

RADIOGENIC ISOTOPE GEOCHEMISTRY: THE MANTLE II

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. Our next step, therefore, is to see if Pb isotopes are consistent with the picture provided by Sr, Nd, and Hf. First we need to consider the special features of the Pb isotope system. We noted earlier that the slope on a plot of $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ is proportional to time. Since Pb is a volatile element, we cannot assume the U/Pb ratio of the Earth is the same as the chondritic one. 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 4.55 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 4.55 Ga and which passes through Canyon Diablo initial Pb (Figure 17.1; Table 17.1). 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 4.55 Ga ago, but the accretion of the inner

TABLE 17.1. Pb ISOTOPE 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

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. On the other hand, several lines of evidence suggest the Earth could be no younger than about 4.45 Ga. This evidence includes terrestrial Xe isotope data, which we will discuss subsequently, and the presence of 4.45 Ga rocks on the Moon. It is clear from isotope data among other evidence that the Earth and Moon are closely related planetary bodies, and it is unlikely the Moon is substantially older than the Earth. The point is that we

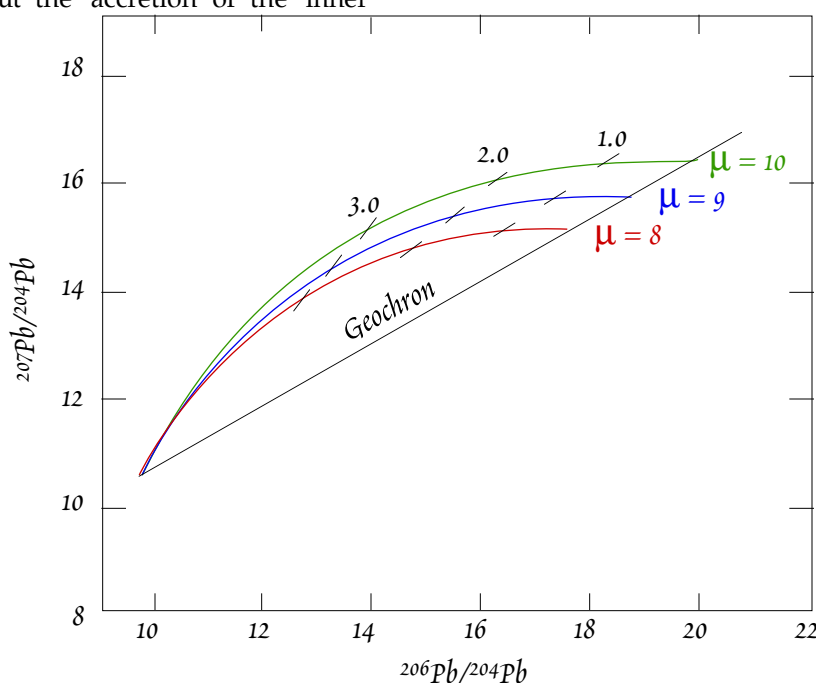


Figure 17.1. Evolution of Pb isotope ratios. The curve lines represent the evolutionary paths for systems having μ values of 8, 9, and 10. The hash marks on the evolution curves mark Pb isotope compositions 1.0, 2.0, and 3.0 Ga ago.

cannot be quite certain that bulk Earth Pb isotope ratios must lie on the geochron shown in Figure 17.1. But they must lie between this line and a 4.45 Ga isochron, which on Figure 17.1 would be essentially parallel to the 4.55 Ga geochron shown but shifted to higher $^{206}\text{Pb}/^{204}\text{Pb}$ by about 0.6.

