Radiogenic Isotope Geochemistry I: The Mantle

INTRODUCTION

The initial use of radioactive and radiogenic isotopes in geology was directed exclusively toward geochronology. The potential geochemical applications became apparent only later. One of the first to recognize the potential of radiogenic isotope studies was Paul Gast, who was a student of Al Nier, whom we have already met. In what was one of the first papers to apply radiogenetic isotopes to a geochemical problem (the composition of the mantle), Gast (1960) described the principles of Sr isotope geochemistry as follows:

In a given chemical system the isotopic abundance of $^{87}\text{Sr}$ is determined by four parameters: the isotopic abundance at a given initial time, the Rb/Sr ratio of the system, the decay constant of $^{87}\text{Rb}$, and the time elapsed since the initial time. The isotopic composition of a particular sample of strontium, whose history may or may not be known, may be the result of time spent in a number of such systems or environments. In any case the isotopic composition is the time-integrated result of the Rb/Sr ratios in all the past environments. Local differences in the Rb/Sr will, in time, result in local differences in the abundance of $^{87}\text{Sr}$. Mixing of material during processes will tend to homogenize these local variations. Once homogenization occurs, the isotopic composition is not further affected by these processes. Because of this property and because of the time-integrating effect, isotopic compositions lead to useful inferences concerning the Rb/Sr ratio of the crust and of the upper mantle. It should be noted that similar arguments can be made for the radiogenic isotopes of lead, which are related to the U/Pb ratio and time.

Gast’s first sentence is simply a statement of the radiogenic growth equation for the Rb-Sr system:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0 + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} \left(e^{\lambda t} - 1\right)$$

Gast’s statement remains a valid and succinct summary of the principles of isotope geochemistry. The only change we need to make is to modify the last sentence to add mention of the radiogenic isotopes of Nd, Hf, Os, etc.

A principal objective of geology is to understand how the Earth evolved from its initial state to its present one. Radiogenic isotope geochemistry is uniquely suited for this sort of study because an isotope ratio such as $^{87}\text{Sr}/^{86}\text{Sr}$ is a function not only of the differentiation processes which fractionate Rb from Sr, it is also a function of the time at which the fractionation occurred. On a continuously evolving Earth, ancient features tend to be destroyed by subsequent processes. For example, erosion of rock to form a new sedimentary rock destroys information about the large-scale structure of the pre-existing rock. If the sediment is sufficiently coarse-grained, some information about the fine-scale structure of parent rock will be preserved. If the sediment produced is fine-grained, such as shale, no structural information is preserved. Some chemical information might be preserved in this case, although often very little. Isotopic ratios of the shale, however, preserve information not only about the chemistry of the parent, but also about its age of formation. Similarly, melting of the sediment to form granite destroys all structural information, but often considerable chemical information is preserved. Isotope ratios, however, preserve, albeit incompletely, information about both chemistry and time.

As Gast said, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is a function of the time-integrated Rb/Sr. Ultimately, we can draw much broader inferences than merely the time-integrated Rb/Sr ratio. Rb and Sr are both trace ele-
ments, and together account for only a few ppm of the mass of the Earth. However, Rb and Sr share some of their properties with other elements of their group: Rb with the alkalis, Sr with the alkaline earths. So Rb/Sr fractionations tell us something about alkali/alkaline earth fractionations. In addition, since Rb is highly incompatible and Sr only moderately so, Rb/Sr fractionations tell us something about the fractionation of incompatible elements from compatible or less incompatible elements. Similarly Sm/Nd variations are related to variations between light and heavy rare earths, as well as incompatible–less incompatible element variations. We have some knowledge of the processes that fractionate the alkalis and alkaline earths and the light and heavy rare earths. Thus knowledge of variations in these element ratios allows us to limit the range of possible processes occurring within the Earth; the time parameter in equation 6.01 allows us the limit the range of possible times at which this fractionation occurred.

DEFINITIONS: TIME-INTEGRATED AND TIME AVERAGED

Gast stated that the $^{87}\text{Sr}/^{86}\text{Sr}$ is a function of the time-integrated Rb/Sr ratio. What did he mean by “time-integrated”?

Suppose the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio evolves in some reservoir in some complex way. Let’s allow the $^{87}\text{Rb}/^{86}\text{Sr}$ to be an arbitrary function of time such as $^{87}\text{Rb}/^{86}\text{Sr} = t + \sin(5 \times t/\pi) + 1$. This is shown plotted in Fig. 6.01a. If we integrate $^{87}\text{Rb}/^{86}\text{Sr}$ with respect to time, we get the area under the curve, of course. From that, we can find the average $^{87}\text{Rb}/^{86}\text{Sr}$ simply by dividing the area under the curve by $(t - t_0)$, which is 3.3. The $^{87}\text{Sr}/^{86}\text{Sr}$ would evolve as shown by the solid line in Fig. 6.01b. Just as we can calculate the average $^{87}\text{Rb}/^{86}\text{Sr}$ ratio from the area under the curve in figure

![Graph](image_url)
Isotope Geochemistry

Chapter 6

Spring 2011

6.01a, we can deduce the average \(^{87}\text{Rb}/^{86}\text{Sr}\) in a reservoir if we know the initial and final values of \(t\) and \(^{87}\text{Sr}/^{86}\text{Sr}\). It is in this sense that \(^{87}\text{Sr}/^{86}\text{Sr}\) yields a time-integrated value of \(^{87}\text{Rb}/^{86}\text{Sr}\).

Notice that the same final \(^{87}\text{Sr}/^{86}\text{Sr}\) value in Fig. 6.01b would have been reached if \(^{87}\text{Rb}/^{86}\text{Sr}\) had a constant value of 3.3 (\(^{87}\text{Sr}/^{86}\text{Sr}\) evolves along the dashed line). It could have been reached by an infinite other number of paths as well. Thus, while we can deduce the time-averaged \(^{87}\text{Rb}/^{86}\text{Sr}\) of a reservoir over its history from the \(^{87}\text{Sr}/^{86}\text{Sr}\), we cannot decipher the details of the evolution (i.e., the exact path) of the \(^{87}\text{Rb}/^{86}\text{Sr}\) ratio. An interesting feature of the U-Pb system is that we can constrain, though not specify exactly, the evolutionary path. This is because the two isotopes of U have very different half-lives.

We will begin our study of isotope geochemistry with an examination of mantle geochemistry. We will then turn to the geochemistry of the continental crust. The two problems are closely related, so ultimately, we will attempt to understand the relationship between chemical evolution of the crust and of the mantle.

**ISOTOPE GEOCHEMISTRY OF THE EARTH’S MANTLE**

The mantle constitutes two thirds of the mass of the Earth and very nearly the entire mass of the silicate Earth. The relative abundances of many elements in the mantle, therefore, should be close to that of the Earth as a whole, most particularly for those elements that do not partition into either the core or the crust. We will begin with a working hypothesis that the crust, which constitutes only 0.5% of the mass of the Earth, has been created by partial melting of the mantle. This is one of only two possible alternatives: either the crust was formed at the same time as the Earth or it grew out of the mantle. There is no a priori reason why either of these two must be the case; we simply arbitrarily chose the second (in due course we will see that isotopic data substantiate our choice).

Doing so allows us to define a reservoir that we shall call **primitive mantle** and is equivalent to the composition of the bulk Earth less the composition of the core. In mathematical notation, then:

\[
m_{PM}[E]_{PM} = m_E[E]_E - m_C[E]_C
\]

where \(m\) denotes mass, the subscripts PM, E, and C denote primitive mantle, bulk Earth, and core respectively, and \([E]\) is a \(1 \times 92\) matrix containing the concentrations of the elements in the reservoir. Thus the relative abundances of lithophile elements (those elements for which \(E_C = 0\)) in the primitive mantle are the same as in the bulk Earth. The average modern mantle composition is then equal to the primitive mantle less the present composition of the crust:

\[
m_M[E]_M = m_{PM}[E]_{PM} - m_K[E]_K
\]

where the subscript \(K\) denotes continental crust and \(M\) the mantle. Our formulation implicitly assumes the core was formed before the crust. Again this is a somewhat arbitrary choice, but we have seen that deviation of terrestrial \(^{182}\text{W}/^{183}\text{W}\) from chondritic suggests the core formed early. Similar mass balance equations may be written for isotope ratios (though not for ratios involving different elements – this introduces non-linearities and requires slightly more complex mass balance equations).

The mantle is not generally accessible for direct sampling, so geochemists must resort to indirect samples. Much of the information we have about the geochemistry of the Earth’s mantle comes from studies of mantle-derived magmas; other samples of the mantle include peridotite* massifs and xenoliths.

