio by a factor of more than 10^3 in terrestrial materials. Helium-4, the most abundant isotope, produced by radioactive decay of uranium and thorium, was discovered in the atmosphere of the Sun, from which it takes its name. The cosmic abundance of helium is about 10 percent, making it second only to hydrogen in the composition of stars, such as the Sun, and presumably the preplanetary solar nebula. In the Sun helium is about 100 times more abundant than oxygen and 3000 times more abundant than silicon. The Earth has clearly not received its solar complement of this element, but the small amount that it has

TABLE 10-3
Argon and Helium Abundances

	Units	Atmosphere	Crust	MORB	Plume
^{36}Ar	10^{19}cm^3	12.46	0.04	—	—
	$10^{-8}\text{cm}^3/\text{g}$	2	<3	0.005–0.013	3.3–5.9
^{40}Ar	10^{21}cm^3	36.78	4.6–14	—	—
	$10^{-5}\text{cm}^3/\text{g}$	—	—	0.2–0.4	2
$^{40}\text{Ar}/^{36}\text{Ar}$	10^3	0.2955	1	24.5	0.35–0.50
He	$10^{-10}\text{cm}^3/\text{g}$	—	—	0.2–0.7	10–36
^4He	$10^{-6}\text{cm}^3/\text{g}$	—	—	2–6	28–170
He/ ^4He	10^{-5}	0.14	10^{-2} – 10^{-3}	1.2	>6
$^4\text{He}/^{40}\text{Ar}$	—	10^{-3}	—	2–10	1.4–1.7
$^4\text{He}/^{36}\text{Ar}$	10^4	10^{-4}	—	1.6–2.9	0.05–0.09
$^3\text{He}/^{36}\text{Ar}$	—	—	—	0.16–1.4	0.03–0.06
$(^3\text{He}/^{36}\text{Ar})_N$	—	—	—	20 ± 6	1
$(^{36}\text{Ar})_N$	—	—	—	1	250–1100
$(^3\text{He})_N$	—	—	—	1	5
$^3\text{He}/\text{U}$	—	—	—	-10^{-5}	10^{-3}

Hart and others (1985).

trapped, as primordial helium-3, provides important clues regarding differentiation and outgassing of the Earth.

The atmospheric $^3\text{He}/^4\text{He}$ ratio is about 1.4×10^{-6} (Table 10-3). A small amount of helium-3 is produced by nuclear reactions involving lithium, but most of the helium-3 in the mantle is thought to be original or primordial. The high $^3\text{He}/^4\text{He}$ ratio of mantle gases indicates that the Earth is not completely outgassed. Both isotopes escape from the atmosphere because of their low masses. The residence time of the helium in the atmosphere is about 10^6 years, thus a geochemical mass balance cannot be attempted, but the mantle flux rate can be estimated.

The $^3\text{He}/^4\text{He}$ ratio in gas-rich meteorites is about 3×10^{-4} , about 200 times greater than the atmospheric ratio. About half of the production of helium-4 in the Earth takes place in the continental crust. The $^3\text{He}/^4\text{He}$ ratio in helium from the mantle is at least 100 times greater than the ratio produced in the crust.

The $^3\text{He}/^4\text{He}$ ratio, R, of terrestrial samples varies from less than 10^{-8} to more than 10^{-3} with a general increase from old, stable terranes to currently active regions. These bracket the current atmospheric value of 1.4×10^{-6} and are generally much less than the presumed "cosmic" value of about 10^{-4} . The highest values are found in regions of recent volcanism such as Hawaii, Iceland and Yellowstone and in diamond inclusions, which are probably armored from the addition of radiogenic helium-4. Some hot-spot islands and other plume-like basalts have low R values, suggesting the addition of a low-R component, such as sediments or seawater, or a decrease of R with time due to helium-4 production by uranium and thorium. Studies in Hawaii suggest that the earliest magmas to emerge in a given region are the most enriched in the "primitive" helium-3 component, and R decreases as volcanism pro-

ceeds. R is higher in tholeiites than in alkalis and is relatively low in olivine inclusions.

Midocean-ridge tholeiites average about 8.5 times the atmospheric ratio for $^3\text{He}/^4\text{He}$, and this ratio is remarkably constant. The MORB reservoir, therefore, must be extremely uniform. Basalts and phenocrysts from Hawaii range up to 37 times atmospheric. The $^3\text{He}/^4\text{He}$ ratio in natural diamond crystals from kimberlites ranges up to 280 times atmospheric, close to the solar value. $^3\text{He}/^4\text{He}$ values found in Iceland and Hawaii and along the Reykjanes Ridge can be modeled as two-component mixtures with MORB and Loihi being the end-members. Other islands have lower $^3\text{He}/^4\text{He}$ ratios than MORB, suggesting a third component, or a variably outgassed enriched reservoir. The $^3\text{He}/^4\text{He}$ ratio for oceanic-island basalts is highly variable.

Values of the $^3\text{He}/^4\text{He}$ ratio in some natural diamond crystals range up to 3.2×10^{-4} (Ozima and Zashu, 1983), suggesting that the primitive ratio has been preserved, that these samples have been isolated from uranium and thorium and that crystals can hold helium for long periods of time. These values are close to the solar value ($\sim 4 \times 10^{-4}$) and exceed the value commonly attributed to meteorites and planets. Some of these diamonds appear to be nearly as old as the Earth itself. They appear to have retained high $^3\text{He}/^4\text{He}$ values by being completely isolated from the uranium in the surrounding mantle. This may be evidence that a cold and thick continental lithosphere (refractory and buoyant assemblages of olivine) was an early result of terrestrial differentiation. Cold proto-continental rafts moving away from the hotter regions of the mantle offer a possible explanation for the helium data and other evidence for ancient mantle under some cratons.

The $^3\text{He}/^4\text{He}$ ratio in some oceanic-island basalts is very high. The correlation of $^3\text{He}/^4\text{He}$ with $^{87}\text{Sr}/^{86}\text{Sr}$ on oceanic

islands and along ridge segments is not simple, leading to the speculation that helium and the other incompatible elements are decoupled. Primordial helium-3 is often assumed to come from primordial or undifferentiated mantle, but it can be extracted from primitive mantle in a melt phase and stored elsewhere. If the melt is high in uranium and thorium, the $^3\text{He}/^4\text{He}$ ratio will, of course, decrease with time.

Large oceanic islands such as Hawaii and Iceland not only have some magmas with high $^3\text{He}/^4\text{He}$ but also exhibit a very large variation in $^3\text{He}/^4\text{He}$ for relatively constant $^{87}\text{Sr}/^{86}\text{Sr}$. The wide range of $\delta^{18}\text{O}$ values of basalts from these islands, as well as the low $^3\text{He}/^4\text{He}$ values, indicate involvement of the atmosphere, meteoric water and older altered basaltic crust. Low $^3\text{He}/^4\text{He}$ ratios in island basalts are not necessarily representative of the mantle source region. In Hawaii, the highest $^3\text{He}/^4\text{He}$ ratios are found for the youngest volcanoes and the smallest edifices. This suggests that the gases in the earliest stage of volcanism are representative of the mantle source and gases at later stages are more representative of the lithosphere (Kurz and others, 1983) or that shallow mantle gases are flushed out by the earliest volcanism.

