RADIOGENIC ISOTOPE GEOCHEMISTRY: 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 radiogenic 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 $^{87}$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 $^{87}$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 $^{87}$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:

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

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 $^{87}$Sr/$^{86}$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. Isotopic ratios, however, preserve, albeit incompletely, information about both chemistry and time.

As Gast said, the $^{87}$Sr/$^{86}$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 elements, 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 13.1 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 $^{87}\text{Rb}/^{86}\text{Sr} = t + \sin(5t/\pi) + 1$. This is shown plotted in Fig. 13.1a. 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. 13.1b. Just as we can calculate the average $^{87}\text{Rb}/^{86}\text{Sr}$ ratio from the area under the curve in figure 13.1a, 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. 13.1b 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, 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:

$$m_{\text{PM}}[\text{E}]_{\text{PM}} = m_{\text{E}}[\text{E}]_{\text{E}} - m_{\text{C}}[\text{E}]_{\text{C}}$$  

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:

$$m_{\text{M}}[\text{E}]_{\text{M}} = m_{\text{PM}}[\text{E}]_{\text{PM}} - m_{\text{K}}[\text{E}]_{\text{K}}$$

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 $^{182}\text{W} / ^{184}\text{W}$ 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† 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

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* Peridotite is a rock which consists of greater than 50% olivine, $[\text{Mg,Fe}]\text{SiO}_4$; 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 ($[\text{Mg,Fe}]\text{CaSi}_2\text{O}_6$) and orthopyroxene ($[\text{Mg,Fe}]\text{Si}_2\text{O}_5$), and an aluminous phase, either plagioclase ($\text{CaAl}_2\text{Si}_2\text{O}_8$), spinel ($\text{MgAl}_2\text{Si}_2\text{O}_8$), or garnet ($[\text{Mg,Fe,Ca}]\text{Al}_2\text{Si}_2\text{O}_{12}$) 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 ($\text{Mg,Fe,Ca}\text{Si}_2\text{O}_6$) and magnesiowüstite ($\text{Mg,FeO}$).

† 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.
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.

We will begin by concentrating on the picture of the mantle provided by isotopic compositions of basalts derived from the suboceanic mantle. We initially avoid continental basalts 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

![Diagram](Figure 13.2. 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.)
not be as well mixed and as representative of the mantle as oceanic basalts derived from the convecting mantle.

**The Sr-Nd-Hf Picture**

Figure 13.2 shows the Sr and Nd isotopic characteristics of the Earth’s major silicate reservoirs, and Figure 13.3 shows the isotopic compositions of oceanic basalts – mid-ocean ridge basalts (MORB) and oceanic island basalts (OIB). The first observation is that MORB have the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ and highest $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. We immediately interpret this as an indication that the mantle source of MORB has

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‡ 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.
low Rb/Sr and high Sm/Nd ratios relative to the source of OIB. Furthermore, these low ratios must have existed for a geologically significant time, hundreds of millions or billions of years, though without information on the parent/daughter ratios, we cannot be certain of how long.

Nd isotopes provide particularly useful information because we know the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of the whole earth or primitive mantle. We see that all of the MORB and most of the OIB have positive $\varepsilon_{\text{Nd}}$, i.e., they have $^{143}\text{Nd}/^{144}\text{Nd}$ greater than bulk earth. We associate positive $\varepsilon_{\text{Nd}}$ ratios with light-rare-earth (LRE) depletion. MORB are themselves LRE depleted, so this comes as no surprise. From what we know of mineral-melt partition coefficients, it was clear before Nd isotopic data were available that the source of MORB was also LRE depleted. The Nd isotopic data confirmed this, but also made it clear that this light-rare-earth depletion must have existed for a considerable length of time (in order for the high $^{143}\text{Nd}/^{144}\text{Nd}$ to evolve). It was surprising that most OIB also had positive $\varepsilon_{\text{Nd}}$ and hence time-integrated LRE depleted rare earth patterns because they are generally LRE enriched. While it is possible to create LRE enriched melts from LRE depleted sources, this requires rather small degrees of partial melting.