---

* Peridotite is a rock which consists of greater than 50% olivine, \([\text{Mg,Fe}]_2\text{SiO}_4\); the term peridotite comes from the gem name of olivine, peridot. Various lines of evidence, including density, seismic velocities, and the assumption of an approximately chondritic Earth, indicate the mantle must consist of peridotite. Other essential minerals in the upper mantle are clinopyroxene (\([\text{Mg,Fe}]_2\text{SiO}_4\) and orthopyroxene (\([\text{Mg,Fe}]_2\text{SiO}_4\), and an aluminous phase, either plagioclase (\(\text{CaAl}_2\text{Si}_2\text{O}_8\)), spinel (\(\text{MgAl}_2\text{Si}_2\text{O}_6\)), or garnet (\([\text{Mg,Fe}]_3\text{Al}_2\text{Si}_3\text{O}_12\)) depending on pressure. Most other elements will be dissolved in these 4 phases. In the lower mantle, this assemblage is replaced by one consisting primarily of Mg-perovskite (\(\text{Mg,Fe,Al}_2\text{Si}_3\text{O}_7\)) and magnesiowüstite (\(\text{Mg,Fe}\)).
liths” in magmas. The utility of the peridotite massifs is limited by their rarity and metamorphic and metasomatic processes associated with emplacement in the crust; information from xenoliths is limited both by their rarity and their small size; the information from basalts is limited because all structural information is lost and much of the chemical information is ‘distorted’ by the partial melting process. But all three types of samples have particular advantages as well. Together, they provide a picture of the composition and structure of the mantle complimentary to the information derived from geophysical observations such as seismic waves, free oscillations, etc.

A xenolith is any foreign rock found in an igneous rock. Xenoliths of peridotite in igneous rocks are often pieces of mantle that have been carried to the surface by ascending magma.

Figure 6.02. Sr and Nd isotopic systematics of the crust and mantle. Oceanic island basalts and MORB sample major reservoirs in the mantle. Continental basalts represent mixtures of various components, including mantle plumes, subcontinental lithosphere, and continental crust. Horizontal grey band is the estimated $\varepsilon_{\text{Nd}}$ of the bulk silicate of Caro and Bourdon (2010); vertical gray band between dashed lines in their estimated bulk silicate Earth $^{87}\text{Sr}/^{86}\text{Sr}$.
The Sr-Nd-Hf Picture

Figure 6.02 shows the Sr and Nd isotopic characteristics of the Earth’s major silicate reservoirs. We begin by focusing on the picture of the mantle provided by isotopic compositions of basalts† derived from the suboceanic mantle. Initially, we’ll focus on oceanic basalts and avoid continental ones for two reasons: 1.) many are contaminated by the continental crust through which they ascend and 2.) the subcontinental lithosphere, from which some of the continental basalts are derived, does not convect and hence many not be as well mixed and as representative of the mantle as oceanic basalts derived from the convecting mantle.

Figure 6.03 shows the isotopic compositions of oceanic basalts – mid-ocean ridge basalts and oceanic island basalts in detail. Mid-ocean ridge basalts (MORB) are those erupted at plate boundaries along the Earth’s 50,000 km mid-ocean ridge system. Oceanic island basalts (OIB) are those that erupt on oceanic island volcanoes, such as the Hawaiian ones, and include oceanic islands, such as Iceland, that lie on mid-ocean ridges. The first observation is that Nd and Sr isotope ratios are inversely correlated and

---

† By definition, basalt is an extrusive igneous rock (i.e., lava) with less than 52% SiO$_2$. Basalt is the primary product of melting of the mantle. Mid-ocean ridge basalts are simply those lavas erupted at mid-ocean ridge spreading centers, i.e., divergent plate boundaries.
the region occupied by the oceanic basalt data is often referred to as the “mantle array”. The second observation is that, although there is overlap, MORB have the lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and highest $\varepsilon_{\text{Nd}}$ than OIB. Variations in radiogenic isotope ratios in basalts result from variations in parent-daughter ratios in the mantle over great lengths of time. For example, to create a $\varepsilon_{\text{Nd}}$ variation in $^{147}\text{Sm}/^{144}\text{Nd}$ would require a variation in $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.02, or about 10%, that existed for 1.4 Ga. We infer MORB come from a source with lower time-integrated $^{87}\text{Rb}/^{86}\text{Sr}$ and higher $^{147}\text{Sm}/^{144}\text{Nd}$ than OIB.

Nd isotopes systematics can help put the relative differences between MORB and OIB in context because $^{142}\text{Nd}/^{144}\text{Nd}$ ratios provide some constraints on the Sm/Nd ratio of the silicate Earth and primitive mantle. As we saw in the last Chapter, $^{142}\text{Nd}/^{144}\text{Nd}$ ratios of all modern terrestrial materials are about 18 ppm higher than those of ordinary chondrites. How different the Sm/Nd ratio of the Earth must be from chondritic depends somewhat on the very early history of the Earth, but Caro and Bourdon (2010) estimate the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the bulk Earth as 0.2082±0.004 compared to a chondritic value in the range of 0.1960−0.1966. This would mean that the bulk silicate Earth, or at least the observable part of it (if a hidden low $^{147}\text{Sm}/^{144}\text{Sm}$ reservoir exists), has $\varepsilon_{\text{Nd}} = 6.9±1.9$. Assuming the “mantle array” in Figure 6.03, Caro and Bourdon estimated the $^{87}\text{Sr}/^{86}\text{Sr}$ of the bulk (observable) silicate Earth as 0.7030±0.004. These values are illustrated on Figure 6.02 as grey bands. On average, MORB have $\varepsilon_{\text{Nd}} = 8.53$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.70289$, so-called “normal MORB”, which are those that are light rare earth depleted, have $\varepsilon_{\text{Nd}} = 9.25$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.70273$ (White, 2011). Thus MORB have higher time-integrated $^{147}\text{Sm}/^{144}\text{Nd}$ lower $^{87}\text{Rb}/^{86}\text{Sr}$ than bulk Earth, – one that is relatively depleted in more incompatible elements, such as Rb and Nd compared to more compatible ones such as Sr and Sm. For this reason, we often speak of MORB as being derived from a “depleted”, meaning incompatible element-depleted, reservoir.

Although we tend to think of MORB and OIB as being isotopically distinct, there is in fact consider-

Figure 6.04. Comparison of Nd isotope ratio analyses of 1679 MORB and 2380 OIB from the PetDB and GEOROC databases. While distributions overlap, the two groups have different means and different spreads, with these differences being highly statistically significant.
able overlap in the isotopic compositions of these groups. This is illustrated in Figure 6.04 for $\varepsilon_{\text{Nd}}$. Nevertheless, the means of the two are quite different, 8.5 and 5.0 respectively. MORB also clearly have a more uniform isotopic compositions with less dispersion than OIB, implying the reservoir from which MORB are derived is less heterogeneous.

In the above discussion, we have transformed the isotopic information into information about parent-daughter ratios. The next step is to consider those processes that can fractionate, or change, the parent-daughter ratios. Rb is more incompatible than Sr, while Nd is more incompatible than Sm. This suggests the mantle has been affected by a process that removes the more incompatible elements. Partial melting and extraction of the melt is such a process. If, as we supposed above, the crust has formed by extraction of the mantle, then the depleted isotopic signature of the mantle might just reflect formation of the continental crust. The source of MORB appears to have been more depleted, perhaps having lost a greater melt fraction, than the source of OIB. There are, however, other explanations for the difference between MORB and OIB, which we will consider later.

Figure 6.05 shows $^{176}\text{Hf}/^{177}\text{Hf}$ ratios plotted against Nd isotope ratios. As we expect from what we know of the behavior of the parents relative to the daughters, $\varepsilon_{\text{Hf}}$ is negatively correlated with $^{87}\text{Sr}/^{86}\text{Sr}$ and positively correlated with $\varepsilon_{\text{Nd}}$. From the intersection of the $\varepsilon_{\text{Hf}}$–$\varepsilon_{\text{Nd}}$ array with $\varepsilon_{\text{Nd}} = 6.9$, Caro and
Bourdon (2010) estimate the $^{177}$Hf/$^{176}$Hf ratio of the bulk (observable) silicate Earth as 0.28313, compared to a chondritic value of 0.282786, corresponding to an $\varepsilon_{116}$ of +12±3. MORB have average $\varepsilon_{116}$ of 14.2, implying the come from a reservoir with higher time-integrated Lu/Hf than the bulk silicate Earth. Because Hf is more incompatible than Lu, this is entirely consistent with the inference of incompatible element-depletion of the MORB source made from the Sm-Nd and Rb-Sr systems.

**ISOTOPE GEOCHEMISTRY OF THE MANTLE: THE Pb PICTURE**

Pb is by far the most powerful of the isotopic tools available to us because three parents decay to three isotopes of Pb. We have seen that the two U decay systems make Pb isotopes particularly useful in geochronology. The same is true in isotope geochemistry. Let’s consider the special features of the Pb isotope system. We noted earlier that the slope on a plot of $^{207}$Pb/$^{204}$Pb–$^{206}$Pb/$^{204}$Pb is proportional to time. Since Pb is a volatile element, and also somewhat siderophile and chalcophile, the U/Pb ratio of the silicate Earth is unlikely to be the same as the chondritic one. Indeed, it is demonstrably not. Hence the Pb isotope ratios of the bulk Earth are not readily constrained from chondritic values. Pb isotope ratios are, however, constrained by the assumptions that (1) the solar nebula has a uniform Pb isotopic composition when it formed (which we take to be equal to the composition of Pb in troilite in the Canyon Diablo iron meteorite) and (2) the Earth formed from this nebula 4.56 Ga ago. Thus the $^{207}$Pb/$^{204}$Pb and $^{206}$Pb/$^{204}$Pb ratios of the Earth today must lie on a unique isochron, called the Geochron, whose slope corresponds to 4.56 Ga and which passes through Canyon Diablo initial Pb (Figure 6.06; Table 6.01). Indeed, all planetary bodies that formed from the solar nebula at that time (4.55 Ga ago), and have remained closed system since then must plot on this isochron.

