Isotope Geochem Notes (U,Th-Pb; Sm-Nd; Re-Os; Lu-Hf)

Reading for this topic: White, Nos. 7,8,9,11.

Guide questions:
What are the special features of the U, Th - Pb system that make it uniquely useful for age dating very old rocks?
What are the special properties of Zircon that make it uniquely useful?
How can we combine the two U-Pb geochronometers in a way that makes the combined geochronometer more useful than either one alone?
How have geoscientists been able to infer the ages of the oldest rocks on earth, even though the zircons they used had leaked daughter nuclides at some point?
What is the special feature of the Sm-Nd geochronometer that makes it a more robust age dating tool than Rb-Sr?
Why have the earth’s mantle and crust evolved to different Nd isotope values over time?
How can the Sm-Nd system be used to infer the times at which various areas of the continental crust were generated from the earth’s mantle?
How is Lu-Hf similar to, and different from, the Sm-Nd system?
What mineral takes in Hf readily and is a durable recorder of past Hf isotope values?
Why have the Os isotope compositions of the earth’s mantle and crust evolved toward very different values over time?
How can the various isotope ratios tell us about the history of formation of continental masses on planet earth?

U, Th - Pb geochronology

Used to determine the ages of the oldest rocks on the earth’s surface

\[
\begin{align*}
^{238}\text{U} & \rightarrow ^{206}\text{Pb} + 8\alpha + 6\beta^+ + Q \quad \quad Q=1.55125 \times 10^{10} \quad \quad t_{1/2}= 4.468 \times 10^9 \text{ y} \\
^{235}\text{U} & \rightarrow ^{207}\text{Pb} + 7\alpha + 4\beta^+ + Q \quad \quad Q=9.8485 \times 10^{10} \quad \quad t_{1/2}= 0.7038 \times 10^9 \text{ y} \\
^{232}\text{Th} & \rightarrow ^{208}\text{Pb} + 6\alpha + 4\beta^+ + Q \quad \quad Q=4.9475 \times 10^{11} \quad \quad t_{1/2}= 14.010 \times 10^9 \text{ y}
\end{align*}
\]

Also see Table 8.1 from White Lecture 8

There are several alpha decays and several beta decays required for each U or Th isotope to reach a stable Pb isotope, but the intermediate nuclides are all ephemeral (short half-lives- effectively instantaneous decay if you are concentrating on age dates of millions to billions of years) and we can ignore them for now (we will get back to them soon). If you are curious, Fig. 10.1 from White’s Lecture 10 gives the U and Th Series decay chains.

The strengths of this system:
1) 3 different geochronometers involve three different Pb daughters
2) AND two U parents with different half-lives decay to two Pb daughters
   • you might think that the two geochronometers would just be redundant, but they are not (see below)
**Zircons** (ZrSiO$_4$) are nearly ideal crystals for age dating:
- Very resistant to weathering and melting
- U-rich, Th-rich, almost Pb-free when they form.

There are 3 possible isochron ages from a single rock. These would be redundant, though obviously useful to check each other. But for age dating very old zircons, Isochron methods are not used frequently.

We usually use the Concordia method. This approach takes advantage of the fact that the RATIO of two geochronometers with different decay rates is itself a geochronometer. We do this because Pb loss is common in old zircons- they’ve all been metamorphosed. The combined geochronometer is less affected by Pb loss- see below.

Here’s how we can obtain an equation that lets us use the combined the $^{207}$Pb-$^{206}$Pb approach:

$$\frac{^{206}Pb}{^{204}Pb} = \frac{^{206}Pb}{^{204}Pb} + \frac{^{238}U}{^{204}Pb} \left( e^{\lambda t} - 1 \right)$$

This is the normal isochron equation, written for U-Pb

$$\frac{^{207}Pb}{^{204}Pb} \frac{^{207}Pb}{^{204}Pb} = \frac{^{235}U}{^{204}Pb} \left( e^{\lambda t} - 1 \right)$$

Divide $^{235}$U-$^{207}$Pb eqn. by the $^{238}$U-$^{206}$Pb eqn.

$$\frac{^{207}Pb}{^{206}Pb} \frac{^{207}Pb}{^{206}Pb} = \frac{^{235}U}{^{238}U} \left( e^{\lambda t} - 1 \right)$$

Cancel out the $^{204}$Pb’s...

$$\frac{^{207}Pb}{^{206}Pb} = \frac{^{235}U}{^{238}U} \left( e^{\lambda t} - 1 \right)$$

Where the * means the ingrown Pb only; this is usually appropriate for zircons

This is great! We can measure $^{207}$Pb/$^{206}$Pb, and we know $^{235}$U/$^{238}$U because all U was inherited from the beginning of the solar system!