When the Earth formed its Pb isotope ratios were (roughly) the same 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 $^{207}\text{Pb}/^{204}\text{Pb}$ ratio increased rapidly because there was about as much ^{235}U as ^{238}U around and ^{235}U was decaying to Pb more rapidly than ^{238}U . But as the ^{235}U was consumed, the rate of increase of $^{207}\text{Pb}/^{204}\text{Pb}$ slowed until the present when there is very little ^{235}U left to produce additional ^{207}Pb . Thus growth of Pb isotope ratios through time in any system follows a curved path, such as those in Figure 17.1, that depends on the $^{238}\text{U}/^{204}\text{Pb}$ (μ) ratio. If the system has remained closed (no change in μ) for the entire 4.55 Ga, it starts

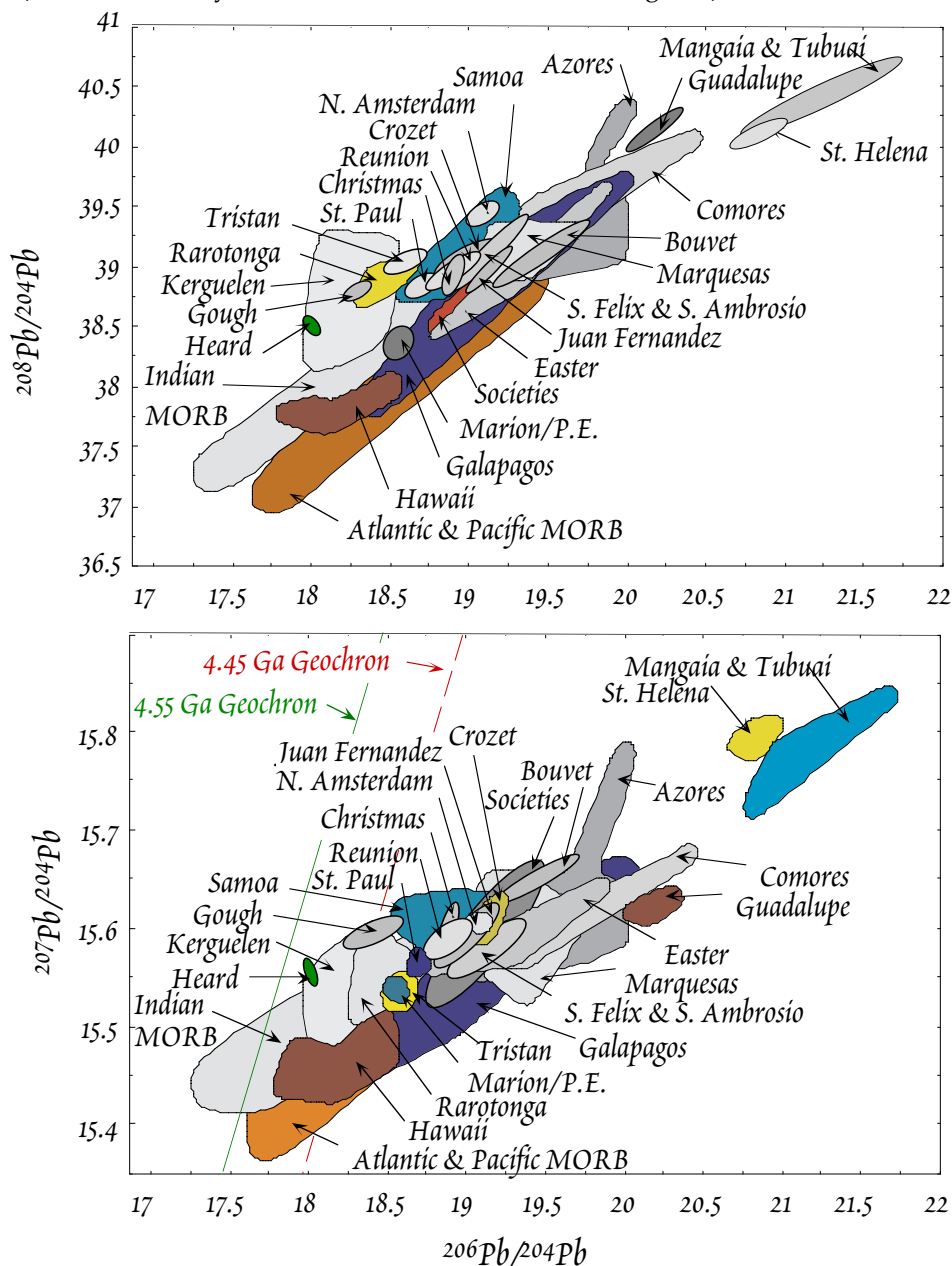


Figure 17.2. Pb isotope systematics of oceanic basalts on the $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams.

