

## RADIOGENIC ISOTOPE GEOCHEMISTRY: THE MANTLE I

### 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  $^{87}\text{Sr}$  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:

$$\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}} = \left( \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}} \right)_0 + \frac{{}^{87}\text{Rb}}{{}^{86}\text{Sr}} (e^{\lambda t} - 1) \quad 16.1$$

Gast's statement remains a valid and succinct summary of the principles of isotope geochemistry. The only change we need to make is the addition of other systems, Sm-Nd, Re-Os, Lu-Hf, La-Ce, and K-Ar, and U-Th-Pb.

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 continuing 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 a shale, no structural information is preserved. Some chemical information might be preserved in this case, though 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 a 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 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 a 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 16.1 allows us the limit the range of possible times at which this fractionation occurred.

### DEFINITIONS: TIME-INTEGRATED AND TIME AVERAGED

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

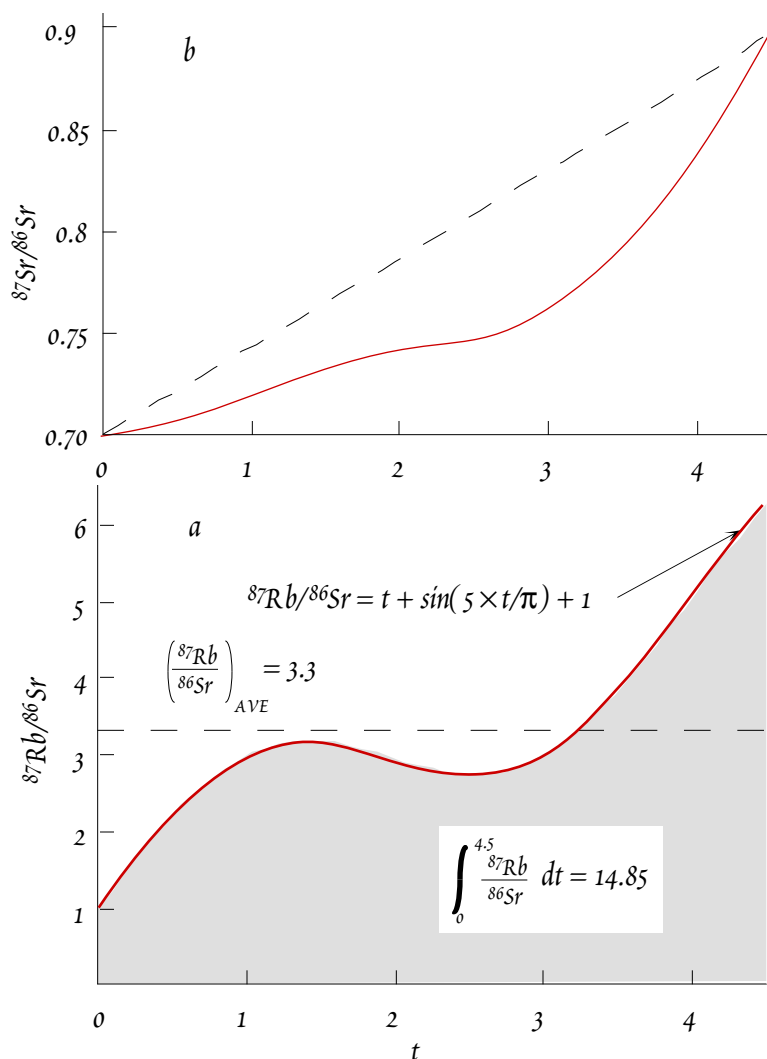


Figure 16.1. (a)  $^{87}\text{Rb}/^{86}\text{Sr}$  is shown as changing in a hypothetical reservoir as some arbitrary function of time. The average  $^{87}\text{Rb}/^{86}\text{Sr}$  may be calculated by integrating  $^{87}\text{Rb}/^{86}\text{Sr}$  with respect to time, and then dividing by  $(t - t_0)$ . (b) Evolution of  $^{87}\text{Sr}/^{86}\text{Sr}$  for the case where  $^{87}\text{Rb}/^{86}\text{Sr}$  is a function of time as shown in Fig. 16.1a. the dashed line shows the growth of  $^{87}\text{Sr}/^{86}\text{Sr}$  if  $^{87}\text{Rb}/^{86}\text{Sr}$  is constant and equal to 3.3.

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. 16.1a. 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. 16.1b. Just as we can calculate the average  $^{87}\text{Rb}/^{86}\text{Sr}$  ratio from the area under the curve in figure 16.1a if we know the initial and final values of  $t$ , we can deduce the average  $^{87}\text{Rb}/^{86}\text{Sr}$  in a reservoir if we know the initial and final values of  $^{87}\text{Sr}/^{86}\text{Sr}$ . It is in this sense that  $^{87}\text{Sr}/^{86}\text{Sr}$  yields a *time-integrated*, or *time-averaged* value of  $^{87}\text{Rb}/^{86}\text{Sr}$ .