The low $^3\text{He}/^4\text{He}$ and high helium-4 content of olivine xenocrysts in Hawaiian basalts indicate that helium can be trapped in significant quantities in crystals and that this gas can contribute to low measured $^3\text{He}/^4\text{He}$ values of some alkali basalts (Kurz and others, 1983). These observations also indicate that rare gases can be trapped in the upper mantle. The high helium content of xenocrysts relative to glasses also shows that the effective crystal-melt partition coefficient for helium can be high relative to other incompatible elements. The high $^3\text{He}/^4\text{He}$ and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of some Hawaiian basalts show that these basalts are not directly derived from "primitive" mantle. The relation $^3\text{He}/^4\text{He}$ versus $^{40}\text{Ar}/^{39}\text{Ar}$ of hotspot magmas suggests an atmospheric component (Kaneoka and others, 1983).

The $^3\text{He}/^4\text{He}$ ratio of a melt or basalt increases with time at a rate determined by the abundance of uranium and thorium (Craig and Lupton, 1981):

$$J = 0.2355 \times 10^{-12} (\text{U}) \times [1 + 0.123(\text{Th}/\text{U} - 4)]$$

where J is the growth of helium-4 in units of cm^3/g year and U is in ppm. The total $^3\text{He}/^4\text{He}$ is therefore

$$^3\text{He}/^4\text{He} = \frac{(^3\text{He}/^4\text{He})_o \times \frac{[^4\text{He}]_o}{[^4\text{He}]_R} + \left(\frac{^3\text{He}}{^4\text{He}}\right)_R}{\frac{[^4\text{He}]_o}{[^4\text{He}]_R} + 1}$$

where $(^3\text{He}/^4\text{He})_R$ is the production ratio of $^3\text{He}/^4\text{He}$, about 10^{-8} for basalt. Assimilation of deeply buried older basalts by new magma will decrease both $^3\text{He}/^4\text{He}$ and $\delta^{18}\text{O}$.

Mixing calculations are shown in Figure 10-6 with two assumptions about the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the depleted end-member. The highest $^3\text{He}/^4\text{He}$ samples from Loihi can be matched with about 18 percent of the enriched end-member

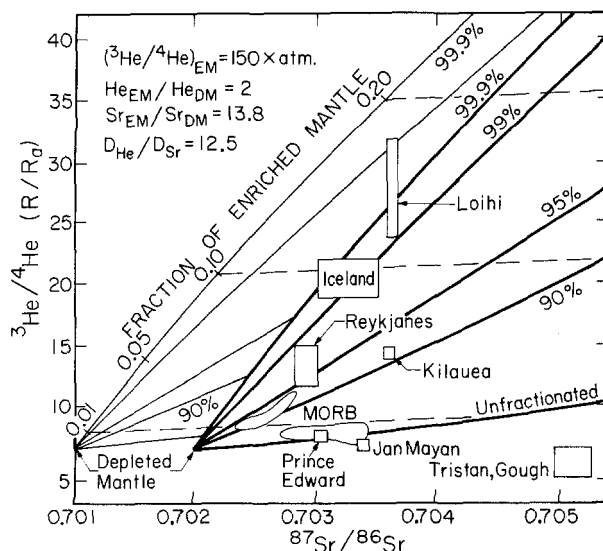


FIGURE 10-6

Mixing curves for $^3\text{He}/^4\text{He}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$. Two choices for the depleted end-member (DM) are shown. Hawaiian basalts imply 90 to over 99 percent crystal fractionation and 5–18 percent contamination from enriched mantle (EM) (Anderson, 1985).

($^3\text{He}/^4\text{He} = 150 \times$ atmospheric) combined with 99.9 percent crystal fractionation of the depleted magma. Islands such as Prince Edward (in the Southern Ocean) and Jan Mayen can be modeled as mixtures involving nearly unfractionated MORB. Tristan da Cunha and Gough may require a third component, such as subducted sediments, or may have experienced previous outgassing. In order to cover the entire range by two-component mixing and fractionation, it is necessary to assume that the helium abundance in the enriched reservoir is about twice the abundance in the depleted reservoir and that the partition coefficient for helium is much greater than for strontium. The partition coefficient for helium in basalt is unknown, but it is not obvious that it will behave as a classic incompatible element. The total helium abundances in some diamonds and xenoliths are higher than in some basalts, suggesting that appreciable helium can be trapped in crystals.

The clinopyroxene-melt partition coefficients for argon and krypton are 0.2 to 0.5, and there is some indication that the value increases with decreasing atomic weight (Hiyagon and Ozima, 1982). These surprisingly high values for the rare gases, compared to the values for other incompatible elements, are of the order of those required to explain the helium and strontium isotopic results by the fractionation mixing, two-components model.

The olivine-basalt partition coefficients for helium, neon and argon are ≈ 0.07 , 0.006–0.08 and 0.05–0.15, respectively (Hiyagon and Ozima, 1986). Clinopyroxene values may be an order of magnitude higher. In the eclogite fractionation model the important phases are clinopyroxene and garnet, but the partitioning of helium into either is un-

known. Garnet might be an important accommodator for the rare gases.

The distribution of $^3\text{He}/^4\text{He}$ in the enriched reservoir is likely to be uneven because it depends on the amount of trapped primordial helium-3, as well as the uranium and thorium content, and age of the enrichment. It therefore depends on the outgassing history as well as the magmatic and metasomatic history of the reservoir. If part of the LIL enrichment is due to reinjection of oceanic crust and sediments, this part of the enriched reservoir will have a low $^3\text{He}/^4\text{He}$ ratio.

Nevertheless, combined crystal fractionation and contamination, utilizing only two end-members, can explain much of the range and several of the trends observed in oceanic basalts. For example, the MORB–Loihi and Kilauea–Loihi trends can be due to increasing fractionation and contamination. The MORB trends require only small differences in the amount of contamination.

The $^3\text{He}/^4\text{He}$ ratio of hotspot magmas may help constrain the enrichment process. Subducted material, a possible candidate for enrichment in LIL, $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$, has low $^3\text{He}/^4\text{He}$, and the ratio decreases with time. Ancient subducted crust or sediment, therefore, cannot be the source of high- $^3\text{He}/^4\text{He}$ basalts. Some oceanic islands are low in $^3\text{He}/^4\text{He}$, and these may have a subducted component. Except for the high $^3\text{He}/^4\text{He}$ found in kimberlitic diamonds, there are few data on kimberlitic material, so this source cannot be evaluated.

If we admit the possibility that helium-3, uranium and thorium can all be concentrated in the enriched source region by upward migrating melts or fluids, then the present-day $^3\text{He}/^4\text{He}$ ratio depends on the $^3\text{He}/(\text{Th}+\text{U})$ ratio and the age of enrichment events and, of course, the degree of outgassing.