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at Canyon Diablo and ends (at present) at some point on the Geochron determined by its $^{238}\text{U}/^{204}\text{Pb}$ ratio.

It seems pretty clear that the Earth has remained a closed system with respect to Pb since its formation, but no reservoir within the Earth need have remained closed for this period. Systems that have experienced a net increase in μ over the past 4.55 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 is still a lot of ^{238}U around but not much ^{235}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 μ at some time later than 4.55 Ga would plot to the low $^{206}\text{Pb}/^{204}\text{Pb}$ side of the Geochron (note that changes in μ at 4.55 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 μ in any subsystem or reservoir within the Earth relative to the Earth as a whole. U is more incompatible than Pb, so increases in μ should accompany increases in Rb/Sr and decreases in Sm/Nd and Lu/Hf. Th is slightly more incompatible than U.

With this in mind, we can now consider the available Pb isotopic data on the mantle, which is shown in Figure 17.2. As we expect, Pb isotope ratios in OIB are generally, though not uniformly, higher than in MORB. However, it is surprising to find that nearly all oceanic basalts, including most MORB, plot to the high $^{206}\text{Pb}/^{204}\text{Pb}$ side of the Geochron, implying the mantle has experienced a net increase in μ (this is still true if we take 4.45 Ga as the age of the Earth). So either (a) U is not more incompatible than Pb, (b) partial melting is not the process responsible for changing U/Pb, Rb/Sr, Sm/Nd and Lu/Hf ratios, or (c) the U/Pb ratio has been affected by some process that has not significantly affected the other ratios. Figure 17.2 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 17.2. 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 17.2 can be interpreted as a mixing line between components at each end, in which case the age means very little. Alternatively, the age may date a single differentiation event, or represent the average age of a series of differentiation events.

Sm, Nd, Lu, Hf, Rb, and Sr all appear to be behaving in a generally coherent manner in the mantle, but one or all of U, Th, and Pb appears 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 17.3. 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 ratio, or μ , 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 κ . This is done as follows. We can write two equations:

$$^{208}\text{Pb}^* = ^{232}\text{Th}(e^{\lambda_{232}t} - 1) \quad 17.1$$

$$\text{and} \quad ^{206}\text{Pb}^* = ^{238}\text{U}(e^{\lambda_{238}t} - 1) \quad 17.2$$

where the asterisks denotes the radiogenic component. Dividing 17.1 by 17.2, we obtain:

$$\frac{^{208}\text{Pb}^*}{^{206}\text{Pb}^*} = \kappa \frac{(e^{\lambda_{232}t} - 1)}{(e^{\lambda_{238}t} - 1)} \quad 17.3$$