Although we tend to think of MORB and OIB as being isotopically distinct, there is in fact considerable overlap in the isotopic compositions of these groups. This is illustrated in Figure 13.4 for $\varepsilon_{\text{Nd}}$. Nevertheless, the means of the two are quite different, 8.7 and 5.0 respectively. MORB also clearly have a more uniform isotopic composition, and this is reflected by a standard deviation that is significantly smaller than that of OIB.

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

![Figure 13.4. 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.](image)
the difference between MORB and OIB, which we will consider later.

In the past, the “depleted” isotopic signatures of oceanic basalts have been explained in just this way, i.e., production of the crust, either continental, oceanic, or both. Extraction of high Rb/Sr, low Sm/Nd crust would leave a mantle with low Rb/Sr and high Sm/Nd that evolved toward low \(^{87}\text{Sr}/^{86}\text{Sr}\) and high \(\varepsilon\text{Nd}\). However, the new \(^{142}\text{Nd}/^{144}\text{Nd}\) measurements force us to rethink this assumption. The \(^{142}\text{Nd}/^{144}\text{Nd}\) of the accessible Earth, including MORB and OIB, is about 20 ppm higher than chondritic. This implies that the Sm/Nd ratio of the accessible Earth is 5\% or more higher than chondritic. This translates to an \(\varepsilon\text{Nd}\) of the accessible Earth of +5 or more, i.e., near the mean value for OIB. In other words, the average oceanic basalt may come from a mantle whose composition is close to that of primitive mantle. We do not have the same constraints on the Rb/Sr ratio of the Earth, but given the strong correlation between \(^{87}\text{Sr}/^{86}\text{Sr}\) and \(\varepsilon\text{Nd}\), it seems reasonable to assume that the Rb/Sr ratio was similarly affected (albeit in the opposite sense) by early differentiation.

Figure 13.5 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 \(\varepsilon\text{Nd}\). The bulk Earth \(^{177}\text{Hf}/^{176}\text{Hf}\) ratio is 0.2828, so we also see that MORB have positive \(\varepsilon\text{Hf}\), as do many OIB. Because Hf is more incompatible than Lu, the information provided by the Hf is entirely consistent with the information 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 \(^{207}\text{Pb}/^{204}\text{Pb}\) vs \(^{206}\text{Pb}/^{204}\text{Pb}\) is proportional to time. Since Pb is a volatile element, and also somewhat siderophile and chalcophile, we cannot assume the U/Pb ratio of the silicate Earth is the same as the chondritic one. Indeed, it is demonstrably not. Hence the Pb isotope ratios of the bulk Earth are not known precisely, as is the Nd or Hf isotope ratio.
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 $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ 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 13.6; Table 13.1). 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 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 13.6, 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. (Even if the Earth is a few 10’s of millions of years younger than the solar system, the U/Pb ratio in the solar nebula would have been so low that the increase in $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ would have been negligible.) As time passed the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios increased. At first, the $^{208}\text{Pb}/^{204}\text{Pb}$ 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 13.5, 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.

Figure 13.6. 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.

| TABLE 13.1. Pb ISOTYPE RATIOS IN CANYON DIABLO TROILITE |
|-----------------|-----------------|
| $^{206}\text{Pb}/^{204}\text{Pb}$ | 9.307 |
| $^{207}\text{Pb}/^{204}\text{Pb}$ | 10.294 |
| $^{208}\text{Pb}/^{204}\text{Pb}$ | 29.476 |
With this in mind, we can now consider the available Pb isotopic data on the mantle, which is shown in Figure 13.7. 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

