Radiogenic Isotope Geochemistry – applications to igneous systems

Reading – White Chapter Ch 8.3 and Ch11.5-11.6
(this is the last assigned reading for the semester; you’ve already read parts of these chapters earlier).

Today
1. Overview.

Radiogenic Isotopes in Igneous Systems

Like stable isotopes, radiogenic isotopes play many roles in different branches of Earth science. They are among the most powerful tools geochemists have.

We’ve already discussed some of the isotopic evidence for the ages and timing of various events in Earth and early solar system history. But we haven’t yet examined exactly how this evidence works in detail.

quick review of radioactive decay again:

Recall the decay equation: $N_t = N_0 e^{-\lambda t}$

where $N$ is the radioactive parent, $t$ is the time of decay, and “$o$” is the initial condition (at $t=0$).
Radiogenic Isotopes in Igneous Systems

(1) \[ N_t = N_0 e^{-\lambda t} \]
One can determine an age by comparing \( N_t \) and \( N_0 \).

We can also determine ages if we don’t know \( N_0 \), because \( N \) decays to a daughter isotope, \( D \), such that
\[ N_0 = N_t + D_t \], assuming that \( D \) is also not radioactive (we will discuss that special case later)

Substituting into eqn (1) \( N_t + D_t = N_0 e^{\lambda t} \) yields:

(2) \[ D_t = N_t e^{\lambda t} - N_t \]

\( D_t = N_t(e^{\lambda t} - 1) \) In many cases, \( D_0 \neq 0 \), so we need to include it:

\[
D_t = D_0 + N_t(e^{\lambda t} - 1) \quad \text{or} \quad \frac{D_t}{d} = \frac{D_0 + N_t(e^{\lambda t} - 1)}{d}
\]

Where \( d \) = a non-radiogenic isotope of the daughter element; it is called the normalizing isotope.

Radiogenic Isotopes in Igneous Systems

\[
(D/d)_t = (D/d)_0 + (N/d)_t(e^{\lambda t} - 1)
\]

Commonly, \( D/d \) and \( N/d \) are symbolized as \( R \) and \( P \), respectively.

We usually measure ratios rather than absolute amounts of isotopes because we can measure isotope ratios far more precisely.

Two uses of the above equation:
1. it serves as the basis for several powerful radiometric dating methods; i.e., where the goal is to measure \( t \), the age of geological samples. This branch of geochemistry is called geochronology. Your reading describes some of the details and gives several good examples.

2. An equally important application involves using radiogenic isotope ratios as tracers of the composition and history of sources and geochemical processes.

This latter application follows directly from our discussions of trace elements and planetary differentiation, so we’ll start with it first.
Radiogenic Isotopes in Igneous Systems

In the past few weeks, we’ve learned that:

1. Igneous rock compositions reflect the processes that formed the rocks (“petrogenesis”), and we can investigate these processes with a range of geochemical tools.

2. Planetary-scale differentiation has produced crustal and mantle reservoirs within the silicate Earth; these reservoirs have distinctly different compositions.

Radiogenic Isotopes in Igneous Systems

Compositional variability in igneous rocks can result from both
a. effects of past planetary differentiation on mantle
b. crustal compositions the magmatic activity that forms the rocks and the ongoing.

We use radiogenic isotopes of heavy elements to disentangle and illuminate these different processes, and to tell us about the time scales over which they operate.
Radiogenic Isotopes in Igneous Systems

We use radiogenic isotopes that are heavy, and produced from radioactive parents with *very long half lives*, because

- **they can** distinguish ancient from recent/modern processes and

- ratios of two isotopes of a heavy element are **generally not fractionated during melting or crystallization** (or we can correct for any minor fractionation); i.e., isotope ratios allow us to “see through” petrogenesis.

The second point is a fundamental difference between heavy-element isotopes and light-element isotopes, such as those of H, C, and O. As we saw earlier this semester, the light isotopes *can be* fractionated significantly by natural processes. For the light isotopes, it is the fractionation itself that makes them so useful.

Radiogenic Isotopes in Igneous Systems

Consider how the mantle operates to see why time is an important aspect of this process:

Each new mantle melting makes event the mantle a little bit more depleted in lithophile and atmophile elements, so differentiation of Earth is ongoing.

However, subduction of oceanic lithosphere also returns some lithophile and atmophile material back into the mantle.