But the real strength of this approach is the way in which we can correct for Pb loss during metamorphism. Pb loss, at the time it occurs, does not affect the $^{207}$/$^{206}$ ratio.

There is a sneaky way to use this fact to correct for Pb loss. To do this, we use a **CONCORDIA Plot**
Here’s how this plot works:

1. The curved line is the closed system line, where the two geochronometers give exactly the same age, i.e., ages are concordant. Such lines are called concordia lines. Example, the dot on the plot above is where a 4 billion year old zircon would plot if it had no Pb loss.

2. Pb loss today moves composition directly toward the origin.
   a. Complete Pb loss completely resets the geochronometers
   b. Partial loss leaves the composition BELOW the concordia line

3. Pb loss in the past
   a. Complete loss at some time in the past: The original age information is completely wiped out; the zircon plots on the concordia line today, and the age it gives is the age of the heating that caused Pb loss.
   b. Partial loss: The zircon plots below the concordia line today, on the straight line that connects the crystal age to the age of the Pb loss event.

Procedure:
- Measure $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ on a collection of zircons
- Plot on Concordia Diagram
- If you get a linear array, the points where this line intersects the concordia line gives the time of crystallization and the time of lead loss.

see: Science 27 July 2001; 293: 619-620
http://www.sciencemag.org/cgi/content/full/293/5530/619?maxtoshow=&HITS=10&hits=10&RESULTFORMAT=&fulltext=zircon+gneiss&searchid=1093997195230_11399&stored_search=&FIRSTINDEX=10

http://www.nature.com/cgi-taf/DynaPage.taf?file=/nature/journal/v409/n6817/full/409175a0_fs.html

Zircons often have old cores with overgrowths of newer zircon. Machines have been invented that can make good Pb and U isotope measurements on very small spots, so you can probe various spots and use only the oldest parts of the crystals.

If you are curious about these machines:
OR http://shrimprg.stanford.edu/
and here is an even newer method: http://pubs.nrc-cnrc.gc.ca/mineral/tcm-27341-2.html
Sm-Nd geochronology

\[ ^{147}\text{Sm} \rightarrow ^{143}\text{Nd} + \text{a} \]

\[ ^{147}\text{Sm} \text{ decay const} = 6.54 \times 10^{-12}, \text{ half-life} = 1.06 \times 10^{11} \text{ years} \]

Sm\(^{3+}\) and Nd\(^{3+}\) are REE’s: large, highly charged ions, all with same outer electron config.

They fit into crystal lattices, i.e., slow diffusion compared to Ar
But... awkward fit into most common crystals
Exceptions are garnet, which accepts heavy REE’s, and some unusual minerals (fluorapatite, allanite, monazite and zircon)

Because of high charge density, REE’s are not very soluble and hence, not very mobile in aqueous solutions, e.g., during metamorphic events.
Thus, Sm-Nd ages are resistant to resetting by heating and fluid transport, and whole rock isochrons are especially useful

Use of Nd Isotope Ratios to Reveal How the Continents were Produced from the Earth’s Mantle

Assume 4.5Ga birth of the Earth, core formation soon after
Crust formation at 4.0 Ga or earlier (Zircons dated at 4.0 Ga, the oldest so far)

Partitioning of elements- Mantle versus crust.
As the earth’s crust forms via melting of the mantle, some elements become concentrated in magma and thus in the crust-
For example, Rb is strongly concentrated in the crust (more so than Sr), and thus the crust develops high \(^{87}\text{Sr}/^{86}\text{Sr}\) (relative to the mantle) over time.