Figure 13.7. Pb isotope systematics of oceanic basalts on the $^{207}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$ diagrams. $\Phi$ is the mean of 10 estimates of BSE compiled by Halliday (2004).
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 plots significantly to the high $^{206}\text{Pb} / {^{204}\text{Pb}}$ side of the Geochron. The mean of these estimates, 18.10 and 15.50, is shown in Figure 13.7. If this is indeed the BSE isotopic composition, it means that the silicate Earth must be significantly younger (50–100 Ma younger) than 4.66 Ga. Since Pb is siderophile and U is lithophile, this young age could reflect late core formation. This would appear to conflict with the evidence from W isotopes that the Earth formed, and its core segregated, within 30 Ma of 4.56 Ga. Halliday (2004) considered this problem and concluded that a probable explanation for discrepancy in Hf-W and U-Pb ages of the Earth is that the planetesimals that accreted to form the Earth had already differentiated into silicate mantles and metal cores. He suggests that the cores of these impacting planetesimals did not always mix efficiently with the silicate portions of the Earth before being added to the Earth’s core. As a result, Hf-W ages reflect more the age of planetesimals cores than the Earth’s core. Although Pb is similar to W in being siderophile, it is different from it in being volatile. Significant amounts of Pb could have been lost from the Earth as a result of impact-driven volatile loss. Halliday suggests that the U-Pb system might provide a more accurate age of the Earth than the Hf-W one. Yet another possibility is that the apparently $^{206}\text{Pb}$-rich nature of the accessible 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 if $U / \text{Pb}$ 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 $^{208}\text{Pb} / {^{204}\text{Pb}}$ 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 $U / \text{Pb}$ 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 $\text{Rb} / \text{Sr}$ and decreases in $\text{Sm} / \text{Nd}$ and $\text{Lu} / \text{Hf}$. $Th$ is slightly more incompatible than $U$.

Looking at Figure 13.7, 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 greater complexity of the U-Pb system. Figure 13.7 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 13.6. This age is on the order of 1.5–2 Ga. Exactly what this age means, if indeed it is meaningful at all, is unclear. The array in figure 13.7 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.

$\text{Sm-Nd}$, $\text{Lu-Hf}$, and $\text{Rb-Sr}$ 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 13.8. We know that the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios provide information about the time-integrated U/Pb ratio, 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:

$$^{208}\text{Pb}^* = ^{232}\text{Th}(e^{\lambda_{232}t} - 1)$$  \hspace{1cm} 13.4

and

$$^{206}\text{Pb}^* = ^{238}\text{U}(e^{\lambda_{238}t} - 1)$$  \hspace{1cm} 13.5

where the asterisks denotes the radiogenic component. Dividing 13.4 by 13.5, we obtain:

$$\frac{^{208}\text{Pb}^*}{^{206}\text{Pb}^*} = \frac{^{232}\text{Th}}{^{238}\text{U}} = \kappa \frac{(e^{\lambda_{232}t} - 1)}{(e^{\lambda_{238}t} - 1)}$$  \hspace{1cm} 13.6

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:

![Figure 13.8. $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of the suboceanic mantle as sampled by oceanic basalts.](image)
where the subscript $i$ denotes the initial ratio. By substituting a value for time in equation 13.6, and picking appropriate initial values for equation 13.7, we can calculate the time-integrated value of $\kappa$ over that time. For example, picking $t = 4.55$ Ga and initials equal to Canyon Diablo, we calculate the time-averaged $\kappa$ over the past 4.55 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 13.9 shows $\varepsilon_{\text{Nd}}$ plotted against $^{208}\text{Pb}^{*}/^{206}\text{Pb}^{*}$.

Figure 13.9. $\varepsilon_{\text{Nd}}$ vs. $^{208}\text{Pb}^{*}/^{206}\text{Pb}^{*}$ ratios of the suboceanic mantle as sampled by oceanic basalts.
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 geophysical 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. The idea of early enriched and depleted reservoirs in the mantle, derived from the non-chondritic nature of the terrestrial $^{142}$Nd/$^{144}$Nd ratio, encounters an even more severe problem. 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. 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.

REFERENCES AND SUGGESTIONS FOR FURTHER READING