Notice that the same final  $^{87}\text{Sr}/^{86}\text{Sr}$  value in Fig. 16.1b could have been reached had  $^{87}\text{Rb}/^{86}\text{Sr}$  had a constant value equal to its average 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. While we can deduce the average  $^{87}\text{Rb}/^{86}\text{Sr}$  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-

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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:

$$m_{PM}[E]_{PM} = m_E[E]_E - m_C[E]_C \quad 16.2$$

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:

$$m_M[E]_M = m_{PM}[E]_{PM} - m_K[E]_K \quad 16.3$$

where the subscript K denotes continental crust. Our formulation implicitly assumes the core was formed quite early and has not exchanged with the mantle since that time. Again this is an arbitrary choice, and we will examine it in more detail a bit later. 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 because of 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 complementary to the information derived from geophysical observations such as seismic waves, free oscillations, etc.

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\* Peridotite is a rock which consists of greater than 50% olivine ( $[Mg,Fe]SiO_4$ , the term peridotite comes from the gem name of olivine, peridot). Various lines of evidence, including both seismic velocities and the assumption of an approximately chondritic Earth, indicate the mantle must consist of peridotite. Other essential minerals are clinopyroxene ( $[Mg,Fe]CaSi_2O_6$ ) and orthopyroxene ( $[Mg,Fe]SiO_3$ ), and an aluminous phase, either plagioclase ( $CaAl_2Si_2O_8$ ), spinel ( $MgAlSiO_4$ ), or garnet ( $[Mg,Fe,Ca]_3Al_2Si_2O_{12}$ ) depending on pressure. Most other elements will be dissolved in these 4 phases.

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

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 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 16.2 shows the Sr and Nd isotopic characteristics of the Earth's major silicate reservoirs, and Figure 16.3 shows the isotopic compositions of oceanic basalts. The open circles are mid-ocean ridge basalts<sup>‡</sup> (MORB), the other symbols are basalts from various oceanic islands (oceanic island basalts or 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