While there are no good grounds to question assumption 1, assumption 2 might be questioned in detail. The solar system certainly formed 4.56 Ga ago, but the accretion of the inner planets may have required a significant amount of time. Indeed, computer models of planetary accretion suggest the process may take as much as 100 Ma. In this case, the Earth might be as young as 4.45 Ga, and would have begun with slightly different initial Pb isotope ratios, because of growth of radiogenic Pb over this 100 Ma period. However, the W isotope evidence we discussed in Lecture 11 appears to constrain the age of the Earth to no more than a few 10’s of millions of years younger than the 4.456 Ga age for the solar system.

**Table 6.01. Pb Isotope Ratios in Canyon Diablo Troilite**

<table>
<thead>
<tr>
<th>Pb Isotope Ratio</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{206}$Pb/$^{204}$Pb</td>
<td>9.307</td>
</tr>
<tr>
<td>$^{207}$Pb/$^{204}$Pb</td>
<td>10.294</td>
</tr>
<tr>
<td>$^{208}$Pb/$^{204}$Pb</td>
<td>29.476</td>
</tr>
</tbody>
</table>

Figure 6.06. Evolution of Pb isotope ratios. The curve lines represent the evolutionary paths for systems having $\mu$ values of 8, 9, and 10. The hash marks on the evolution curves mark Pb isotope compositions 1.0, 2.0, and 3.0 Ga ago.
of the solar system. The point is that we cannot be quite certain that bulk Earth Pb isotope ratios must lie on the geochron shown in Figure 6.06, but it certainly must lie close to it.

When the Earth first formed, its Pb isotope ratios should have been similar as that of the Canyon Diablo iron. As time passed the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios increased. At first, the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio increased rapidly because there was about as much $^{235}\text{U}$ as $^{238}\text{U}$ around and $^{235}\text{U}$ was decaying to Pb more rapidly than $^{238}\text{U}$. But as the $^{235}\text{U}$ was consumed, the rate of increase of $^{207}\text{Pb}/^{204}\text{Pb}$ slowed until the present when there is very little $^{235}\text{U}$ left to produce additional $^{207}\text{Pb}$. Thus growth of Pb isotope ratios through time in any system follows a curved path, such as those in Figure 6.05, that depends on the $^{238}\text{U}/^{204}\text{Pb}$ ratio ($\mu$). For a system that has remained closed (no change in $\mu$) for the entire 4.56 Ga, it starts at Canyon Diablo and ends (at present) at some point on the Geochron determined by its $^{238}\text{U}/^{204}\text{Pb}$ ratio.

With this in mind, we can now consider the available Pb isotopic data on the mantle, which is shown in Figure 6.07. Perhaps somewhat surprisingly, almost all oceanic basalts plot to the high $^{206}\text{Pb}/^{204}\text{Pb}$ side of the Geochron. Taken together, these basalts likely represent the isotopic composition of the convecting mantle. As we shall see in future lectures, the average isotopic composition of the bulk continental crust also plots high $^{206}\text{Pb}/^{204}\text{Pb}$ side of the Geochron (average lower continental crust probably plots slightly to the low $^{206}\text{Pb}/^{204}\text{Pb}$ side). Thus the terrestrial reservoirs available to us, the accessible Earth, seems to have a mean isotopic composition falling off the Geochron. Halliday (2004) compiled 10 estimates of the Pb isotopic composition of the bulk silicate Earth (BSE). These estimates vary widely, from $^{206}\text{Pb}/^{204}\text{Pb} = 17.44$ and $^{207}\text{Pb}/^{204}\text{Pb} = 15.16$ to $^{206}\text{Pb}/^{204}\text{Pb} = 18.62$ and $^{206}\text{Pb}/^{204}\text{Pb} = 15.565$, reflecting our uncertainty in this BSE Pb isotopic composition. However, all of these plot significantly to the high $^{206}\text{Pb}/^{204}\text{Pb}$ side of the Geochron. The mean of these estimates, 18.1 and 15.5, is shown in Figure 6.07. If this is indeed the BSE isotopic composition, it means that the silicate Earth must be significantly younger (50-100 Ma younger) than 4.56 Ga.

The U/Pb ratio in carbonaceous chondrites, and thus presumably in the solar nebula, was so low that any increase in $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ during the time Pb spent in the solar nebula would have been negligible. The silicate Earth has a much higher U/Pb ratio than carbonaceous chondrites, and the Pb-Pb age of the Earth reflects the timing of this change in U/Pb ratio. The change could be due either to Pb loss to its volatility or sequestering of Pb in the core. It is possible, if not likely that both played a role. If the latter stages of Earth’s formation involved violent collisions between large proto-planets, this would have provided energy to vaporize Pb. And we saw in the previous chapter that growth of the Earth’s core probably occurred in parallel with accretion of the Earth. The relatively young Pb-Pb age of the Earth is more or less consistent with evidence of W isotope for relatively late formation of the Earth that we discussed in the last chapter. Yet another possibility is that the apparently $^{206}\text{Pb}$-rich nature of the observable silicate Earth reflects differentiation of the Earth into early enriched and depleted reservoirs as suggested by Boyet and Carlson (2005). Perhaps the early enriched reservoir plots to the low $^{206}\text{Pb}/^{204}\text{Pb}$ side of the Geochron. We simply don’t know if this is the case because we do not know the nature of this early enriched reservoir, if it exists.

While the Earth has remained a closed system with respect to Pb since its formation (indeed, a reasonable definition of the “age” of the Earth is the time since it became a closed system), but no reservoir within the Earth need have remained closed for this period. Systems that have experienced a net increase in $\mu$ over the past 4.56 Ga will plot today to the high $^{206}\text{Pb}/^{204}\text{Pb}$ side of the Geochron. Thus is because U/Pb would be high in later parts of the system’s history, when there was still a lot of $^{238}\text{U}$ around but not much $^{235}\text{U}$, leading to high $^{206}\text{Pb}/^{204}\text{Pb}$ ratios relative to $^{207}\text{Pb}/^{204}\text{Pb}$ ratios. Conversely, a system experiencing a net decrease in $\mu$ at some time later than 4.56 Ga would plot to the low $^{206}\text{Pb}/^{204}\text{Pb}$ side of the Geochron (note that changes in $\mu$ at 4.56 Ga affect only the ultimate position of the system on the Geochron — they do result in the system plotting off the Geochron). Thus despite our lack of knowledge about the Earth’s U/Pb ratio, we can still draw inferences about changes in $\mu$ in any subsystem or reservoir within the Earth relative to the Earth as a whole. U is more incompatible
than Pb, so increases in $\mu$ should accompany increases in Rb/Sr and decreases in Sm/Nd and Lu/Hf. Th is slightly more incompatible than U.

Looking at Figure 6.07, we see that Pb isotope ratios in OIB are generally, though not uniformly, higher than in MORB. This is what we expect if Pb is more compatible than U. On the other hand, there is a lot more overlap between MORB and OIB than for the other decay systems, suggesting

![Figure 6.07. Pb isotope systematics of oceanic basalts on the $^{207}$Pb/$^{204}$Pb – $^{206}$Pb/$^{204}$Pb and $^{208}$Pb/$^{204}$Pb – $^{206}$Pb/$^{204}$Pb diagrams. $\Phi$ is the mean of 10 estimates of BSE compiled by Halliday (2004).](image-url)
greater complexity of the U-Pb system. Figure 6.07 also shows the relationship between $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$. The two ratios are reasonably well correlated, implying U and Th have behaved rather similarly.

Since slopes on $^{207}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$ plots are proportional to time, we can associate an age with the overall slope of the array in Figure 6.06. The slope corresponds to an age of about 1.68 Ga (White, 2010). Exactly what this age means, if indeed it is meaningful at all, is unclear. The array in figure 6.07 can be interpreted as a mixing line between components at each end, in which case the age is only the minimum time that the two components must have been isolated. Alternatively, the age may date a single differentiation event, or represent the average age of a series of differentiation events, with the latter case being the most likely.