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

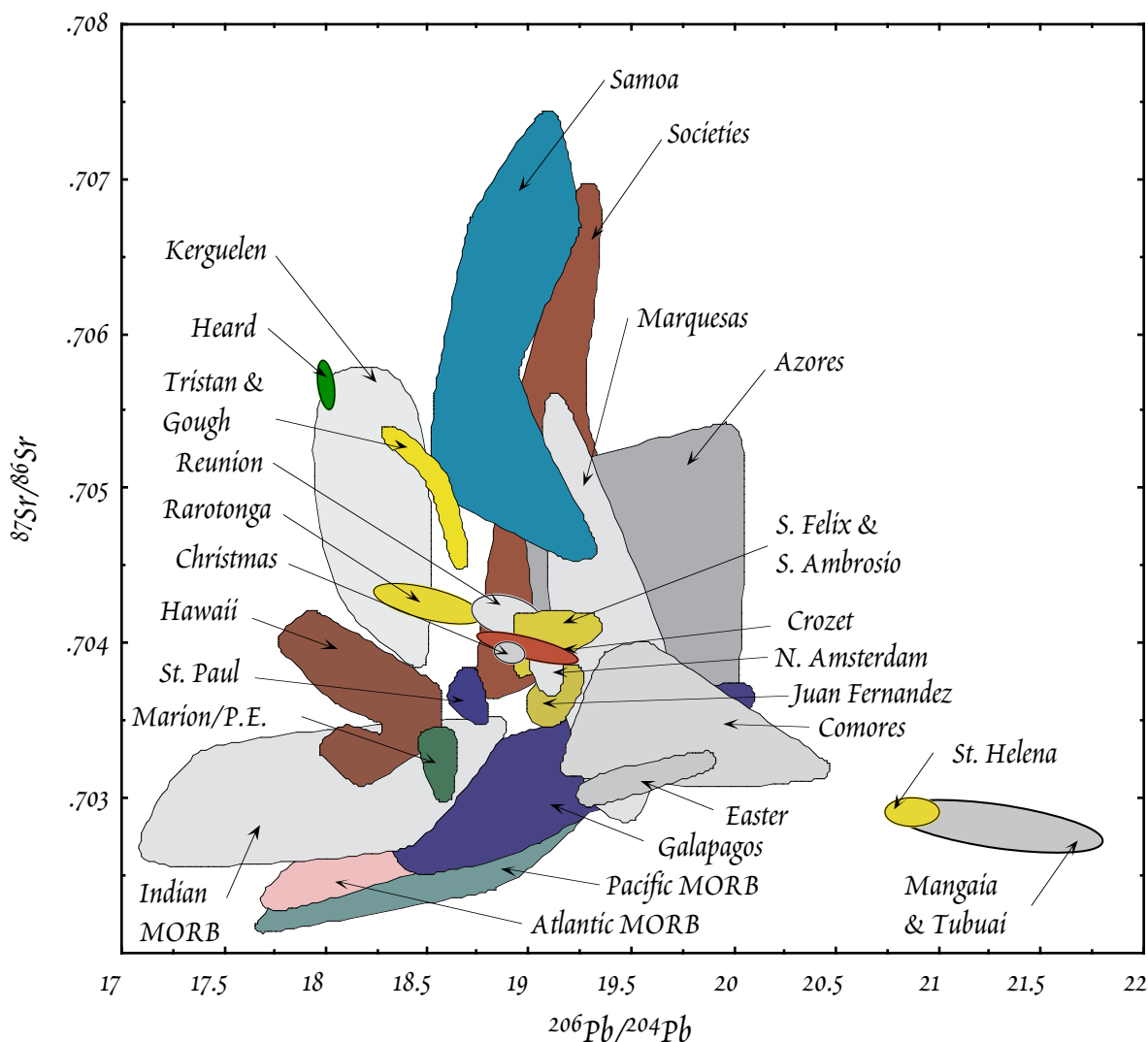


Figure 17.3. $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of the suboceanic mantle as sampled by oceanic basalts.

$$\frac{{}^{208}\text{Pb}^*}{{}^{206}\text{Pb}^*} = \frac{{}^{208}\text{Pb}/{}^{204}\text{Pb} - ({}^{208}\text{Pb}/{}^{204}\text{Pb})_i}{{}^{206}\text{Pb}/{}^{204}\text{Pb} - ({}^{206}\text{Pb}/{}^{204}\text{Pb})_i} \quad 17.4$$

where the subscript i denotes the initial ratio. By substituting a value for time in equation 17.3, and picking appropriate initial values for equation 17.4, we can calculate the time-integrated value of κ over that time. For example, picking $t = 4.55$ Ga and initials equal to Canyon Diablo, we calculate the time-averaged κ over the past 4.55 Ga.