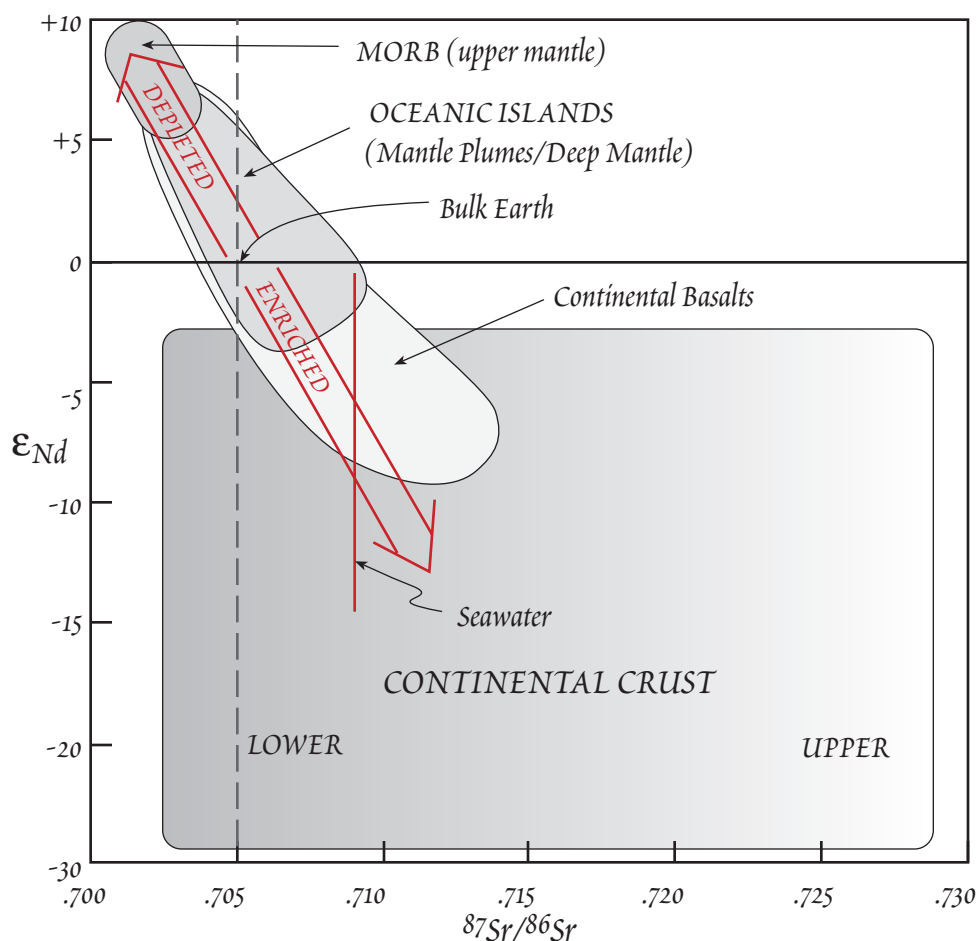


Figure 16.2. Sr and Nd isotopic systematics of the crust and mantle. Oceanic island basalts and MORB sample major reservoirs in the mantle. Continental basalts represent mixtures of various components, including mantle plumes, subcontinental lithosphere, and continental crust.

<sup>‡</sup> By definition, basalt is an extrusive igneous rock (i.e., lava) with less than 52%  $\text{SiO}_2$ . 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.

has low Rb/Sr and high Sm/Nd ratios relative to the source of OIB. Furthermore, these low ratios must have existed for some time, 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  $\epsilon_{\text{Nd}}$ , i.e., they have  $^{143}\text{Nd}/^{144}\text{Nd}$  greater than bulk earth. We associate positive  $\epsilon_{\text{Nd}}$  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  $\epsilon_{\text{Nd}}$  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 seems to require rather small degrees of partial melting.

In the above discussion, we have transformed the isotopic information into information about par-