Sm-Nd, Lu-Hf, and Rb-Sr all appear to be behaving in a generally coherent manner in the mantle, but one or all of U, Th, and Pb appear to behave ‘anomalously’. Pb isotope ratios generally show only poor correlations with other isotope ratios, for example $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ shown in Figure 6.08. We know that the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios provide information about the time-integrated U/Pb ra-

![Diagram](image)

Figure 6.08. $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of the suboceanic mantle as sampled by oceanic basalts.
Isotope Geochemistry

Chapter 6

Spring 2011

tio, or \( \mu \), and \( ^{208}\text{Pb} / ^{204}\text{Pb} \) provides information about time-integrated Th/Pb. The Pb isotope system can also provide information about the time-integrated Th/U ratio, or \( \kappa \). This is done as follows. We can write two equations:

\[
^{208}\text{Pb}^* = 232\text{Th} (e^{\lambda_{232}t} - 1) \quad 6.04
\]

and

\[
^{206}\text{Pb}^* = 238\text{U} (e^{\lambda_{238}t} - 1) \quad 6.05
\]

where the asterisks denotes the radiogenic component. Dividing 6.04 by 6.05, we obtain:

\[
\frac{^{208}\text{Pb}^*}{^{206}\text{Pb}^*} = \frac{232\text{Th}}{238\text{U}} = \kappa \frac{(e^{\lambda_{232}t} - 1)}{(e^{\lambda_{238}t} - 1)} \quad 6.06
\]

Thus the ratio of radiogenic \( ^{208}\text{Pb} \) to radiogenic \( ^{206}\text{Pb} \) is proportional to the time-integrated value of \( \kappa \). This ratio may be computed as:

\[
\frac{^{208}\text{Pb}^*}{^{206}\text{Pb}^*} = \frac{^{208}\text{Pb} / ^{204}\text{Pb} - (^{208}\text{Pb} / ^{204}\text{Pb})_i}{^{206}\text{Pb} / ^{204}\text{Pb} - (^{206}\text{Pb} / ^{204}\text{Pb})_i} \quad 6.07
\]

where the subscript \( i \) denotes the initial ratio. By substituting a value for time in equation 6.06, and picking appropriate initial values for equation 6.07, we can calculate the time-integrated value of \( \kappa \) over that time. For example, picking \( t = 4.56 \) Ga and initial ratios equal to Canyon Diablo, we calculate the time-averaged \( \kappa \) over the past 4.56 Ga.

Now let’s see how \( ^{208}\text{Pb}^* / ^{206}\text{Pb}^* \), and hence \( \kappa \) relates to other isotope ratios, and hence other parent-daughter ratios. Figure 6.09 shows \( \varepsilon_{\text{Nd}} \) plotted against \( ^{208}\text{Pb}^* / ^{206}\text{Pb}^* \). We can see that the two are reasonably well correlated, implying the fractionations of Sm from Nd and U from Th in the mantle have been closely related. From this, we conclude that the lack of correlation of ‘first-order’ Pb isotope ratios with Sr, Nd, and Hf isotope ratios is due to ‘anomalous’ behavior of Pb.

We have seen that there are systematic differences in isotopic composition between MORB and OIB. Thus, there are at least two major reservoirs in the mantle – although deducing the physical relationship between these reservoirs is more problematic. The conventional interpretation is that MORB are derived from the uppermost mantle, which we can see is the most depleted of the reservoirs sampled by oceanic volcanism. Oceanic islands are thought to be surface manifestations of mantle plumes, which rise from, and therefore ‘sample’, the deeper mantle. A standard interpretation would thus be of a layered mantle. However, this interpretation encounters the difficulty that there is little or no geo-physical evidence for a layered mantle. Seismic tomography, in particular, has imaged subducted oceanic lithosphere extending to near the core-mantle boundary, suggesting free communication between deep and shallow mantle. Furthermore, there is no convincing evidence of reflections or seismic velocity discontinuities that would be expected from a boundary between distinct and isolated mantle layers, with the possible exception of the D” region occupying the lowermost 200 km of the mantle. The magma flux of mantle plumes is, however, small compared to the magmatic flux at mid-ocean ridges. Thus the volume required of a plume reservoir could be quite small, perhaps no bigger than the seismically distinct D” layer at the base of the mantle.

The idea of early enriched and depleted reservoirs in the mantle, derived from the non-chondritic nature of the terrestrial \( ^{142}\text{Nd} / ^{144}\text{Nd} \) ratio, encounters similar problems. The hypothesis of Boyet and Carlson (2005) effectively requires that the early enriched reservoir remain isolated, not just for a couple of billion years, but throughout Earth’s history. As we noted in the previous chapter, such a reservoir would contain a significant fraction of the Earth’s radiogenic heat production, and it seems particularly unlikely that such an energy-rich reservoir would remain isolated. The difficulty in associating ‘reservoirs’ deduced from isotope geochemistry with physical features in the mantle remains one of the most pressing problems in understanding the Earth’s deep interior.
Most of the geochemistry of the MORB source can be described in terms of depletion in incompatible elements due to partial melting and removal of the melt. But how are we to interpret the OIB data? There are a number of possible interpretations. One of the earliest was OIB sources were mixtures of lower primitive mantle and upper depleted mantle. Such an interpretation does not explain those OIB with negative $\varepsilon_{\text{Hf}}$ and $\varepsilon_{\text{Nd}}$ and it is completely at odds with the Pb data. If this interpretation were correct, OIB should lie between MORB and the Geochron, but they clearly do not. An interpretation that OIB sources are simply less depleted than the MORB source also does not account for those OIB with negative $\varepsilon_{\text{Hf}}$ and $\varepsilon_{\text{Nd}}$. A final possibility is that OIB sources are depleted mantle that has experienced some incompatible element re-enrichment. These alternative hypotheses are not mutually exclusive, all may have affected all OIB reservoirs, or each of the alternatives may exclusively account for a portion of OIB sources. Our next step is to consider the OIB data and seek any regularities in it that might suggest a process or processes to explain their isotopic compositions.

Figure 6.09. $\varepsilon_{\text{Nd}}$ vs. $\frac{^{208}\text{Pb}^*}{^{206}\text{Pb}^*}$ ratios of the suboceanic mantle as sampled by oceanic basalts.
The crust of the Earth is relatively enriched in incompatible elements. This is true of both the oceanic and continental crust, although the continental crust is much more incompatible element-enriched than the oceanic crust. This is entirely consistent with our hypothesis that the crust was created through partial melting of the mantle. We can then ask, from what fraction of the mantle have these incompatible elements been extracted to account for their abundance in the crust? Since its ephemeral, on average only 60 million years old, let’s ignore the ocean crust for the moment and just focus on continental crust. We have seen that MORB have “depleted” Nd, Sr and Hf isotopic compositions — let’s assume that the MORB source is residual mantle remaining after extraction of the continental crust. How much undepleted mantle would remain?

This is essentially a problem mass balance among a number of reservoirs, so we begin by writing a series of mass balance equations. The first is mass of the reservoirs:

$$\sum_j M_j = 1$$  
6.08

where $M_j$ is the mass of reservoir $j$ as a fraction of the total mass of the system, in this case the silicate Earth. We can also write a mass balance equation for any element $i$ as:

$$\sum_j M_j C_j^i = C_0^i$$  
6.09

where $C_j$ is the concentration in the silicate Earth.

For an isotope ratio, $R$, of element $i$, or for an elemental ratio of which element $i$ is the denominator, the mass balance equation is:

$$\sum_j M_j C_j^i R_j^i = C_0^i R_0^i$$  
6.11

Our problem assumes the existence of 3 reservoirs: the continental crust, the mantle depleted by crust formation, and the undepleted, or primitive, mantle. These mass balance equations can be combined to solve for the mass ratio of continental crust to depleted mantle:

$$\frac{M_{DM}}{M_{CC}} = C_{CC}^i \left( \frac{R_C^i - R_{DM}^i}{R_0^i - R_{DM}^i} \right) - 1$$  
6.12

where the subscripts $DM$ and $CC$ refer to depleted mantle and continental crust respectively. A number of solutions to the mass balance equations are possible, but we choose this form because it does not contain the concentration term for the depleted mantle. We can judge the isotopic composition of mantle sources because the magmas they produce have the same isotopic composition, but this is not true of elemental concentrations. Once we have solved for the mass of depleted mantle, however, it is straightforward to solve for the depleted mantle concentration term:

$$C_{DM}^i = \frac{C_0^i \left( M_{DM} + M_{CC} \right) - M_{CC} C_{CC}^i}{M_{DM}}$$  
6.13

Another difficulty arises with the isotopic composition of the continental crust, which is not well known. On the other hand, there are a number of estimates of elemental composition of the continental crust based on compilations of data, as well as on the age of the crust. With some assumptions, however, we can combine the information that we do have to arrive at an estimate of the volume of mantle depleted by crust formation.