The study of $^3\text{He}/^4\text{He}$ has led to several important conclusions:

1. Primordial helium-3 is present; hence, the Earth is not completely outgassed.
2. The results from submarine basalts indicate a uniform, probably well-mixed reservoir. The similarity in results from the Atlantic and the Pacific suggests that the depleted reservoir is global. This suggests that the depleted reservoir is deep.
3. The variability in island basalts shows that the whole mantle does not share this homogeneity. Either the enriched source region is heterogeneous or melts from the enriched source region are variably mixed with depleted basalts.

The Earth is an extensively differentiated and probably well-outgassed planet. The crust, for example, contains 35–58 percent of the estimated mantle-plus-crustal abundances for various incompatibles (Rb, Cs, K, Ba, Th and U). The amount of argon-40 in the atmosphere represents 77 percent of the total produced by 152 ppm potassium that is esti-

mated to reside in the mantle-plus-crust. Since argon-40 is produced slowly over time, its presence in the atmosphere cannot be the result of an early catastrophic outgassing. Helium-3 is probably more outgassed than argon-40, but we do not know what fraction of the primordial component still resides in the mantle.

O’Nions and Oxburgh (1983) concluded that the uranium and thorium abundance in the mantle required to support the observed radiogenic helium flux into the atmosphere would only provide about 5 percent of the mantle heat flux. That can be raised to 10 percent if half the mantle heat flow is due to secular cooling. This implies that vastly more helium is being generated in the Earth than is being outgassed, or that the time constants for the loss of heat and loss of helium differ greatly. Helium brought into the shallow mantle can only escape at ridges and hotspots and only then if magmas are brought close enough to the surface to vesiculate. By contrast heat is continuously lost from the mantle as the seafloor spreads and as continents cool from their last thermal event. Magmas solidifying at depth can even recycle helium back into the mantle. The diffusion distances for helium are relatively short, and therefore helium can be trapped at any depth, not just the lower mantle.

If outgassing was more efficient in early Earth history, then a larger fraction of the mantle argon-40 may reside in the atmosphere than is the case for helium-4 because of the short half-life of potassium-40. It also appears that potassium is more efficiently concentrated in the crust than uranium or thorium and therefore can more readily dump its decay products into the atmosphere. The present rate of outgassing also may not be typical of that integrated over the past 200 Ma. If oceanic islands, plateaus and continental flood basalts are any indication, there may have been more hotspot activity and outgassing during the breakup of Pangaea. Seafloor spreading, and therefore ridge-crest volcanism, was much greater in the recent past than at present.

Two sources of mantle helium can clearly be identified, MORB helium and a high $^3\text{He}/^4\text{He}$ source. The latter is, unfortunately, often called undepleted, undegassed or primitive mantle. The range of isotopic abundances, and correlations, or lack thereof, with other isotopes can be produced by mixing, crystal fractionation, degassing, and subsequent addition of radiogenic ^4He . The location of the high $^3\text{He}/^4\text{He}$ source is not known. It may be inside of crystals, such as garnet or diamond or in a separate part of the mantle, for example, in depleted harzburgites. The shallow mantle may be the best storage place since it is relatively cold and probably buoyant. Entrainment of upward migrating helium by previously depleted harzburgite would make the harzburgite a secondary, rather than primitive, source.

Argon and Helium

The argon-40 in the atmosphere is produced from the decay of potassium-40 in the crust and mantle via the decay equation

$$^{40}\text{Ar} = \lambda_1 ^{40}\text{K}(e^{\lambda_1 \tau} - 1)/\lambda$$

where λ_1 is the decay constant for decay of potassium-40 to argon-40 ($0.581 \times 10^{-10}/\text{yr}$) and λ is the total decay constant of potassium-40 to calcium-40 and argon-40 ($0.5543 \times 10^{-9}/\text{yr}$). The $^{40}\text{K}/\text{K}$ ratio is about 1.17×10^{-4} . The total argon-40 in the atmosphere is then

$$^{40}\text{Ar} = ^{40}\text{Ar}_0 + 1.39 \times 10^{-4} \text{ K}$$

where $\tau = 4.5 \times 10^9$ yr and $^{40}\text{Ar}_0$ is the initial argon-40 content, which is probably negligible compared to that produced and outgassed over the age of the Earth.

The decay equation for helium is

$$^4\text{He} = 8 ^{238}\text{U}(e^{\lambda_8 \tau} - 1) + 7 ^{235}\text{U}(e^{\lambda_5 \tau} - 1) + 6 ^{232}\text{Th}(e^{\lambda_2 \tau} - 1)$$

where the decay constants are $\lambda_8 = 1.551 \times 10^{-10}/\text{yr}$, $\lambda_5 = 9.85 \times 10^{-10}/\text{yr}$ and $\lambda_2 = 4.948 \times 10^{-10}/\text{yr}$. The amount of helium-4 generated in 4.5×10^9 yr is approximately

$$^4\text{He} = 16.64 \text{ U}$$

which gives

$$^4\text{He}/^{40}\text{Ar} = 1.22 \times 10^5 \text{ (U/K)}$$

The predicted bulk Earth value for $^4\text{He}/^{40}\text{Ar}$ is about 1.5 ± 0.2 , which is about 10^5 higher than the atmospheric ratio. The difference is due to the rapid escape of helium from the atmosphere. The bulk Earth value, however, is in the range of both MORB and hotspot magmas.

On the basis of $^3\text{He}/^4\text{He}$ versus $^{40}\text{Ar}/^{36}\text{Ar}$ systematics, there are four discrete reservoirs: atmosphere, continental crust, MORB and "plume." Most basalts appear to be mixtures of material from these reservoirs. Hotspot or "plume," magmas have $^{40}\text{Ar}/^{36}\text{Ar}$ ratios similar to atmospheric values but have $^3\text{He}/^4\text{He}$ up to two orders of magnitude higher. This suggests that hotspot basalts or their source region are contaminated with atmospheric, seawater or sedimentary components or that the present atmosphere is mainly generated by outgassing of the plume source with differential escape of helium-3 relative to helium-4. In any event the mixing of plume magmas with atmosphere, seawater or sediments does not change the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio. Plume magmas therefore appear to be homogeneous in $^{40}\text{Ar}/^{36}\text{Ar}$ just as MORB appears to be homogeneous with respect to $^3\text{He}/^4\text{He}$. If most magmas are mixtures, then He/Ar for the MORB reservoir is greater than He/Ar for the plume source (Hart and others, 1979).