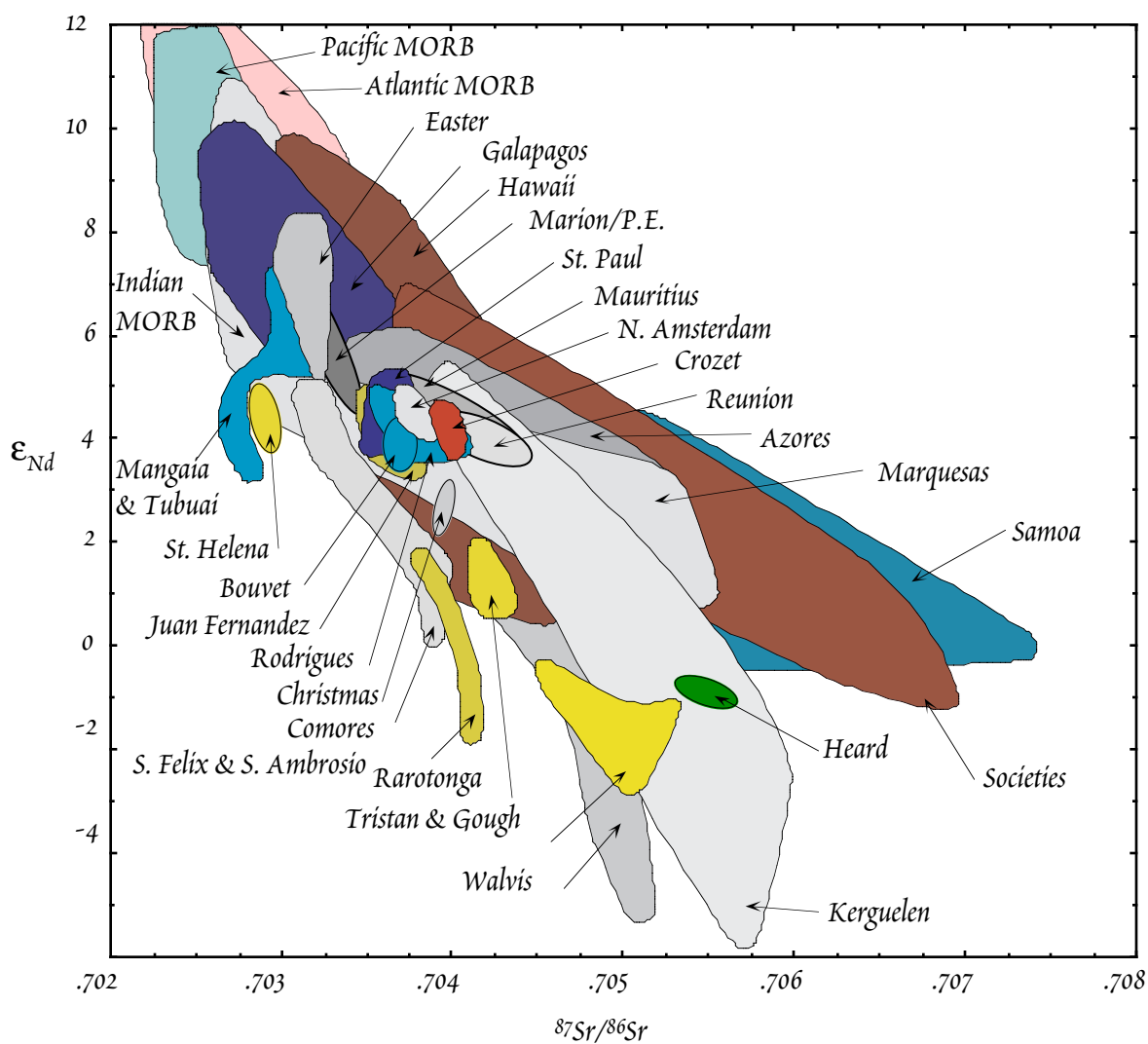


Figure 16.3. Sr and Nd isotope ratios of the suboceanic mantle as sampled by oceanic basalts. Three fields are shown for MORB from the 3 ocean basins, other symbols are various oceanic islands and island chains.

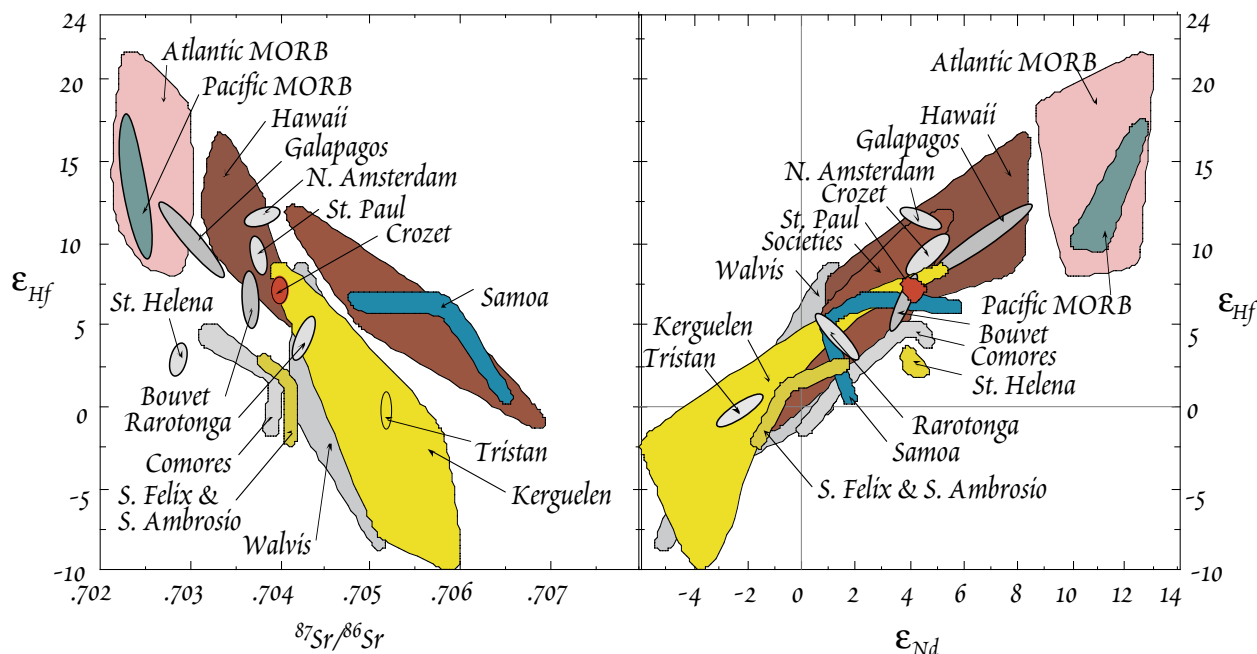


Figure 16.4. Hf, Sr, and Nd isotope ratios of the suboceanic mantle as sampled by oceanic basalts. Note that the  $\epsilon_{Nd}$ - $\epsilon_{Hf}$  array passes nearly through the 0-0 bulk Earth point.

ent-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. This would be consistent with our working hypothesis: extraction of a melt enriched in incompatible elements to form the continental crust left a mantle depleted in these incompatible elements. Thus the dominant process affecting the composition of the mantle appears to be extraction of a partial melt. The source of MORB appears to have been more depleted than the source of OIB. There are a number of possible reasons for this, which we will consider later.

Let's test this hypothesis further by considering an additional decay system, namely Lu-Hf. Figure 16.4 shows  $^{176}Hf/^{177}Hf$  ratios plotted against Nd isotope ratios. As we expect from what we know of the behavior of the parents relative to the daughters, the two are positively correlated. The bulk Earth  $^{177}Hf/^{176}Hf$  ratio is 0.28282, so we also see that MORB have positive  $\epsilon_{Hf}$  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.

### REFERENCES AND SUGGESTIONS FOR FURTHER READING

Gast, P. W. 1960. Limitations on the composition of the upper mantle. *J. Geophys. Res.* 65: 1287-1297.