The Nd isotope system is perhaps best suited for this question since $^{142}$Nd/$^{144}$Nd ratios constrain the Nd isotopic composition of the Earth and, being a refractory lithophile element, its concentration in the
Isotope Geochemistry

Chapter 6

Spring 2011

bulk silicate Earth is also constrained (though not precisely). The Nd concentration in the continental crust are also better constrained than many other elements. The Sm/Nd ratio and $^{143}\text{Nd}/^{144}\text{Nd}$ of the crust are related through isotopic evolution, specifically:

$$^{143}\text{Nd}/^{144}\text{Nd} = (^{143}\text{Nd}/^{144}\text{Nd})_0 + ^{147}\text{Sm}/^{144}\text{Nd}(e^{\lambda T} - 1)$$

6.14

Because the half-life of $^{147}\text{Sm}$ is long compared to the age of the Earth and because we do not need the level of precision necessary for geochronology, we can linearize this equation as:

$$^{143}\text{Nd}/^{144}\text{Nd} = (^{143}\text{Nd}/^{144}\text{Nd})_0 + ^{147}\text{Sm}/^{144}\text{Nd} \lambda T$$

6.15

Let’s assume for simplicity that the some fraction of silicate Earth differentiated in a single event into a continental crust and depleted mantle at some time $T$. This is certainly not the case, as we shall see, but because of the linearity of the equation 6.15, even if the crust formed through similar events over a range of times, our approach is still valid if $T$ is the average age of the crust. At time $T$, the continental crust and depleted mantle both had the same isotopic composition as undepleted mantle; i.e., the composition of the undepleted mantle becomes the initial ratio in version of 6.14 written for depleted mantle and continental crust. For the continental crust:

$$\left(^{143}\text{Nd}/^{144}\text{Nd}\right)_{CC} = (^{143}\text{Nd}/^{144}\text{Nd})_{PM} + \left([^{147}\text{Sm}/^{144}\text{Nd}]_{CC} - [^{147}\text{Sm}/^{144}\text{Nd}]_{PM}\right) \lambda T$$

6.16

where the superscript $T$ denotes the value at time $T$. We can calculate that value from the present-day $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ of primitive mantle. Substituting, we have:

$$\left(^{143}\text{Nd}/^{144}\text{Nd}\right)_{CC} = (^{143}\text{Nd}/^{144}\text{Nd})_{PM} + \left([^{147}\text{Sm}/^{144}\text{Nd}]_{CC} - (^{147}\text{Sm}/^{144}\text{Nd})_{PM}\right) \lambda T$$

6.17

The value thus calculated can then be used in equation 6.12 to calculate the mass fraction of depleted mantle. Figure 6.10 shows the mass fraction of the depleted mantle as a function of the ratio of the concentration of Nd in the crust to the bulk silicate Earth; i.e., the enrichment of Nd in the continental crust. It assumes that the average age of the crust is 2.0 Ga and that its $^{147}\text{Sm}/^{144}\text{Nd}$ ratio is 0.1228. If the $\varepsilon_{\text{Nd}}$ of the Earth is around +6.9, as suggested by Caro and Bourdon (2010), then the mantle depleted by crust extraction occupies at least 75% of the entire mantle and possibly all of it.

This is quite a different picture of the mantle from the one that has prevailed for the last 30 years or so derived from assumption that the Earth has chondritic Sm/Nd and therefore $\varepsilon_{\text{Nd}} = 0$. Mass balance calculations such as those of Jacobsen and Wasserburg (1979), O’Nions et al. (1979) and DePaolo (1980) concluded that the mass of the depleted mantle is was only 25% to 50% the total mass of the mantle, and therefore that a large “primitive mantle” reservoir existed. The lower end of this range corresponds to the mass fraction of mantle above the 660 km seismic discontinuity. This coincidence led to models of the mantle in which a depleted reservoir occupied the upper mantle, the region above the 660 km discontinuity, and the region below it, the lower mantle, consisted of primitive mantle. Maintaining two distinct reservoirs for the age of the Earth in turn implied that convection in the mantle was layered and that the 660 km discontinuity represented a boundary to mass transport. Eventually, however, new evidence from other branches of earth science raised questions about this model. Experimental studies revealed that increase in seismic velocity at 660 km depth resulted from a phase change resulting from a fundamental change in silicate structure, and that while the phase change might retard mass transport across the boundary, it probably did not prohibit it. The development of seismic tomography in the 1990’s confirmed that subducting lithosphere did, at least sometimes, pass through the 660 km discontinuity into the lower mantle, and in some cases could be traced nearly to the core-mantle boundary. Thus isotope geochemistry, which seemed to support two layered convection in the mantle, was at odds with geophysics, which favored whole mantle convection. This conflict is resolved is the Earth is non-chondritic and has a high $\varepsilon_{\text{Nd}}$. Any surviving “primitive mantle” reservoir would be small; most of the mantle likely consists of the kind of depleted mantle that produces MORB. This accords with the observation that no mantle or mantle-derived materials having $\varepsilon_{\text{Nd}} = 0$ and other chemical and isotopic characteristics expected of primitive mantle have been identified.
MULTI-RESERVOIR MANTLE MODELS

Wasserburg and DePaolo (1976) termed the linear correlation originally observed between Sr and Nd isotope ratios the "mantle array". Even though it is now clear that mantle does not always plot on the linear array, the term has survived, and is useful for reference. If we consider where individual oceanic islands or island chains plot on various isotope ratio plots, we can see that there are some systematic features. For example, several islands, including St. Helena Island in the Atlantic and the Austral Chain in the Pacific, plot on Figure 6.03 slightly below the Sr-Nd mantle array with $^{87}\text{Sr}/^{86}\text{Sr}$ about 0.7029, only slightly higher than MORB. Basalts from these same islands also plot below the Hf-Nd isotope correlation (Figure 6.05). In addition, they have remarkably radiogenic Pb, with $^{206}\text{Pb}/^{204}\text{Pb} > 20$ (Figure 6.07, 6.08). Based on observations such as these, White (1985) grouped oceanic island basalts into 5. It is reasonable to suppose that this reflects the existence of 5 reservoirs, or perhaps more accurately, 5 types of reservoirs within the mantle. Although this need not necessarily be the case, the idea has been accepted as a sort of working hypothesis by mantle geochemists (although it is unclear exactly how many classes there are, some prefer 4 or 6).

The next question to ask is what processes have lead to the distinct identities of these reservoirs. For the MORB reservoir, this question is relatively easy to answer: extraction of partial melt. Two of the reservoirs types, called Kerguelen and Society by White (1985) but subsequently termed EM I and EM II ('enriched mantles 1 and 2') by Zindler and Hart (1986), have some characteristics of continental crust and sediment, and hence it is suspected that recycling of crustal material, via subduction, has been the principal process in the evolution of these reservoirs. White and Hofmann (1982) suggested EMII could be produced by recycling of oceanic crust and sediment and EM I by oceanic crust alone, but it is unclear whether oceanic crust is ever subducted without sediment, and consequently not clear why recycling should lead to two apparently distinct reservoirs. Numerous authors have suggested the St. Helena reservoir type, whose most distinctive characteristic is high Pb isotope ratios, and which Zindler and Hart (1986) called HIMU (for high-$\mu$), has also been produced by recycling of the oceanic crust. The basis for this argument is the effects of ridge-crest hydrothermal activity, which apparently removes Pb from the oceanic crust, but transfers seawater U (which is ultimately of continental crustal derivation) to the oceanic crust, effectively increasing its $\mu$. For the most part, it must be admitted that we do not yet understand the evolution of the OIB source reservoirs. It does seem, however, that a number of processes have operated over geologic time to produce reservoirs in the mantle that are distinct from both depleted mantle and primitive mantle. The reservoir types of White (1985) and components of Zindler and Hart (1986) are shown in Figures 6.11 and 6.12.
We should note that the existence of multiple reservoirs in the mantle does not necessarily invalidate the mass balance models discussed above if the mass of the various OIB reservoirs is insignificant. Since the volume of OIB is small compared to MORB, this is certainly a possibility. Mass balance models also neglect the mass of the subcontinental mantle lithosphere. Although significant parts of the subcontinental lithosphere appear highly incompatible element enriched, it is probably not a significant reservoir of incompatible elements.

A different view of the mantle has been taken in papers by Galer and O’Nions (1985) and White (1993). The models we have discussed thus far assume that isotope ratios in mantle reservoirs reflect the time-integrated values of parent-daughter ratios in those reservoirs. Indeed, we devoted some time to the concept of time-integrated parent-daughter ratios in the previous lecture. Wasn’t this, after all, what Gast said, that (among other things) an isotope ratio reflects the time-integrated parent-daughter ratio?

Indeed, what did Gast say? He said “The isotopic composition of a particular sample of strontium... may be the result of time spent in a number of such environments. In any case, the isotopic composition is the time-integrated result of the Rb/Sr ratios in all past such environments.” If for example, a sample of Sr from the depleted upper mantle (we’ll adopt the acronym DUM* for this reservoir) had spent the past 4.55 Ga in

---

* You may get the impression that to really succeed in mantle isotope geochemistry you need to be good at thinking
that reservoir, its isotopic composition should indeed reflect the time-integrated Rb/Sr in that reservoir. But suppose that sample of Sr had spend only the last few hundred million years in the DUM? Its isotopic composition will be more of a reflection of the Rb/Sr ratios in the previous environments than in DUM. This is exactly the point made by Galer and O’Nions.