ISOTOPIC CONSTRAINTS ON MAGMA GENESIS

Midocean-ridge basalts (MORB) are the most depleted (low concentrations of LILs, low values of Rb/Sr, Nd/Sm, $^{87}\text{Sr}/$

^{86}Sr , $^{144}\text{Nd}/^{143}\text{Nd}$, $^{206}\text{Pb}/^{204}\text{Pb}$) and the most voluminous magma type. They erupt through thin lithosphere and have apparently experienced some crystal fractionation prior to eruption. Isotopic ratios show that the MORB reservoir was outgassed and depleted more than 10^9 years ago. There is growing evidence that there is also an ancient enriched reservoir in the mantle and that the continental crust is not the only complement to the MORB reservoir (Menzies and Murthy, 1980; Anderson, 1981, 1983; McCulloch and others, 1983). The most enriched mantle magmas are lamproites, kimberlites, and basalts from islands such as Kerguelen, St. Helena and Tristan da Cunha. There is a complete spectrum of basalts lying between these extremes. The presence of helium-3 in MORB and the fact that its $^3\text{He}/^4\text{He}$ is higher than atmospheric (Hart and others, 1979; Kaneoka, 1983) suggests that outgassing was not 100 percent efficient, or that MORB is contaminated. Lead isotopes suggest that MORB has experienced some contamination prior to eruption (Anderson, 1982). Therefore, MORB itself may be a hybrid magma.

The geochemistry of various magma types requires at least two distinct reservoirs in the mantle. The relatively uniform depleted mantle suffered an ancient depletion event, presumably by removal of a residual fluid. The other reservoir, enriched mantle, is less homogeneous and is presumed to provide the enriched signature of hotspot magmas. Correlated LIL and isotopic variations in mantle magmas are often explained by mixing of material from the two reservoirs.

Basalts with high Rb/Sr, La/Yb, and Nd/Sm generally have high $^{87}\text{Sr}/^{86}\text{Sr}$ and low $^{143}\text{Nd}/^{144}\text{Nd}$. These can be explained by binary mixing of depleted and enriched magmas or by mixtures of a depleted magma and a component representing varying degrees of melting of an enriched reservoir (Anderson, 1982). The variable LIL ratios of such an enriched component generates a range of mixing hyperbolas or "scatter" about a binary mixing curve, even if there are only two isotopically distinct end-members. Thus a model with two isotopically distinct reservoirs can generate an infinite variety of mixing lines (Anderson, 1982). In some regions, however, the inverse relationship between LIL and isotopic ratios cannot be explained by binary mixing (Lipman and Mehnert, 1975; Dunlop and Fitton, 1979; Barberi and others, 1980; Menzies and Murthy, 1980b; Zhou and Armstrong, 1982; Chen and Frey, 1983). These regions are all in midplate or thick lithosphere environments, and sublithospheric crystal fractionation involving garnet and clinopyroxene might be expected prior to eruption.

The wide range of isotopic ratios in island and continental basalts has led to the view that the mantle is heterogeneous on all scales. The failure of simple binary mixing to explain the spread of isotopic and trace-element ratios, and the presence of LIL-enriched basalts with time-integrated depleted isotopic ratios, has also given rise to the

concept that recent mantle metasomatism has affected the source region and may even be a prerequisite for magmatism (Boettcher and O'Neil, 1980).

Some of the observations that have been interpreted in terms of metasomatism, or an extremely heterogeneous mantle, are (1) scatter of $^{143}\text{Nd}/^{144}\text{Nd}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ values about the mantle array, (2) lack of correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ or $^3\text{He}/^4\text{He}$, and (3) inverse correlations between La/Ce or Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$. However, if one or both end-members of a hybrid is a fractionated melt, or represents varying degrees of partial melting, then these observations do not necessarily require multiple sources. If melts from one reservoir must traverse the other reservoir on their way to the surface, there is no need for a "plum pudding" mantle or recent metasomatism of the source.

The cases where a depleted magma causes variable degrees of melting of an enriched reservoir or where an undepleted magma partially melts a depleted layer have already been treated (Anderson, 1982; Chen and Frey, 1983). We now treat a fractionating depleted magma interacting with an enriched reservoir. To fix ideas, consider the depleted magma from the depleted-mantle reservoir to be the parent of MORB. If this magma is brought to a near-surface environment, it may fractionate olivine, plagioclase and orthopyroxene. If arrested by thick lithosphere it will fractionate garnet and clinopyroxene. Assume that the fractionating crystals and melt are in equilibrium. I emphasize varying degrees of crystal fractionation, but these results are applicable to the case where the depleted component represents varying degrees of partial melting of a garnet- and clinopyroxene-rich region, such as a garnet pyroxenite lower oceanic lithosphere or an eclogite slab (Chen and Frey, 1983).

There are two situations that have particular relevance to mantle-derived magmas. Consider a "normal" depleted mantle magma. If it can rise unimpeded from its source to

the surface, such as at a rapidly spreading ridge, it yields a relatively unfractionated, uncontaminated melt—MORB. Suppose now that the magma rises in a midplate environment, and its ascent is impeded by thick lithosphere. The magma will cool and crystallize, simultaneously partially melting or reacting with the surrounding shallow mantle. Thus, crystal fractionation and mixing occur together, and the composition of the hybrid melt changes with time and with the extent of fractionation. Fractionation of garnet and clinopyroxene from a tholeiitic or picritic magma at sublithospheric depths (>50 km) can generate alkalic magmas with enriched and fractionated LIL patterns. Let us investigate the effects of combined eclogite fractionation (equal parts of garnet and clinopyroxene) and "contamination" on melts from depleted mantle. "Contamination" is modeled by mixing an enriched component with the fractionating depleted magma. This component is viewed as a partial melt generated by the latent heat associated with the crystal fractionation. The assumed geochemical properties of the end-members, the enrichment factors of the elements in question and the partition coefficients, D , assumed in the modeling are given in Table 10-4. D for six elements (Rb, Sr, Sm, Nd, La and Ce) are the mean for clinopyroxene and garnet (Frey and others, 1978). The figures that follow show various ratios for mixes of a fractionating depleted melt and an enriched component. We assume equilibrium crystal fractionation, as appropriate for a turbulent or permeable magma body, and constant D .

La/Ce Versus $^{87}\text{Sr}/^{86}\text{Sr}$

La/Ce is high in melts relative to crystalline residues containing garnet and clinopyroxene. It is low in depleted reservoirs and high in enriched reservoirs. Low and high values of $^{87}\text{Sr}/^{86}\text{Sr}$ are characteristics of time-integrated depleted and enriched magmas, respectively. Since high $^{87}\text{Sr}/$

TABLE 10-4
Parameters of End-Members

Parameter	Depleted Mantle (1)	Enriched Mantle (2)	Enrichment Ratio (2)/(1)
$^{87}\text{Sr}/^{86}\text{Sr}$	0.701–0.702	0.722	Sr_2/Sr_1 13.8
ϵ_{Nd}	24.6	–16.4	Nd_2/Nd_1 73.8
$^{206}\text{Pb}/^{204}\text{Pb}$	16.5–17.0	26.5	Pb_2/Pb_1 62.5
$^3\text{He}/^4\text{He}$ (R.)	6.5	150	He_2/He_1 2.0
$\delta^{18}\text{O}$ (permil)	5.4	17	O_2/O_1 1.0
La/Ce	0.265	0.50	Ce_2/Ce_1 165.0
Sm/Nd	0.50–0.375	0.09–0.39	
Partition Coefficients			
Rb	0.02	Sr	0.04
La	0.012	Ce	0.03
Sm	0.18	Pb	0, 0.002
He	0.50	Nd	0.09

^{86}Sr implies a time-integrated enrichment of Rb/Sr, there is generally a positive correlation of Rb/Sr and LdCe with $^{87}\text{Sr}/^{86}\text{Sr}$. Some magmas, however, exhibit high LdCe and low $^{87}\text{Sr}/^{86}\text{Sr}$.⁹ This cannot be explained by binary mixing of two homogeneous magmas.