Together, they form a compositional cycle within the silicate Earth that operates very much like the hydrologic cycle (although at rates that are far slower).
Radiogenic Isotopes in Igneous Systems

Over time, the mantle has developed compositional variability through this cycle. We see the evidence for this variability in igneous rocks from around the world.

Using trace elements, it’s usually very difficult or impossible to tell whether compositional differences were produced by past melting and crystallization events or very recently, possibly even in the same melting event that formed a particular sequence of magmas.

In contrast, ratios of radiogenic isotopes to non-radiogenic isotopes provide a record of ancient events that is not erased or overprinted by recent melting or crystallization events, including the chemical fractionation that accompanies the formation of an igneous rock itself.

We usually use isotope ratios, R, where

- one isotope is radiogenic (produced from the decay of another)
- the other is a stable, non radiogenic isotope.

\[ R = \frac{\text{radiogenic daughter}}{\text{non-radiogenic isotope}} \]

The parent and daughter element always have somewhat different incompatibility, so the ratio of radiogenic to non-radiogenic isotopes in a rock or mineral reflects the composition of the source…

but in a time-integrated way because the half lives of the parent isotopes are very long. For example, high R records a high time-integrated parent-daughter ratio, and thus preserves information on the time-integrated chemical composition and history of a mantle source.
Radiogenic Isotopes in Igneous Systems

In a material that has remained a chemically closed system for a long time the daughter isotope will closely reflect the concentration of the parent.

Let’s use the Rb-Sr system as an example.

Given enough time, $^{87}\text{Sr}/^{86}\text{Sr}$ will reflect $^{87}\text{Rb}/^{86}\text{Sr}$ via $^{87}\text{Rb}$ decay and $^{87}\text{Sr}$ ingrowth.

The evolution of the system over time is described by the radioactive decay equation we derived a few minutes ago, which can be written here as:

$$
^{87}\text{Sr}_{\text{today}} = ^{87}\text{Sr}_{\text{initial}} + ^{87}\text{Rb}_{\text{today}}(e^{\lambda t} - 1) \\
^{86}\text{Sr}_{\text{today}} = ^{86}\text{Sr}_{\text{initial}} + ^{87}\text{Rb}_{\text{today}}(e^{\lambda t} - 1)
$$

$^{86}\text{Sr}$ is the normalizing isotope used in Rb-Sr work. It is stable and non-radiogenic.

Radiogenic Isotopes in Mantle Evolution

An isochron diagram illustrates how an isotope ratio changes in a closed system after an initial fractionation event.

Example: let’s say our closed system is a rock composed of several minerals that formed from a melt of the mantle at some time $t$ in the past.

For the Rb-Sr system:

$$
^{87}\text{Sr}_{\text{today}}^{86}\text{Sr} = ^{87}\text{Sr}_{\text{initial}}^{86}\text{Sr} + ^{87}\text{Rb}(e^{\lambda t} - 1)
$$

For the bulk rock and for each phase in it, we can measure the present-day Sr isotope ratio and parent/daughter ratio and determine the age and the initial Sr isotope ratio.
Radiogenic Isotopes in Mantle Evolution

We do this with an isochron diagram, based on compositional relationships between different phases in a sample having the same age.

$^{(87\text{Sr}/86\text{Sr})}_{\text{today}} = (^{87\text{Sr}/86\text{Sr}})_{\text{initial}} + (^{87\text{Rb}/86\text{Sr}})_{\text{today}}(e^{\lambda t} - 1)$

$y = b + x \cdot m$

This is an equation for a straight line with $m = (e^{\lambda t} - 1)$ and $b = (^{87\text{Sr}/86\text{Sr}})_{\text{initial}}$.

We obtain the age, $t$, from the slope of the line, since $m = (e^{\lambda t} - 1)$ and the initial ratio from the intercept.

Each dot in the isochron plot at the left represents values for a given mineral or the bulk rock at a given time. The heavy lines connecting the dots are called isochrons.

As a rock ages, the slope of the isochron increases. Each dot evolves as indicated by the arrows.

Radiogenic Isotopes in Igneous Systems

$^{87}\text{Sr}/^{86}\text{Sr}_{\text{today}} = ^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}} + ^{87}\text{Rb}/^{86}\text{Sr}(e^{\lambda t} - 1)$

Open systems: material from which Rb and/or Sr were recently extracted will have Rb/Sr (and therefore $^{87}\text{Rb}/^{86}\text{Sr}$) different from the value we would predict from the present-day $^{87}\text{Sr}/^{86}\text{Sr}$ of the material.