We have seen in previous lectures that the time integrated Th/U ratio is recorded by the $^{208}\text{Pb^*/206}\text{Pb^*}$ ratio. Galer and O’Nions (1985) found that the average $^{208}\text{Pb^*/206}\text{Pb^*}$ in MORB corresponded to a time-integrated Th/U ratio of about 3.75. The chondritic Th/U ratio, according to several compilations, is about 3.9. Since Th and U are both refractory elements, this should be the ratio of the bulk Earth as well. The present-day Th/U ratio of the mantle source of a basalt can be deduced from Th isotope systematics, as we have seen. According to the compilation made by Galer and O’Nions, $\chi$ in DUM, based on Th isotope ratios in MORB, is about 2.5. That the present ratio is lower than the chondritic one makes perfect sense because Th is more incompatible than U, so we would expect this ratio to be low in

up acronyms. As near as I can tell, this is true. This acronym is due to Claude Allegre.
DUM. Assuming the upper mantle started out with a chondritic $\kappa$ of 3.9 at 4.55 Ga, and has decreased through time to 2.5, the time-integrated ratio should be somewhere in between these two values. Indeed, it is. However, the time-integrated value of 3.75 is surprisingly close to the initial value. This would imply in a simple evolutionary model of the mantle that the depletion in Th relative to U must have occurred relatively recently. Indeed, as illustrated in Figure 6.13, this depletion must have occurred only 600 Ma ago. This is a surprising result, and one that is inconsistent with other evidence. If the depleted mantle is the complimentary reservoir to the continental crust, time-integrated parent-daughter ratios should indicate a depletion age of about 2-2.5 Ga.

Galer and O’Nions (1985) concluded that something was very wrong with conventional views of the mantle. They suggested that Pb now in the upper mantle had not resided there for long, that it was ultimately derived from a lower mantle reservoir that had a primitive (i.e., chondritic) Th/U ratio. In other words, the upper mantle had not evolved simply by losing melt fractions to the continental crust, but was a completely open system, with fluxes into it as well as out of it. They argued that the apparent depletion time of 600 Ma was in reality simply the residence time of Pb in the upper mantle. Galer and O’Nions may have underestimated the value of $\kappa$ in the Earth; it is very possible that the value for the bulk Earth is higher than 3.9, perhaps in the range of 4.0 to 4.2 (and even as high as 4.3). However, this only extends the residence time to about 1 to 1.2 Ga, still much less than the average age of continents, so their point remains valid.

**GEOPHYSICAL VARIATIONS IN MANTLE ISOTOPIC COMPOSITION**

Can geographic variations in mantle chemistry be identified on a larger scale that of individual volcanic island chains? The answer turns out to be yes. The first such variation observed was on the Mid-Atlantic Ridge. Sr and Pb isotope ratios in MORB were observed to decrease with distance from Iceland and the Azores. This was interpreted as ‘contamination’ of the asthenosphere by the Azores and Iceland mantle plumes (Hart et al., 1973; White et al., 1976). Somehow, the rising mantle plume mixes with asthenosphere through which it ascends, with the effect on isotopic compositions being noticeable up to 1000 km from the center of the plume. Subsequent studies showed similar effects even a ridge is located in proximity to a hot spot or mantle plume, including Easter Island, the Galapagos, and several

---

$\tau = \frac{C_i M_i}{f_i}$

where $\tau$ is the residence time, $C_i$ is the concentration of element $i$ in the reservoir, $M_i$ is the mass $i$ in the reservoir, and $f_i$ is the flux of $i$ into or out of the reservoir. The residence time of Pb in the depleted mantle is the average time an atom of Pb will spend there between entering and leaving.
of the islands in the South Atlantic and Indian Oceans (Schilling, 1985). These variations can be seen in Figure 6.14. Other variations along the ridge, however, cannot be directly related to mantle plumes.

Is there evidence for larger scale geochemical provinces in the mantle, comparable to say tectonic provinces of the continents? The answer is again yes. Perhaps the first such ‘province’ to be identified was the Indian Ocean geochemical province. Data published as early as the early 1970’s suggested MORB from the Indian Ocean were distinct from those of the Pacific and the Atlantic, having higher $\frac{{^{87}Sr}}{^{86}Sr}$ ratios. However, the scarcity and poor quality of data on Indian Ocean MORB left the issue in doubt for more than a decade. It was resolved with a flood of data on Indian Ocean MORB, beginning with a paper by Dupré and Allègre (1983). Dupré and Allègre found Indian Ocean MORB has higher $\frac{{^{87}Sr}}{^{86}Sr}$ ratios but lower $\frac{{^{206}Pb}}{^{204}Pb}$/ $\frac{{^{207}Pb}}{^{204}Pb}$ ratios compared to MORB from other oceans. They also have high $\frac{{^{207}Pb}}{^{204}Pb}$ and $\frac{{^{208}Pb}}{^{204}Pb}$ ratios for a given value of $\frac{{^{206}Pb}}{^{204}Pb}$ than other MORB. This is can be seen in Figure 6.07. Furthermore, these characteristics seem to be shared by many of the oceanic islands in the Indian Ocean. Subsequent work that showed Indian Ocean MORB have low $\epsilon_{Nd}$ as well. Finally, MORB from the Pacific Ocean can be distinguished from Atlantic MORB by having lower $\frac{{^{87}Sr}}{^{86}Sr}$ ratios for a given $\epsilon_{Nd}$.

Hart (1984) noticed that oceanic basalts with high $\frac{{^{207}Pb}}{^{204}Pb}$ and $\frac{{^{208}Pb}}{^{204}Pb}$ ratios for a given value

Figure 6.14. Variation of Sr and Pb isotope ratios with angular distance along the mid-ocean ridge system. The "0" point is the location of the northernmost sample site of the Gakkel Ridge at 85.64°N, 85.05°E. From White and Klein (in press).
Isotope Geochemistry

Chapter 6

Spring 2011

of $^{206}\text{Pb}/^{204}\text{Pb}$ come mainly from a belt centered at about $30^\circ$ S. Hart named this feature the DUPAL anomaly (after Dupré and Allègre). He defined the DUPAL isotopic signature as having higher $\Delta\text{Sr}$ ($\Delta\text{Sr} = [^{87}\text{Sr}/^{86}\text{Sr} - 0.7030] \times 10^4$) and high $\Delta\text{Sr}/4$ and $\Delta\text{Sr}/4$. The value of $\Delta\text{Sr}/4$ and $\Delta\text{Sr}/4$ are percent deviations from what Hart defined as the Northern Hemisphere Regression Line, regression lines through the $^{208}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$ arrays for northern hemisphere data:

$$\Delta\text{Sr}/4 = \left[ ^{208}\text{Pb}^{204}\text{Pb} - ^{206}\text{Pb}^{204}\text{Pb}_{\text{NHRL}} \right] \times 100$$

where

$$^{208}\text{Pb}^{204}\text{Pb}_{\text{NHRL}} = 15.627 + 1.209 ^{206}\text{Pb}^{204}\text{Pb} \quad 6.19$$

and

$$^{207}\text{Pb}^{204}\text{Pb}_{\text{NHRL}} = 13.491 + 0.1804 ^{206}\text{Pb}^{204}\text{Pb} \quad 6.22$$

Subsequently, Castillo (1989) suggested that Hart’s “DUPAL anomaly” actually consisted of two separate regions: the DUPAL in the Indian Ocean, and the “SOPITA” (South Pacific Isotope and Thermal Anomaly) in the South Pacific and pointed out they correspond to regions of slow mantle seismic velocities, which in turn imply high mantle temperatures. Castillo’s map is shown in Figure 6.14.

Interestingly, the DUPAL characteristic is shared by both Indian Ocean OIB and MORB, but this does not seem to be the case in the Atlantic and Pacific. The DUPAL signature has not been observed in Atlantic or Pacific MORB, except in the immediate vicinity of the Tristan da Cunha mantle plume in the south Atlantic. An additional question relates to sampling coverage. Nearly two-thirds of oceanic island occur in this belt, so it is not surprising that a particular chemistry in often found there. Nevertheless, it is clear that there is something anomalous about this region.

The Galapagos Archipelago provides another example of geographic variation of isotope composition in the mantle. The Galapagos provide an unusually favorable opportunity for producing a geochemical map of the mantle because they consist of 20 or so volcanoes that have all been active over the past 2 or 3 million years. Combining Nd isotope ratio determined on basalts from these volcanoes as well as data from previous geochemical studies of the Galapagos Spreading Center (GSC) just to the north, White et al. (1993) produced the contour map of Nd isotope ratios shown in Figure 6.16. The contours reflect regional geochemical variations in the mantle below.

The contouring reveals a horseshoe-shaped region around the western, northern, and southern periphery of the archipelago in which low $\varepsilon_{\text{Nd}}$ values occur, and a region in the center of the archipelago in which high $\varepsilon_{\text{Nd}}$ values occur. The high $\varepsilon_{\text{Nd}}$ values are more typical of MORB than of oceanic island basalts. This pattern was unexpected. From what was observed along the MAR (Figure 6.14), one might expect $\varepsilon_{\text{Nd}}$ to decrease radially from the center of the archipelago.