Now let's see how $^{208}\text{Pb}^*/^{206}\text{Pb}^*$, and hence κ relates to other isotope ratios, and hence other parent-daughter ratios. Figure 17.4 shows ϵ_{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. Clearly, there are at least two major reservoirs in the mantle. The conventional interpretation is that MORB are derived from the uppermost mantle, which we can see is the most depleted of the

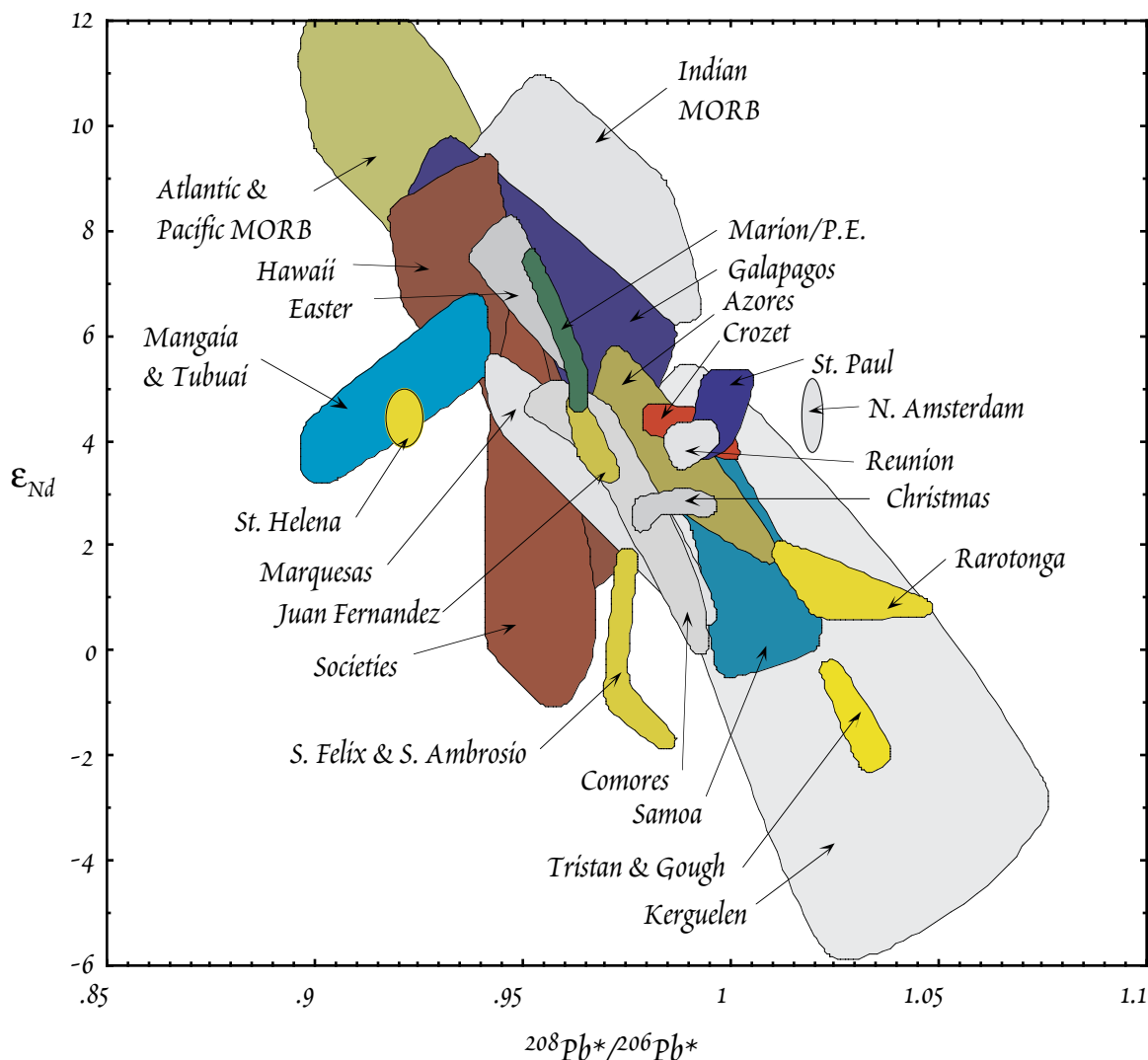


Figure 17.4. ϵ_{Nd} vs. $^{208}Pb^*/^{206}Pb^*$ ratios of the suboceanic mantle as sampled by oceanic basalts.

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. 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 ϵ_{Hf} and ϵ_{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 ϵ_{Hf} and ϵ_{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.