On a theoretical La/Ce versus $^{87}\text{Sr}/^{86}\text{Sr}$ plot (Figure 10-7), the mixing lines between the crystallizing MORB and enriched mantle components reverse slope when MORB has experienced slightly more than 99 percent crystal fractionation. The relationships for equilibrium partial melting and equilibrium, or batch, crystallization are, of course, the same. Therefore, large degrees of crystallization of a MORB-like melt or small amounts of partial melting of a MORB layer are implied by an inverse relationship between La/Ce (or Rb/Sr, La/Yb, Nd/Sm, and so on) and $^{87}\text{Sr}/^{86}\text{Sr}$ (or $^{143}\text{Nd}/^{144}\text{Nd}$) such as observed at many midplate environments. The apparently contradictory behavior of magmas with evidence for current enrichment and long-term depletion is often used as evidence for "recent mantle metasomatism." Figure 10-7 illustrates an alternative ex-

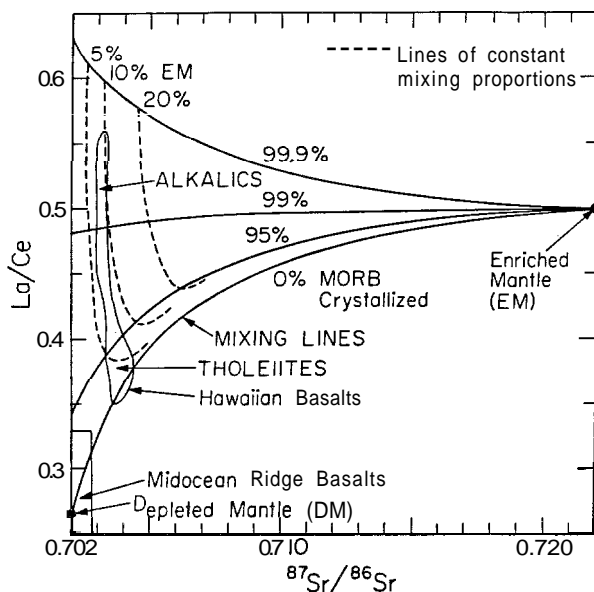


FIGURE 10-7

LdCe versus $^{87}\text{Sr}/^{86}\text{Sr}$ for the fractionation-contamination model, compared with Hawaiian basalts. Unfractionated MORB (DM) has $\text{La/Ce} = 0.265$. La/Ce of the depleted end-member increases as crystal fractionation proceeds. The enriched end-member (EM) has $\text{La/Ce} = 0.5$, in the range of kimberlitic magmas. The Hawaiian tholeiites can be modeled as mixes ranging from pure MORB plus 2–7 percent enriched component to melts representing residuals after 95 percent **clinopyroxene-plus-garnet** crystal fractionation and 5–8 percent enriched component. Alkali basalts involve more crystal fractionation and more contamination. In this and subsequent figures solid curves are mixing lines between EM and melts representing fractionating depleted magmas. Dashed curves are trajectories of constant mixing proportions. Data from Chen and Frey (1983).

planation. Note that, with the parameters chosen, the Hawaiian alkalis have up to 10 percent contamination by the enriched component.

Neodymium Isotopes Versus $^{87}\text{Sr}/^{86}\text{Sr}$

Isotopic ratios for ocean-island and continental basalts are compared with mixing curves (Figure 10-2), these basalts can be interpreted as mixes between a fractionating depleted magma and an enriched component. The value for primitive mantle ($\epsilon_{\text{Nd}} = 0$) is also shown. The primitive mantle value of $^{87}\text{Sr}/^{86}\text{Sr}$ is unknown and cannot be inferred from basalts that are themselves mixtures. For example, the basalts cover a field extending from 0 to 99.9 percent crystal fractionation, and the corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at $s_c = 0$ range from 0.7043 to 0.7066. The extreme situations, constant degree of fractionation combined with variable contamination, and constant mixing proportions combined with variable fractionation, can each explain the trend of the data. Together, they can explain most of the dispersion of the data.

Neodymium Isotopes Versus Sm/Nd

The mixing-fractionation curves for the system ϵ_{Nd} versus Sm/Nd are shown in Figure 10-8. High-Sm/Nd basalts from Iceland, Hawaii, Siberia, Kerguelen, and Brazil all fall near the curve for unfractionated MORB with 1 to 5 percent contamination. Alkalics from large oceanic islands with thick crust (Hawaii, Iceland, and Kerguelen) are consistent with large amounts of crystal fractionation and moderate (5–10 percent) amounts of contamination.

The interpretation is that the more voluminous tholeiites are slightly fractionated and contaminated MORB, while the alkalis have experienced sublithospheric crystal fractionation and contamination prior to eruption. MORB itself has about 1 percent contamination, similar to that required to explain lead isotopes (Anderson, 1982). The Hawaiian tholeiites can be modeled as MORB that has experienced variable degrees of deep crystal fractionation (0 to 95 percent), mixed with 1–5 percent of an enriched component. The alkali basalts represent greater extents of crystal fractionation and contamination. The Columbia River basalts can be interpreted as MORB that has experienced 80 percent crystal fractionation and 5 percent contamination.

Lead and Helium Isotopes

Rubidium, strontium, and the light REEs are classic incompatible elements, and the effects of partial melting, fractionation, and mixing can be explored with some confidence. Relations between these elements and their isotopes

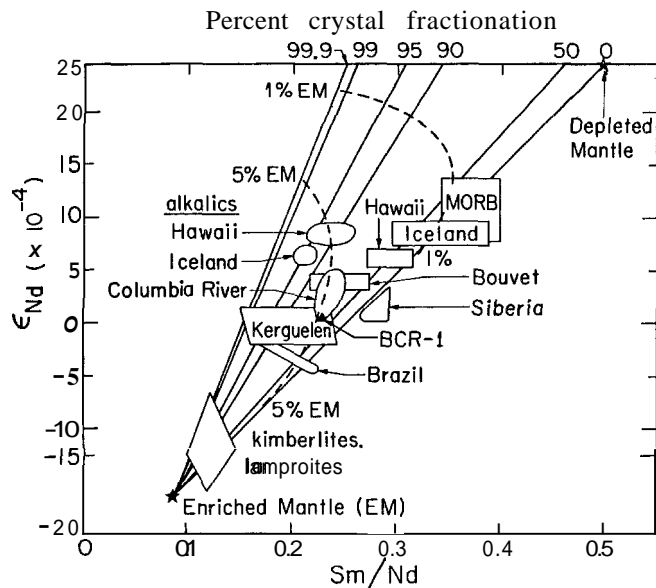


FIGURE 10-8
 $^{143}\text{Nd}/^{144}\text{Nd}$ (relative to primitive mantle) versus Sm/Nd for mixtures of enriched mantle (EM) and residual melts resulting from high-pressure crystal fractionation of MORB-like depleted magma (Anderson, 1985).