IMPORTANT: Here’s the General concept: If the parent and daughter elements are partitioned unequally between two “reservoirs” in the earth, one reservoir will develop a more radiogenic isotope ratio over time relative to the other one.

Radiogenic: Produced by radioactive decay. OR... Containing a relatively large amount of radiogenic isotopes.

Nonradiogenic: Containing relatively small amounts of radiogenic isotopes.

The relative Compatibility of parent versus daughter in the mantle is VERY important. When a magma forms in the mantle, some elements are “unhappy” in the minerals there and thus are driven preferentially into the melt- these are INCOMPATIBLE elements.

Here is a list of distribution coefficients (D = \(C_{\text{min}}/C_{\text{melt}}\), where C is the concentration at equilibrium):

Faure, 1986. Table 12.2

<table>
<thead>
<tr>
<th>Mineral</th>
<th>D(Sm)</th>
<th>D(Nd)</th>
<th>D(Rb)</th>
<th>D(Sr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plagioclase</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>1 to 2</td>
</tr>
<tr>
<td>Clinopyroxene</td>
<td>0.26</td>
<td>0.17</td>
<td>0.003</td>
<td>0.12</td>
</tr>
<tr>
<td>Orthopyroxene</td>
<td>0.022</td>
<td>0.013</td>
<td>0.003</td>
<td>0.02</td>
</tr>
<tr>
<td>Olivine</td>
<td>0.010</td>
<td>0.007</td>
<td>0.0002</td>
<td>0.002</td>
</tr>
<tr>
<td>Amphibole</td>
<td>0.34</td>
<td>0.19</td>
<td>0.045</td>
<td>0.188</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>0.03</td>
<td>0.03</td>
<td>3.0</td>
<td>0.081</td>
</tr>
<tr>
<td>Garnet</td>
<td>0.217</td>
<td>0.087</td>
<td>0.01</td>
<td>0.08</td>
</tr>
<tr>
<td>Apatite</td>
<td>20</td>
<td>26</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Higher D values mean more compatible

List of degree of incompatibility, Parent vs. Daughter
Rb > Sr
Sm < Nd
U, Th > Pb
Lu < Hf
Re >> Os (Os highly compatible)

Look at White fig. 7.4a (or Faure Fig. 12.5)
- Continental crust has relatively small Sm/Nd ratios
- Continental crust initially inherits its \(^{143}\text{Nd}/^{144}\text{Nd}\) ratio from the mantle
- Over time, the mantle evolves \(^{143}\text{Nd}\) via \(^{147}\text{Sm}\) decay
- BUT crust has less Sm, so its \(^{143}\text{Nd}/^{144}\text{Nd}\) increases less rapidly
- Thus, the mantle and crust \(^{143}\text{Nd}/^{144}\text{Nd}\) values diverge over time

We can use this divergence as a way of studying the history of the crust and mantle:
1. We can reconstruct the \(^{143}\text{Nd}/^{144}\text{Nd}\) history of the mantle - see White fig. 7.4a
2. For a rock in the crust, if we measure \(^{143}\text{Nd}/^{144}\text{Nd}\) and \(^{147}\text{Sm}/^{144}\text{Nd}\), we can reconstruct the \(^{143}\text{Nd}/^{144}\text{Nd}\) history of that rock mass
3. The point in time where the mantle and rock \(^{143}\text{Nd}/^{144}\text{Nd}\) coincide must be the point in time at which the magma that produced the rock separated from the mantle

This is called a \textbf{Nd model age} because the answer depends somewhat on what model you construct for mantle evolution- there’s some uncertainty

\section*{Growth of continents as recorded by isotope ratios}

1) \textbf{How have the continents evolved?}
\begin{itemize}
\item Have they grown steadily over time?
\item OR…All formed at 4 Ga, with even addition and recycling since then?
\item OR…Mostly formed recently, with very little early-formed crust?
\end{itemize}

2) \textbf{How were the current continents assembled} (i.e., how old are the basement rocks that form the cores of the terranes that have been shuffled together over time)?

\section*{Question 2 first- Continental Assembly}
We would expect, just by looking at the geology, that continents have been assembled by the addition of blocks of material roughly the size of California.
What are the ages of these blocks?