In the mantle, there’s a wide diversity of $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values, reflecting how and when material has been added to or removed from different parts of it.
### Radiogenic Isotopes in Igneous Systems.

<table>
<thead>
<tr>
<th>Isotope pair</th>
<th>Parent</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>87</strong>Sr/<strong>86</strong>Sr</td>
<td><strong>87</strong>Rb decays to <strong>87</strong>Sr $\left( t_{1/2} = 4.967 \times 10^{10} \text{ yr} \right)$</td>
<td>in a rock, this tells us about Rb/Sr of the source. <strong>Rb is typically more incompatible than Sr.</strong></td>
</tr>
<tr>
<td><strong>147</strong>Sm/<strong>144</strong>Nd</td>
<td><strong>147</strong>Sm decays to <strong>143</strong>Nd $\left( t_{1/2} = 1.06 \times 10^{11} \text{ yr} \right)$</td>
<td>tells us about Sm/Nd of the source. <strong>Sm is typically less incompatible than Nd.</strong></td>
</tr>
<tr>
<td><strong>176</strong>Lu/<strong>177</strong>Hf</td>
<td><strong>176</strong>Lu decays to <strong>176</strong>Hf $\left( t_{1/2} = 3.5 \times 10^{10} \text{ yr} \right)$</td>
<td>tells us about Lu/Hf of the source. <strong>Lu is typically less incompatible than Hf.</strong></td>
</tr>
</tbody>
</table>

### Radiogenic Isotopes in Igneous Systems.

... and these isotopes of Pb

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<tr>
<td><strong>206</strong>Pb/<strong>204</strong>Pb</td>
<td><strong>238</strong>U decays to <strong>206</strong>Pb $\left( t_{1/2} = 4.47 \times 10^{9} \text{ yr} \right)$</td>
<td>in a rock tells us about U/Pb of the source. <strong>Pb is typically less incompatible than U.</strong></td>
</tr>
<tr>
<td><strong>207</strong>Pb/<strong>204</strong>Pb</td>
<td><strong>235</strong>U decays to <strong>207</strong>Pb $\left( t_{1/2} = 7.04 \times 10^{8} \text{ yr} \right)$</td>
<td>same, but with a different time scale for changes. <strong>same</strong></td>
</tr>
<tr>
<td><strong>208</strong>Pb/<strong>204</strong>Pb</td>
<td><strong>232</strong>Th decays to <strong>208</strong>Pb $\left( t_{1/2} = 1.40 \times 10^{10} \text{ yr} \right)$.</td>
<td>in a rock tells us about Th/Pb of the source. <strong>Pb is typically less incompatible than Th.</strong></td>
</tr>
</tbody>
</table>
Radiogenic Isotope (and other) Mixtures

Besides age and source information, isotope ratios are particularly useful for identifying and understanding mixtures.

In igneous rocks, mixtures are produced from melting of mantle with small-scale heterogeneity and from addition of crustal and mantle components to a magma (contamination, assimilation).

In such cases, magmas are mixtures of melts drawn from more than one source, or are from a single source but experienced different additional inputs during ascent and storage.

For a mixture of two end-members (1 and 2), mixtures are described by a hyperbola.

\[
A_{\text{mix}} = B_{\text{mix}} \left( \frac{(A_2 - A_1)}{(B_2 - B_1)} \right) + \frac{A_1 B_2 - A_2 B_1}{B_2 - B_1}
\]

Radiogenic Isotope Mixtures

Mixing of materials with different isotopic ratios and elemental concentrations produces predictable hyperbolic arrays.

These general types of mixing patterns hold for both element concentrations and isotope and trace element ratios.

(You can think of a concentration as a ratio with a denominator of 1; e.g., Sr = Sr/1).

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Radiogenic Isotope Mixtures

Figure 12.20. Plots of ratios of elements or isotopes, D/a vs P/b for mixing of end members 1 and 2. The numbers along the curves are the values for r. From Langmuir et al. (1978).

These equations are used for both isotope and trace element ratios.

The curvature of the mixing hyperbola is determined by a parameter “r”, a function of the concentration contrast between the quantities in the denominator of each component.

Mixing between materials of different isotopic or elemental compositions results in D/a and P/b values that are intermediate between the two end-members.

For element-element plots, note that r = 1 and the mixing hyperbola reduces to a straight line.

In coordinates of an isotope ratio of an element vs. the concentration of the same element, the mixing hyperbola reduces to a parabola.