should be fairly coherent. Some enriched magmas also have high $^3\text{He}/^4\text{He}$, $\delta^{18}\text{O}$, and $^{206}\text{Pb}/^{204}\text{Pb}$. These isotopes provide important constraints on mantle evolution, but they may be decoupled from the LIL variations and are usually assumed to be so. $^3\text{He}/^4\text{He}$ depends on the outgassing and magmatic history of the depleted reservoir and on the uranium and thorium content and age of the enriched component. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^3\text{He}/^4\text{He}$ are sensitive to the age of various events affecting a reservoir because of the short half-life of uranium. The UIPb ratio may be controlled by sulfides and metals as well as silicates. Nevertheless, it is instructive to investigate the effects of contamination and fractionation on these systems to ferret out what other effects or components are involved.

A minimum of three components is required to satisfy the combined strontium and lead isotopic systems when only simple mixing is considered. St. Helena has high $^{206}\text{Pb}/^{204}\text{Pb}$ —low $^{87}\text{Sr}/^{86}\text{Sr}$; Kerguelen has high $^{87}\text{Sr}/^{86}\text{Sr}$ —low $^{206}\text{Pb}/^{204}\text{Pb}$; MORB has low $^{87}\text{Sr}/^{86}\text{Sr}$ —low $^{206}\text{Pb}/^{204}\text{Pb}$. The lead isotopes in MORB are higher than expected for a primitive or depleted reservoir. A mixing-fractionation curve for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ (Figure 10-9) shows that the data can be explained with only two isotopically distinct mantle reservoirs. However, even if the enriched mantle reservoir is global, it can have variable $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ since these are sensitive to the U/Pb ratio and the age of enrichment events. U/Pb and $^3\text{He}/\text{U}$ of the enriched mantle will change locally by the subduction of sediments and oceanic crust and by the insertion of basalts that do not make their way to the surface. Isotopic ratios of

lead and helium, therefore, are variable and change rapidly with time. The various contributions to the enrichment process (subduction, trapped magmas) make it likely that the enriched reservoir is in the shallow mantle and is laterally inhomogeneous. In this sense the mantle contains multiple reservoirs; their dimensions are likely to be of the order of the size of convection cells.

A MODEL FOR MAGMA GENESIS AND EVOLUTION IN THE MANTLE

Chen and Frey (1983) proposed a model for Hawaiian volcanism that involves melting of an enriched mantle plume from the lower ("primitive") mantle. This upwelling plume traverses a depleted (MORB) region, which partially melts (0.05–2.0 percent); these melts mix in varying proportions to form the spectrum of basalts found in Hawaiian volcanoes. With their choice of end-members the MORB component must be small, less than 2 percent.

The results just described suggest an alternative explanation. Melts from the depleted reservoir rise to the base of the lithosphere, fractionate and mix with melts from the enriched reservoir. At midocean ridges the lithosphere is thin, crystal fractionation occurs at shallow depths, and eruption occurs with little contamination. Midplate volcanism involves crystal fractionation at greater depth, deeper than 60 km. Because of slower cooling at depth, there is more chance for mixing with melts from the asthenosphere and lithosphere prior to eruption. Thus, diapirs from a deep depleted reservoir may be the precursors for both midocean and midplate volcanism, but the trace-element and isotopic spectra of basalts depend on the thickness of the lithosphere or crust. Material from the depleted source, which initiates melting in the shallow enriched reservoir, dominates the mix. The choice of a single enriched component is clearly simplistic, but it serves to illustrate the mechanism. On their ascent MORB diapirs can interact with asthenosphere, oceanic or continental lithosphere, sediments, seawater or subducted material.

In the Chen-Frey model the amount of the MORB component decreases as the inferred degree of partial melting of the MORB source increases, the reverse of what might be expected. The relative proportions of the MORB and enriched components are also the reverse of what the $^3\text{He}/^4\text{He}$ data indicate. Kaneoka (1983) suggested that the MORB component of Hawaiian basalts is more than 50–70 percent. In the present model the amount of contamination increases as crystal fractionation proceeds.

Kaneoka (1983) favored a model in which LIL- and ^3He -rich material from a deep primitive mantle reservoir rises through and mixes with a shallow, depleted region. He argued that if the enriched layer is shallow, plumes should

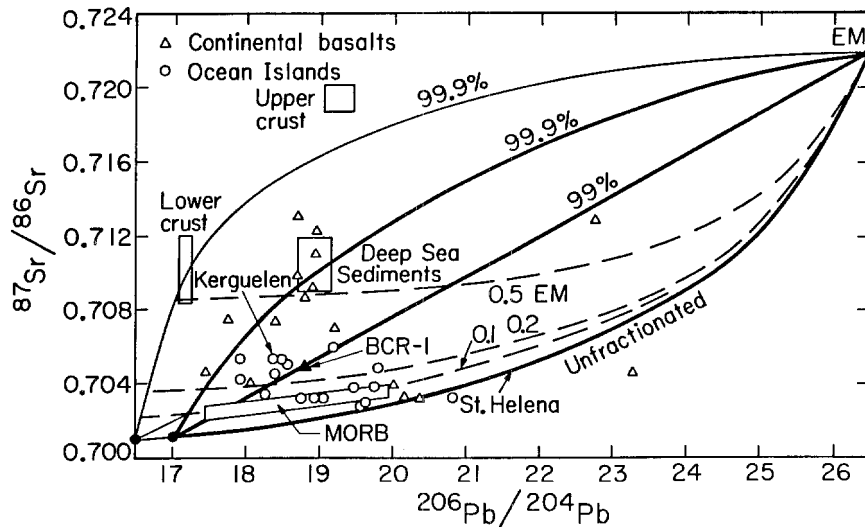


FIGURE 10-9

$^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ trajectories for mixtures of a fractionating depleted MORB-like magma (at two different initial $^{206}\text{Pb}/^{204}\text{Pb}$) and an enriched component. Mixing hyperbolas are solid lines. Hawaiian basalts fall in the region of 50–99 percent crystal fractionation (garnet plus clinopyroxene) and 10–30 percent contamination by EM (dashed lines).

originate at shallow depth, and the only overlying depleted layer is the oceanic lithosphere. However, the distinctive geochemical signature of hotspot basalts may be acquired at shallow depths, and the majority of the erupted material may be depleted basalts rising from greater depth. Continental contamination is an oft-invoked mechanism of this type, although it clearly does not work for the rare gases. An LIL- and ^3He -rich shallow mantle does not imply that plumes originate at shallow depth. In discussions of hotspots it should be recognized that the source of heat, the source of the majority of the magma and the source of the isotopic signatures may be at different depths. Hot regions of the lower mantle, for example, can localize melting in the transition region (400–650 km depth), and depleted melts from this region may become contaminated as they rise. Melts trapped in or rising through the shallow mantle may be responsible for the distinctive physical properties of the low-velocity zone and asthenosphere. Most workers assume that noble gases are strongly partitioned into melts, which then efficiently lose these gases to the atmosphere. Outgassing, however, probably occurs only at relatively shallow depths, where the major gases, such as CO_2 and H_2O , can exsolve (Kaneoka, 1983). If melts are trapped at depth, the noble gases will be as well. The presence of primordial helium-3 and argon-36 in magmas does not require the existence of a previously unmelted or primitive reservoir. The $^3\text{He}/^4\text{He}$ characteristics of hotspot magmas therefore do not require an explanation separate from that for the other isotopes, except that $^3\text{He}/^4\text{He}$ can decrease rapidly with time in a high-uranium reservoir.

