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 $^{207}\text{Pb} / ^{204}\text{Pb} - ^{206}\text{Pb} / ^{204}\text{Pb}$ 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 4.55 Ga ago. Thus the $^{207}\text{Pb} / ^{204}\text{Pb}$ and $^{208}\text{Pb} / ^{204}\text{Pb}$ 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 19.1; Table 19.1). 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 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 16 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 19.1.

![Figure 19.1. 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.](image-url)

| Table 19.1. Pb Isotope Ratios in Canyon Diablo Troilite |
|-----------------|-----------------|
| $^{208}\text{Pb} / ^{204}\text{Pb}$ | 9.307 |
| $^{207}\text{Pb} / ^{204}\text{Pb}$ | 10.294 |
| $^{206}\text{Pb} / ^{204}\text{Pb}$ | 29.476 |
19.1, 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 $^{206}$Pb/$^{204}$Pb and $^{207}$Pb/$^{204}$Pb would have been negligible.) As time passed the $^{207}$Pb/$^{204}$Pb and $^{206}$Pb/$^{204}$Pb ratios increased. At first, the $^{207}$Pb/$^{204}$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 $^{207}$Pb/$^{204}$Pb slowed until the present when there is very little $^{235}$U left to produce additional $^{206}$Pb. Thus growth of Pb isotope ratios through time in any system follows a curved path, such as those in Figure 19.1, that depends on the $^{238}$U/$^{204}$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 $^{238}$U/$^{204}$Pb ratio.

With this in mind, we can now consider the available Pb isotopic data on the mantle, which is shown in Figure 19.2. Perhaps somewhat surprisingly, almost all oceanic basalts plot to the high $^{206}$Pb/$^{204}$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 $^{206}$Pb/$^{204}$Pb side of the Geochron (average lower continental crust probably plots slightly to the low $^{206}$Pb/$^{204}$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 $^{206}$Pb/$^{204}$Pb = 17.44 and $^{207}$Pb/$^{204}$Pb = 15.16 to $^{206}$Pb/$^{204}$Pb = 18.62 and $^{206}$Pb/$^{204}$Pb = 15.565, reflecting our uncertainty in this BSE Pb isotopic composition. However, all of these plot significantly to the high $^{206}$Pb/$^{204}$Pb side of the Geochron. The mean of these estimates, 18.10 and 15.50, is shown in Figure 19.2. 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. 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 planetesimal 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 $^{208}$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 $^{206}$Pb/$^{204}$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 4.55 Ga will plot today to the high $^{206}$Pb/$^{204}$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 $^{206}$Pb/$^{204}$Pb ratios relative to $^{207}$Pb/$^{204}$Pb ratios. Conversely, a system experiencing a net decrease in $\mu$ at some time later than 4.56 Ga would plot to the low $^{206}$Pb/$^{204}$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 19.2, 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 19.2 also shows the relationship between $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$. 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 19.2. 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 19.2 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.

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 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 19.3. 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 $\mu$, 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 fol-

Figure 19.3. $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of the suboceanic mantle as sampled by oceanic basalts.
Lecture 19

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deep and shallow mantle. Furthermore, there is no convincing evidence of reflections or seismic velo

anic 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 $\varepsilon_{Nd}$ and $\varepsilon_{Hf}$ 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 $\varepsilon_{Nd}$ and $\varepsilon_{Hf}$. 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

\begin{align*}
208 \text{Pb}^* &= 232 \text{Th}(e^{\lambda_{232} t} - 1) \\
206 \text{Pb}^* &= 238 \text{U}(e^{\lambda_{238} t} - 1)
\end{align*}

where the asterisks denotes the radiogenic component. Dividing 19.1 by 19.2, we obtain:

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

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

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

where the subscript $i$ denotes the initial ratio. By substituting a value for time in equation 19.3, and picking appropriate initial values for equation 19.4, 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 $^{208}$Pb*/$^{206}$Pb*, and hence $\kappa$ relates to other isotope ratios, and hence other parent-daughter ratios. Figure 19.4 shows $\varepsilon_{Nd}$ plotted against $^{208}$Pb*/$^{206}$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 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.
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