In coordinates of an isotope ratio vs. the inverse concentration, the hyperbola reduces to a straight line (Sr is in the denominator of both axes).

Figure 12.21. Mixing hyperbola formed by components A & B. Isotopic and concentration values in the mixtures were determined using the mixing ratio, r as defined in Fig. 12-20.

In the full form of the mixing equation:

\[ \frac{87\ Sr}{86\ Sr} = \frac{a_1}{a_2} \frac{b_2}{b_1} \]

The right panel is a transformation of the hyperbola into a straight line using reciprocal Sr concentrations in the mixture are used. Modified from White, Geochemistry.
Radiogenic Isotope Mixtures

We can use any combination of radigenic isotopes, stable isotopes or trace element ratios with this equation or diagram.

One very interesting (and useful) application of binary mixing arrays is in assessing magma contamination by either crustal country rock or something in the mantle source, for example, addition of subducted sediments and/or ocean crust.

This Sr-O isotopic diagram is useful for this purpose because the Sr-O isotopic composition of crustal and mantle rocks are often quite distinct, as are their Sr concentrations, whereas O concentrations don’t vary too much.

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Tracing Mixtures in Igneous Petrogenesis with Radiogenic Isotopes

In mantle rock, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio will reflect the time-integrated $^{87}\text{Rb}/^{86}\text{Sr}$ (and thus Rb/Sr), but will not provide information about recent changes in Rb/Sr caused by, for example, melt removal or addition.

Thus, without any idea of how, when, or how often Rb/Sr has changed, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is specifically a general indicator of Rb/Sr in the source averaged over time.
Tracing Mixtures in Igneous Petrogenesis with Radiogenic Isotopes

Since petrogenesis basically does not fractionate the isotopes of Sr from one another

\[ \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{lava}} = \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{source}} \]

if a magma was formed from a single, isotopically homogeneous source and was never contaminated by country rock with a different isotopic value.

This is true for heavy isotope ratios in general:

a lava’s isotope ratio equals the source rock’s ratio under these conditions.

Tracing Mixtures …

The same would be true for two elements, a and b, that are not fractionated from each other by petrogenesis (i.e., that have the same bulk distribution coefficients during melting and crystallization). Then…

\[ \left( \frac{a}{b} \right)_{\text{lava}} = \left( \frac{a}{b} \right)_{\text{source}} \]

i.e., recall invariant ratio discussion of earlier this semester.

However, if a and b have different D values, they will be fractionated from one another by petrogenesis. Then…

\[ \left( \frac{a}{b} \right)_{\text{lava}} \neq \left( \frac{a}{b} \right)_{\text{source}} \]

In this second case, differences between \( \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{lava}} \) (constant if the source is homogeneous) and \( \left( \frac{a}{b} \right)_{\text{lava}} \) (variable, because of different D values) provide a way to distinguish whether petrogenesis or anciently established source differences primarily determines trace element ratios.
Tracing Mixtures …

If the source rock is heterogeneous in $^{87}\text{Sr}/^{86}\text{Sr}$, the heterogeneity pre-dates petrogenesis. Then in lavas that represent mixtures…

1. $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{mix}}$ depends on both $(^{87}\text{Sr}/^{86}\text{Sr})$ and Sr concentration in the end-members…

   \[ \text{and} \]

2. $(a/b)_{\text{mix}}$ depends on both $(a/b)$ and the concentrations of a and b in the end-members and the magmas.

   $(a/b)_{\text{lava}} \neq (a/b)_{\text{source}}$ and $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{lava}} \neq (^{87}\text{Sr}/^{86}\text{Sr})_{\text{source}}$

But the difference between the two ratios is that:

$^{87}\text{Sr}/^{86}\text{Sr}_{\text{lava}}$ depends mainly on the mixing of mantle sources

$^{87}\text{Sr}/^{86}\text{Sr}_{\text{lava}}$ depends on mixing of sources and the processes of petrogenesis.

Tracing Mixtures …

How and when materials are mixed makes some difference in the final result, but once crustal contamination is ruled out, the Sr isotopic heterogeneity is still attributable to variation in the unmelted source, rather than to melting or crystallization.

So differences between $^{87}\text{Sr}/^{86}\text{Sr}_{\text{lava}}$ and $(a/b)_{\text{lava}}$ help us to categorize...

- the types of mantle heterogeneities that exist,
- where they came from,
- when they formed,
- and what sorts of other trace element signatures they might have.

We return to this topic soon with an example to illustrate this.