The magnitude of tholeiitic volcanism, the dominance of the MORB component in mantle magmas, and the close temporal and spatial relationship of depleted and more enriched and evolved alkalic magmas support a controlling role for melts from the depleted reservoir in mantle magma genesis. Oceanic ridges, islands and seamounts may share a common source and mantle magmas may differ primarily because of different degrees of sublithospheric crystal fractionation and contamination, and because of the nature of the (minor) enriched component. Shallow fractionation and crustal contamination, alteration and recycling will be superimposed on the effects considered here. There is also the possibility that the enriched region is inhomogeneously enriched or veined. Lead isotopes, for example, require more than two end-members (Stille and others, 1983). These may differ in age or intrinsic chemistry or both.

The location of the enriched reservoir, the source of the contamination discussed here, cannot be settled by petrological and geochemical arguments alone. It has been a common, but unfortunate, practice in the geochemical literature to beg or prejudice the issue by using the terms lower mantle, primitive mantle, undegassed mantle, plume reservoir and oceanic-island reservoir interchangeably. The similarity in trace-element and isotopic geochemistry between large islands, seamounts, continental rifts, and island arcs suggests that the enriched source is widespread and shallow. The most enriched magmas, kimberlites, appear to originate at a depth of about 200 km. Midocean ridges can be traced by seismic means to depths greater than 200 km, in some cases greater than 400 km (Walck, 1984; Nataf and

others, 1984). The ascent phase of a deep diapir is characterized by melting. Crystallization is caused by entry of the diapir into the cold surface boundary layer. The heat of crystallization causes melting, or wallrock reactions, and hence crystal fractionation and contamination are concurrent processes. The adoption of a single-stage process involving two isotopically distinct end-members, only one of which is allowed to fractionate, is clearly an oversimplification. The enriched component may represent variable degrees of partial melting of an enriched region that is probably inhomogeneous. The shallow mantle is periodically replenished with subducted material and trapped magmas. Some of these processes serve to diminish the extreme amount of crystal fractionation implied by the present calculations, as can non-Henry's Law behavior (Harrison and Wood, 1980; Harrison, 1981). The possibility of large amounts of eclogite or clinopyroxene fractionation has been discussed by O'Hara (1973) and by many others (Frey and others, 1974; O'Hara and others, 1975; Clague and Bunch, 1976; Maaløe and Peterson, 1976; O'Nions and others, 1976; Leeman and others, 1977; de Argollo and Schilling, 1978; Bender and others, 1978).

A thin, shallow layer is unlikely to be globally homogenized by plate tectonic processes. The large-scale isotope anomaly in the southern hemisphere mantle (Hart, 1984) may have been the locus of ancient subduction, just as the circum-Pacific belt is today or the circum-Pangaea belt was in the Cenozoic. In this case the southern hemisphere anomaly would be due to an ancient subducted component in the shallow mantle (high ^{87}Sr , ^{206}Pb , ^4He). Such an anomaly would be smeared out in time, in the direction of mantle flow, but would diffuse only slowly across the upwellings and downwellings that separate upper-mantle convection cells, particularly if it is embedded in buoyant material such as harzburgite.

This model, which has been approached from various lines of evidence in this book, contradicts conventional views of hotspot petrogenesis. The enriched reservoir is shallow rather than deep, and it may be relatively infertile, that is, low in CaO and Al_2O_3 . Being shallow it can collect volatiles and LIL by subduction and by trapping of fluids rising from below. Although global, it is unlikely to be homogeneous. It protects the deeper, depleted but fertile (low LIL, high CaO and Al_2O_3) reservoir from contamination. It is usually assumed that the source of heat, the source of the basalts and the source of the hotspot geochemical signatures are all the same. The relative stationarity of hotspots, the associated swells and high geoid may be due to increased melting in the upper mantle caused by locally high lower-mantle temperatures rather than transfer of material from the lower mantle to the surface. It is the thickness of the lithosphere that controls the geochemical signature of intraplate volcanics, not the ease of communication to the lower mantle. The lower mantle, other than being a source of heat, may not be involved at all in petrogenesis.

References

- Anderson, D. L. (1981) Hotspots, basalts, and the evolution of the mantle, *Science*, *213*, 82–89.
- Anderson, D. L. (1982) Isotopic evolution of the mantle, *Earth Planet. Sci. Lett.*, *57*, 1–24.
- Anderson, D. L. (1983) *J. Geophys. Res.*, *88*, B41–B52.
- Anderson, D. L. (1985) *Nature*, *318*, 145–149.
- Barberi, F., L. Civetta and J. Varet (1980) Sr isotopic composition of Afar volcanics and its implication for mantle evolution, *Earth Planet. Sci. Lett.*, *50*, 247–259.
- Bender, J. F., F. N. Hodges and A. E. Bence (1978) Petrogenesis of basalts from the FAMOUS area; experimental study from 0 to 15 kilobars, *Earth Planet. Sci. Lett.*, *41*, 277–302.
- Boettcher, A. L. and O'Neil, J. R. (1980) *Am. J. Sci.*, *280A*, 594–621.
- Chase, C. G. (1981) Oceanic island Pb; two-stage histories and mantle evolution, *Earth Planet. Sci. Lett.*, *52*, 277–284.
- Chen, C.-Y. and Frey, F. A. (1983) *Nature*, *302*, 785–789.
- Clague, D. and Bunch, T. E. (1976) *J. Geophys. Res.*, *81*, 4247–4256.
- Craig, H. and Lupton, J. (1981) In *Sea I*, (C. Emiliani, ed.) 391–428, Wiley, New York.
- de Argollo, R. M. and Schilling, J. G. (1978) *Nature*, *276*, 24–28.
- Dunlop, H. M. and Fitton, J. G. (1979) *Contr. Miner. Petrol.*, *71*, 125–131.
- Frey, F. A., W. B. Bryan and G. Thomson (1974) Atlantic Ocean floor; geochemistry and petrology of basalts from Legs 2 and 3 of the Deep Sea Drilling Project, *J. Geophys. Res.*, *79*, 5507–5527.
- Frey, F. A., D. H. Green and S. D. Roy (1978) Integrated models of basalts petrogenesis: A study of quartz tholeiites to olivine melilitites from southeastern Australia utilizing geochemical and experimental petrological data, *J. Petrol.*, *19*, 463–513.
- Garlick, G., I. MacGregor, and D. Vogel (1971) Oxygen isotope ratios in eclogites from kimberlites, *Science*, *171*, 1025–1027.
- Gregory, R. T. and H. P. Taylor, Jr. (1981) An oxygen isotope profile in a section of Cretaceous oceanic crust, Samail ophiolite, Oman, *J. Geophys. Res.*, *86*, 2737–2755.
- Harrison, W. J. (1981) *Geochim. Cosmochim. Acta*, *45*, 1529–1544.
- Harrison, W. J. and B. J. Wood (1980) An experimental investigation of the partitioning of REE between garnet and liquid, *Contrib. Mineral. Petrol.*, *72*, 145–155.
- Hart, R., J. Dymond and L. Hogan (1979) Preferential formation of the atmospheric-sialic crust system from the upper mantle, *Nature* *278*, 156–159.
- Hart, R., L. Hogan and J. Dymond (1985) The closed-system approximation for evolution of argon and helium in the mantle, crust and atmosphere, *Chem. Geol.*, *52*, 45–73.
- Hart, S. R. (1984) A large-scale isotope anomaly in the Southern Hemisphere mantle, *Nature*, *309*, 753–757.
- Hiyagon, H. and M. Ozima (1982) Noble gas distribution between basalt melt and crystals, *Earth Planet. Sci. Lett.*, *58*, 255–264.