![Figure 6.15. Map showing the distribution of mantle plumes (triangles), P-wave velocity anomalies (m/sec) averaged over the whole lower mantle (red lines), and location of the DUPAL and SOPITA isotope anomalies (pale red regions). Mantle plumes are located in regions of slow lower mantle seismic velocities, implying high temperatures. After Castillo (1989).](image-url)
The pattern in the Galápagos may reflect the fluid dynamics of plume-asthenosphere interaction. Laboratory experiments have shown that a thermal plume (i.e., one that rises because it is thermal buoyant rather than chemically buoyant) will entrain surrounding asthenosphere if it is bent by asthenospheric motion. This is because the surrounding asthenosphere is heated by the plume, as a result, it also begins to rise.

**The Origin of Mantle Plumes and the Common Component in Plumes**

Determining how the various geochemical reservoirs of the mantle have evolved is among the most vexing problems in geochemistry. The principal observation to be explained is that mantle plumes invariably have less depleted isotopic signatures than MORB, and the isotopic compositions of some indicate net enrichment in incompatible elements. Initially, mantle plumes were initially thought to consist of primitive mantle (e.g., Schilling, 1973). As we have seen, however, oceanic island basalts display a range of compositions and while it is possible that some contain a primitive component (particularly if primitive mantle has $\varepsilon_{Nd}=+7$), other reservoirs with more complex geochemical histories must also be involved. Many, or most, oceanic island basalts have isotopic compositions indicating they have experienced incompatible element-enrichment. How might that enrichment have occurred?

Hofmann and White (1982) suggested mantle plumes obtain their unique geochemical signature through deep recycling of oceanic crust (Figure 6.17). Partial melting at mid-ocean ridges creates oceanic crust that is less depleted in incompatible elements than the depleted upper mantle. The oceanic crust is apparently inevitably subducted as virtually none is preserved at the surface, so it clearly is recycled back into the mantle. The question is what becomes of it? Hofmann and White noted that once oceanic crust reaches depths of about 60 km it converts to eclogite, which is denser than peridotite. Because it is rich in Fe and garnet-forming components, it remains denser than peridotite at all depths greater than 60 km (except, perhaps, just at the 660 discontinuity due to the negative Clapeyron slope). Thus it will sink to the base of the convecting region. If the mantle is chemically stratified, with a Fe-rich lower mantle, oceanic crust would sink to a thermal boundary layer at the 660 discontinuity. If the entire mantle convects as a single unit, that is if it is not chemically stratified, ocean crust will sink to base of the mantle, becoming embedded in thermal boundary layer there (D°). Hofmann and White originally suggested radioactive heating would ultimately cause it to become buoyant. However, heat conducted into it from below, from either the lower mantle or the core, is likely a more important heat source.
source. In any case, upon sufficient heating, it rises, melting near the surface to create intraplate volcanoes.

As we shall see in a subsequent lecture, sediment appears often, if not always, to be subducted along with the oceanic crust. This subducted sediment would also contribute to incompatible element enrichment of plumes. Varying amounts, types, and ages of subducted sediment may be responsible for some of the geochemical variety displayed by plumes. Since sediment is ultimately derived from the continents, recycling of oceanic crust, continental crust, mantle plumes, and oceanic island basalts may all be part of a grand geochemical cycle. Tectonic erosion of continental crust in subduction zones and delamination of continental crust may be alternative mechanisms for deep recycling of continental crust.

Because the major element chemistry of OIB is often similar to that of MORB, it seems unlikely plumes could be composed entirely of recycled oceanic crust. Presumably, they consist primarily of peridotite, with a subordinate fraction of oceanic crust. However, because the oceanic crust has much higher incompatible element concentrations than peridotite, it provides most of the isotopic and incompatible element “flavor” of plumes.

Trace elements provide some evidence that some plumes contain a recycled sediment component. The Pb/Ce ratio is particularly useful indicator of the presence of sediment for several reasons. First, the Pb/Ce ratio is comparatively uniform in MORB and many OIB. Second, the Pb/Ce ratio is an order of magnitude higher in sediments than in the mantle (typically,

Figure 6.17. Cartoon illustrating the oceanic crustal recycling model of Hofmann and White (1982). Oceanic crust is transformed into eclogite and post-eclogite assemblages upon subduction. It separates from the less dense underlying lithosphere and sinks to the deep mantle where it accumulates. Eventually, it becomes sufficiently hot to form plumes that rise to the surface, producing oceanic island volcanism. After Hofmann and White (1982).

Figure 6.18. Pb/Ce and $^{207}$Pb/$^{204}$Pb in basalts from the Society Islands studied by White and Duncan (1996). A calculated mixing line between depleted mantle and sediment passes through the data. Also shown are estimated Pb/Ce ratios of average continental crust and bulk silicate Earth (BSE).
Pb/Ce is greater than 0.3 in sediments and <0.04 in MORB). Third, sediments have two orders of magnitude higher concentrations of Pb (typically 20 ppm or more) than the mantle (less than 0.05 ppm), so that addition of even small amounts of sediment to mantle shifts the Pb/Ce ratio. Finally, the near constancy of Pb/Ce in most basalts suggests this ratio is not significantly changed in by magmatic processes such as partial melting and fractional crystallization. There is a strong correlation between isotopic ratios and Pb/Ce in basalts from the Society Islands. As Figure 6.18 shows, the correlation is consistent with mixing between recycled sediment and mantle. However, most oceanic islands have only mantle-like Pb/Ce ratios.

An alternative origin for mantle plumes was proposed by McKenzie and O’Nions (1983). They noted the common evidence for incompatible element enrichment in the subcontinental lithosphere (which we discuss in the next section) and suggested this material may, because it is cold, occasionally founder and sink to the deep mantle. As in the case of the Hofmann and White model, it would be stored in a thermal boundary layer, heated, and rise in the form of mantle plumes. However, as we shall see in the next section, recent studies have shown that the Os isotope composition of the subcontinental lithosphere is quite distinctive, and quite different from that of mantle plumes. This suggests that “delaminated” subcontinental lithosphere does not contribute to mantle plumes. Because mantle plumes come in several geochemical varieties, it is possible that both mechanisms operate. Indeed, other as yet unknown processes may be involved as well.

Most oceanic islands show some variability in their isotopic compositions, defining elongated arrays on plots of isotope ratios. Such elongated arrays suggest mixing. This raises the rather obvious question of what is mixing with what. In a few cases, the Comores are a good example, the elongate arrays seems to reflect mixing between different plume reservoirs. The Comores data defines a trend in isotopic space that appears to be the result of mixing between an EMI and a HIMU component. In other cases, such as the Galapagos, the plume is clearly mixing with the depleted mantle. However, in many cases, the cause of the isotopic variation is less clear.

Hart et al. (1992) plotted oceanic basalt isotope data in three dimensions, with axes of $\frac{\text{Sr}}{\text{Sr}}$, $\frac{\text{Nd}}{\text{Nd}}$, and $\frac{\text{Pb}}{\text{Pb}}$ (Figure 6.19). Principal component analysis confirmed that 97.5% of the variance in the oceanic basalt isotope data could be accounted for by these ratios (leaving 2.5% to be accounted for by $\frac{\text{Pb}}{\text{Pb}}$, $\frac{\text{Pb}}{\text{Pb}}$, and $\frac{\text{Hf}}{\text{Hf}}$). They found that most of the data plotted within a tetrahedron defined by the hypothetical end members EM1, EM2, HIMU, and DMM. They also noticed that many arrays were elongated toward the base of this tetrahedron on the DMM-HIMU

Figure 6.19. Three dimension plot of $\frac{\text{Sr}}{\text{Sr}}$, $\frac{\text{Nd}}{\text{Nd}}$, and $\frac{\text{Pb}}{\text{Pb}}$. Most oceanic basalt data plot within a tetrahedron defined by the composition of EMI, EMII, HIMU, and DMM components. Oceanic islands and island chains tend to form elongate isotopic arrays, many of which seem to point toward a focal zone (FOZO) at the base of the tetrahedron. Adapted from Hart et al. (1992).
join. From this they concluded that in many, if not most cases, mantle plumes appear to mixing with a previously unidentified component, which they named “FOZO” (an acronym for Focal Zone), that has the approximate isotopic composition of $^{87}\text{Sr}/^{86}\text{Sr} = 0.7025$, $\varepsilon_{\text{Nd}} = +9$, and $^{206}\text{Pb}/^{204}\text{Pb} = 21.5$. They suggested that FOZO is the isotopic composition of the lower mantle and that plumes rising from the core mantle boundary entrain and mix with this lower mantle material. It is unclear, however, whether such a composition for the lower mantle can be fitted to reasonable isotopic mass balances for the Earth.