Look at Nd model ages for granites of the western U.S.;
White, Fig. 20.4 After Bennett and DePaolo, 1987
Data show distinct blocks revealed by model ages with discontinuities at boundaries-
-- “docking” of island arcs is the likely cause of this
**Question #1: How has the continental crust evolved over time?**

3.8 Ga rocks show evidence (high $^{143}$Nd/$^{144}$Nd ratios) that the mantle had previously coughed up large amounts of crust (i.e., it was depleted)!!

White Figs. 19.8 and 19.9: Analyses of rocks that record the evolution of the depleted mantle. Looks like there was an early depletion event and since then the depleted mantle has evolved along a straight line—depletion balanced by recycling or mixing of pristine mantle from below.

Also: Very old marine sediments provide a record of the age of continental crust  
- Nd model ages give “crustal resid. times”  
- Data: Seems close to the case of uniform growth of continents over time. Sediments show a mixture of newer and older crust at all times.  
...Possible problem: Biased sampling - flat crust areas not well represented

**Re-Os and Lu-Hf**

$^{187}$Re $\rightarrow$ $^{187}$Os + $\frac{1}{\lambda}$  
$187$Re decay const = $1.6 \times 10^{-11}$, half-life = $4.5 \times 10^{10}$ years  

$^{176}$Lu $\rightarrow$ $^{176}$Hf + $\frac{1}{\lambda}$  
$176$Lu decay const = about $2 \times 10^{-11}$, half-life = $3.5 \times 10^{10}$ years

Re/Os is very high in the earth’s crust. Os and Re behave very differently when the mantle is partially melted and coughs up magma. Re partitions into magma, whereas Os stays behind.  
- Re/Os in mantle = 0.1  
- Re/Os in basalt = 30!

MEASURE: $^{187}$Os/$^{188}$Os (avoid 186 because it is partially created by Pt decay)

If high $^{187}$Os/$^{188}$Os ratios show up, it clearly indicates a large crust component  
Hawaiian lavas sometimes show high $^{187}$Os/$^{188}$Os, which suggests they are derived from subducted material

Lu-Hf is similar to, but not quite the same, as Sm-Nd because whereas both Nd and Sm are REE’s, Lu is a REE but Hf is a +4 cation like Zr.  
- Thus, more possibility for Lu-Hf to get upset by fractionation of Lu from Hf.  
- BUT, decay of Lu is faster, and Lu/Hf ratios vary more, so $^{176}$Hf/$^{177}$Hf is more sensitive to some earth processes, as we shall see.  
- Also, garnet tends to take in Lu (3+), but not Hf (4+) (high P/D ratio)  
- Hf tends to go into Zircon, Lu does not (Low P/D ratio)- zircons are great indicators of $R_0$  
- GENERAL PRINCIPLE: If parent and daughter nuclides are geochemically different, this is good in that it gives more range in parent to daughter ratio, BUT it is bad in that metamorphism more easily destroys the system

MEASURE: $^{176}$Hf/$^{177}$Hf
Appendix: **How has the mantle evolved isotopically and how heterogeneous is it?**

See White, Lecture 16, 17, 18, and 19. White deals with this in detail; this is his area of research.

- Is the mantle all one well-mixed reservoir? Two reservoirs? Many?
- Can depleted mantle (mantle that has coughed up magma once) melt again?
- What about the subducted crust? Does it melt partially or just mix in?

Sr and Nd evidence from Oceanic basalts: Fig. 13.1 Faure / White figs. 16.2,3,4

Looks like maybe 2 reservoirs works- lower and upper mantle?

**Then look at Pb isotopes, and we find that Pb does not fit.**

To make a long story short: It looks like we have the following different types of mantle material (see Fig. 18.3 and 18.4 in White):

1) Depleted mantle- dominant source of MORB
2) Enriched mantle- Enriched in incompatible elements; Recycled continental crust added back in, perhaps.
3) HiMu- recycled oceanic crust, with little sediment. Gives radiogenic Pb, not radiogenic Sr
4) Prevalent Mantle- all oceanic basalts rooted here