- Hiyagon, H. and M. Ozima (1986) *Geochim. Cosmochim. Acta*, 50, 2045.
- Houtermans, F. G. (1947) *Z. Naturforsch.*, 2a, 322.
- Kaneoka, I. (1983) Noble gas constraints on the layered structure of the mantle, *Nature*, 302, 698–700.
- Kaneoka, I., N. Takaoka and J. D. Clague (1983) Noble gas systematics for coexisting glass and olivine crystals in basalts and dunite xenoliths from Loihi Seamount, *Earth Planet. Sci. Lett.*, 66, 427–437.
- Kramers, J. D. (1977) Lead and strontium isotopes in Cretaceous kimberlites and mantle-derived xenoliths from southern Africa, *Earth Planet. Sci. Lett.*, 34, 419–431.
- Kurz, M. D., Jenkins, W. J., Hart, S. R. and Clague, D. A. (1983) Helium isotopic variations in volcanic rocks from Loihi Seamount and the Island of Hawaii, *Earth Planet. Sci. Lett.*, 66, 388–406.
- Kyser, T. K., J. R. O'Neil and I. S. E. Carmichael (1982) Genetic relations among basic lavas and ultramafic inclusions; evidence from oxygen isotope compositions, *Contrib. Mineral. Petrol.*, 81, 88–102.
- Leeman, W. P., A. V. Murali, M.-S. Ma and R. A. Schmitt (1977) Mineral constitution of mantle source regions for Hawaiian basalts; rare earth element evidence for mantle heterogeneity, *Oregon Dept. Geol. Minerals. Indus. Bull.*, 96, 169–183.
- Lipman, P. W. and H. H. Mehnert (1975) Late Cenozoic basaltic volcanism and development of the Rio Grande Depression in the southern Rocky Mountains, *Geol. Soc. Am. Mem.*, 144, 119–154.
- Maaløe, S. and Peterson, T. S. (1976) *Lithos* 9, 243–252.
- McCulloch, M. T., R. Arculus, B. Anappell and J. Ferguson (1982) Isotopic and geochemical studies of nodules in kimberlites, *Nature* 300, 166.
- McCulloch, M. T., R. T. Gregory, G. J. Wasserburg and H. P. Taylor, Jr. (1981) Sm-Nd, Rb-Sr and O-18/O-16 isotopic systematics in an oceanic section; evidence from the Smail ophiolite, *J. Geophys. Res.*, 86, 2721–2735.
- Menzies, M. and V. R. Murthy (1980a) Enriched mantle; Nd and Sr isotopes in diopsides from kimberlite nodules, *Nature* 283, 634–636.
- Menzies, M. and V. R. Murthy (1980b) Nd and Sr isotope geochemistry of hydrous mantle nodules and their host alkali basalts; implications for local heterogeneities in metasomatically veined mantle, *Earth Planet. Sci. Lett.*, 46, 323–334.
- Nataf, H.-C., Nakanishi, I. and Anderson, D. L. (1984) Anisotropy and shear velocity heterogeneities in the upper mantle, *Geophys. Res. Lett.*, 11, 109–112.
- O'Hara, M. J. (1973) Non-primary magmas and dubious mantle plume beneath Iceland, *Nature*, 243, 507–508.
- O'Hara, M. J., M. J. Saunders and E. L. P. Mercy (1975) Garnet-peridotite, primary ultrabasic magma and eclogite; interpretation of upper mantle processes in kimberlite, *Phys. Chem. Earth*, 9, 571–604.
- Oldenburg, D. W. (1984) The Inversion of Lead Isotope Data, *Geophys. J. R. Astron. Soc.*, 78, 139–158.
- O'Nions, R. K. and Oxburgh, E. R. (1983) Heat and helium in the Earth, *Nature*, 306, 429–431.
- O'Nions, R. K., R. J. Pankhurst and K. Gronvold (1976) Nature and development of basalt magma sources beneath Iceland and the Reykjanes Ridge, *J. Petrol.*, 17, 315–338.
- Ozima, M. and S. Zashu (1983) Primitive helium in diamonds, *Science*, 219, 1067–1068.
- Qzima, M., S. Zashu, D. P. Matley and C. T. Pillinger (1985) Helium, argon and carbon isotopic compositions in diamonds and their implications in mantle evolution, *Geochim. J.*, 19, 127–134.
- Patterson, C. (1956) Age of meteorites and the Earth, *Geochim. Cosmochim. Acta*, 10, 230–237.
- Stille, P., Unruh, D. M. and Tatsumoto, M. (1983) Pb, Sr, Nd and Hf isotopic evidence of multiple sources for Oahu, Hawaii basalts, *Nature* 304, 25–29.
- Sun, S., M. Tatsumoto and J. G. Schilling (1975) Mantle plume mixing along the Reykjanes Ridge axis; lead isotopic evidence, *Science*, 190, 143–147.
- Taylor, H. P., Jr. (1980) The effects of assimilation of country rocks by magmas on $^{18}\text{O}/^{16}\text{O}$ systematics in igneous rocks, *Earth Planet. Sci. Lett.*, 47, 243–254.
- Walck, M. C. (1984) The P-wave upper mantle structure beneath an active spreading center; the Gulf of California, *Geophys. J. Roy. Astron. Soc.*, 76, 697–723.
- Zhou, X. and R. L. Armstrong (1982) Cenozoic volcanic rocks of eastern China; secular and geographic trends in chemistry and isotopic composition, *Earth Planet. Sci. Lett.*, 58, 301–329.