A rather similar idea was presented by Farley et al. (1992), who point out that this additional component, which they called “PHEM”, seems to be associated with high $^3\text{He}/^4\text{He}$. White (1995) concurred with these ideas, but argued that the $^{87}\text{Sr}/^{86}\text{Sr}$ of FOZO is higher, and the $\varepsilon_{\text{Nd}}$ lower, than estimated by Hart et al. (1992) and probably closer to the values chosen by Farley et al. (1992). Hanan and Graham (1996) used Pb and He isotope ratios to deduce yet another potential common component of plumes, which they called “C”. The “C” composition of Hanan and Graham is similar to the PHEM of Farley et al. (1992) and may be just another name for the same thing. “C” and “PHEM” occur in the interior of the tetrahedron shown in Figure 6.19. Hanan and Graham (1996) argued that “C” is the principal component of plumes, the other components just add “flavor”. The “C” and PHEM compositions would have $\varepsilon_{\text{Nd}}$ of about +5. This is fairly close the revised value for the bulk silicate Earth, or the observable part of it if the Boyet and Carlson (2005) model is correct. This is also close the modal (i.e., most common) value of $\varepsilon_{\text{Nd}}$ for oceanic island basalts. This composition may be something approximating a mantle composition that has been minimally modified since either the Earth formed or it initially differentiated and may be quite abundant in the deep Earth. In other words, it might be something close to “primitive mantle”.

**The Subcontinental Lithosphere**

Figure 6.20a shows Sr and Nd isotopic variations in continental basalts. The data span a much larger range than oceanic basalts. Some, but not all, of this variation reflects the effects of assimilation of continental crust on the isotopic signatures of the mantle-derived magmas. Assimilation effects can be avoided by considering only the data on peridotite xenoliths in continental basalts, the data for which is shown in Figure 6.20b. As may be seen, the range of values is reduced, but nevertheless much greater than that observed in oceanic basalts. One needs be cautious in directly comparing the heterogeneity observed in xenolith data to basalt data because the two represent different scales of sampling of the mantle. Basalts are created by melting of regions that have characteristic scales of tens of kilometers, and perhaps greater. The magma generation process undoubtedly averages out very small-scale heterogeneities. Xenoliths, on the other hand, have characteristic dimensions of centimeters. Thus variations in isotopic ratios in basalts reflect large-scale heterogeneity in the mantle, while xenoliths reflect small-scale heterogeneity. Despite this, it appears that the subcontinental lithosphere is more heterogeneous, even on relatively large scales, than is the suboceanic mantle.

It appears that the subcontinental lithosphere can be quite old, and, at least in some cases, has the same age as the crust it underlies. As we saw in previous lecture, studies of xenoliths and inclusions in diamond from South African kimberlites suggests the mantle is 3–3.5 Ga old in this region, ages similar to that of the South African craton. The greater isotopic heterogeneity of the subcontinental lithosphere probably reflects its long-term stability, which allows variations in parent-daughter ratios to be expressed in variations in radiogenic isotope ratios. Convective mixing in the suboceanic mantle will tend to destroy heterogeneity in it.

Though many xenoliths have isotopic compositions indicating incompatible-element enrichment, others xenoliths show parts of the subcontinental lithosphere can be extremely incompatible-element depleted. $\varepsilon_{\text{Nd}}$ values of +500 have been recorded in garnets in eclogites from the Roberts Victor mine kimberlite. These eclogites appear to be rafts of subducted oceanic crust stranded in the subcontinental lithosphere over 3 Ga ago, an interpretation supported by highly variable oxygen isotope ratios in the eclogites. They apparently suffered extreme LRE depletion around that time, perhaps by a small de-
Degree of melting or dehydration after subduction. Much of the subcontinental lithosphere may consist of mantle from which partial melts have been extracted to form the continental crust. Interesting, when the upper mantle undergoes melting both the melt and residual solid will have a density that is less than the original material. This residue is less dense because garnet, a very dense phase, is preferentially removed during melting. Thus both the crustal and mantle parts of the continental lithosphere have relatively low density, which may help to explain its stability.

If the subcontinental lithosphere is residual material from which melts have been extracted, why are xenoliths and basalts with “enriched” isotopic signatures so common? What process or processes could have produced this incompatible element enrichment of many parts of the subcontinental lithosphere? One possibility, first suggested by Brooks et al. (1976), is that partial melts from mantle plumes migrate upward into the lithosphere, where they freeze. The extent to which upwelling mantle can melt will depend on the depth to which it rises. Where continental lithosphere prevents plumes from rising above 200 km depth or so, the degree of melting is likely to be quite small, meaning the melts would be

---

**Figure 6.20.** (a) top. Sr and Nd isotope ratios in continental basalts. (b) bottom. Sr and Nd isotope ratios in xenoliths in continental basalts. After Zindler and Hart (1986).
Isotope Geochemistry

Chapter 6

Spring 2011

Quite incompatible-element enriched. These melts could then migrate upward into the lithosphere, reacting with it, freezing, and enriching it in incompatible elements. Yet another possibility is that hydrous fluids released during dehydration of subducting oceanic lithosphere may migrate into the continental lithosphere and react with it (Hawkesworth, 1990).

Judging from studies of island arc magmas, such fluids appear to be particularly enriched in soluble incompatible elements, such as the alkalis and alkaline earths. These processes in which lithosphere reacts with melts or fluids is known as mantle metasomatism*. Petrographic studies of some xenoliths clearly reveal features, such as the secondary growth of hydrous minerals such as phlogopite (Mg-rich mica) and richterite (an alkali-rich amphibole) indicative of such metasomatism.

Recent studies of Os isotope ratios in xenoliths from the subcontinental lithosphere have been particularly enlightening. Most xenoliths derived from below regions of old continental crust have low Os isotope ratios, which imply that low Re/Os ratios were established long ago. The low Re/Os ratios are consistent with the idea that this material undergone partial melting in the past, since Re is moderately incompatible, and would partition into the melt, while Os is highly compatible, and would remain in the solid. Despite their low $^{187}\text{Os}/^{188}\text{Os}$ ratios, many of these same xenoliths have quite low $\varepsilon_{\text{Nd}}$ (Figure 6.21). The explanation of this paradox appears to be that Os was not affected by the metasomatism that enriched these regions in incompatible elements and decreased Sm/Nd ratios (e.g., Carlson and Irving, 1994). Apparently, neither Re nor Os are transported effectively by metasomatic fluids. If the fluids are aqueous, this is perhaps not surprising, since these elements have low solubilities under reducing conditions. If the fluids are silicate melts, it is unclear why they do not transport Re. The answer may have to do with dependence of the Re partition coefficient on composition and oxygen fugacity.

Regardless of why they arise, these unusual Os-Nd isotope systematics provide the continental lithosphere with a distinctive isotopic signature and geochemists with a means of identifying continental lithosphere. In an earlier section, we discussed the hypothesis of McKenzie and O’Nions that subcontinental lithosphere can delaminate and sink to the bottom of the mantle where it is incorporated into

* Metasomatism is defined in metamorphic petrology as a subsolidus process that results in a net change in the composition of the metamorphic rock. Usually this is accomplished by the flow of aqueous solutions through the rock. The term ‘mantle metasomatism’ is widely used to refer to reaction between rock and silicate liquid as well as between rock and aqueous solution.
mantle plumes. The distinctive isotope signatures of mantle plumes on the one hand and subcontinental lithosphere on the other (Figure 6.21) are inconsistent with this hypothesis.

Continental flood basalts provide another interesting example. These are huge outpourings of basaltic lava that apparently occurred within relatively short time intervals, a few million years and possibly less in some cases. The great oceanic plateaus, such as Ontong-Java and Kerguelen are the marine equivalents. A number of continental flood basalts can be clearly associated with mantle plumes. For example, the Deccan Traps erupted 65 million years ago when India lay directly over the Reunion mantle plume, and the Parana in Brazil and Etendeka in Namibia were erupted 130 million years ago over the Tristan da Cunha mantle plume when Africa and South America were rifting. These observations have given rise to the idea that continental flood basalts are produced when new mantle plumes arrive at the surface.

Fluid dynamic experiments and simulations show that new plumes will have large bulbous heads. When the heads arrive in the upper mantle, they melt, producing a pulse of volcanism. Others, however, have argued on geochemical grounds that continental flood basalts are produced by melting of the continental lithosphere. Because mantle plumes and continental lithosphere have such different Os and Nd isotope signatures, Os-Nd systematics provide a means of discriminating between these possibilities. Because of the difficulties in determining Os isotope ratios in basalts, only one such study has been carried out thus far. In it, Ellam et al. (1992) found that the Karroo flood basalts, erupted in South Africa 190 million years ago, have Os and Nd isotope compositions that lie on mixing lines connecting mantle plume compositions and continental lithosphere compositions (Figure 6.22). Thus at least in this case, both a mantle plume and continental lithosphere appear to have contributed to the magmas. The data also demonstrate the assimilation of continental crust cannot explain the low $\varepsilon_{\text{Nd}}$ observed in these basalts.

REFERENCES AND SUGGESTIONS FOR FURTHER READING


