GEOL5690 Class notes: Radiometric Dates

Text references: Turcotte and Schubert, sections 10-1 to 10-4.

One of the things we banter about quite a bit in tectonics is the age of different rock units. The numerical ages are all derived from radiometric ages, a topic which you have hopefully been exposed to at some point in your education. After a quick reminder of simpler isotopic systems, these notes will briefly cover some of the highlights of uranium-lead concordia, as U-Pb dates appear in both sedimentary provenance estimation and high-precision dating of igneous rocks. Also, the U-Pb concordia diagrams are a bit different than the more straightforward (but practically troublesome) systems such as potassium-argon (K-Ar). We'll leave some of the lower temperature systems, which have some peculiarities all their own, to a possible later discussion.

K-Ar (and Ar-Ar): This is often a nice example system as you can frequently assume there was no Ar when a rock solidified. Recall that ^{40}K decays

$$^{40}\mathrm{K} + e^{-} \rightarrow {}^{40}\mathrm{Ar} \tag{1}$$

with a half-life of 11.8 Gy (billion years). What we often neglect to tell you is that ^{40}K also decays to ^{40}Ca 89.1% of the time (which is why ^{40}K has a much shorter overall half-life of 1.26 Gy). Because measurements are made in mass spectrographs on ratios, we can find the age of a mineral containing potassium:

$$t = \frac{t_{1/2}}{\ln(2)} \ln\left(1 + \frac{^{40}\mathrm{Ar}}{0.109 \cdot {}^{40}\mathrm{K}}\right) \tag{2}$$

where the ratio of Ar to radioactive K is measured at time t after the system closed and $t_{1/2}$ is the halflife of 1.26 Gy. The factor of 0.109 enters to correct for the fraction of decays that go to ^{40}Ar. In some cases, a check on the ^{40}Ar/^{36}Ar ratio can aid in determining if a system was open. Because of the different chemistry of K and Ar, measurements are problematic at times.

The Ar-Ar system relies on the same decay system but ^{39}K is converted to ^{39}Ar by irradiation; then the ratio of ^{40}Ar to ^{39}Ar is measured as a sample is heated. When enough different temperature steps yield the same ratio (a “plateau”), the age can be determined. Because the degree of production of ^{39}Ar is uncertain, a reference standard is irradiated and measured at the same time, so the absolute age of the sample is typically limited more by the age of the standard than the analytical errors in the measurement. A common standard in use now is the Fish Canyon Tuff from the San Juan volcanic field in SW Colorado.

Rb-Sr:

This is a system that was widely used at one time but has been less popular in the past couple of decades for dating (it is relevant, though, for other uses, as we shall discuss). It does illustrate issues relevant to the U-Pb system. Let us begin with the direct relation between the number of atoms of the 87 isotope of strontium, ^{87}Sr, in some volume of rock at a time *t* after the system has been closed to loss or gain of strontium or rubidium:

$$^{87}\mathrm{Sr} = {}^{87}\mathrm{Sr}_{\mathrm{i}} + {}^{87}\mathrm{Rb}\left(e^{\lambda t} - 1\right) \tag{3}$$

where the initial amount of ^{87}Sr is denoted $^{87}\mathrm{Sr}_{\mathrm{i}}$. The half-life of ^{87}Rb is 49 Gy. (You can see this last term most easily from $^{87}\mathrm{Rb} = {}^{87}\mathrm{Rb}_{\mathrm{i}}\, e^{-\lambda t}$ and that $^{87}\mathrm{Sr}_{\mathrm{r}} = {}^{87}\mathrm{Rb}_{\mathrm{I}} - {}^{87}\mathrm{Rb}$ and substituting away). We divide by the number of atoms of a non-radiogenic isotope of strontium, ^{86}Sr to get:

$$\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}} = \left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{\mathrm{i}} + \frac{^{87}\mathrm{Rb}}{^{86}\mathrm{Sr}}\left(e^{\lambda t} - 1\right) \tag{4}$$

Note that this is linear on a plot of ^{87}Sr/^{86}Sr vs ^{87}Rb/^{86}Sr, with the slope related to the age and the intercept to the initial Sr ratio. There is the obvious difficulty that we have one equation and two unknowns, the time *t* and the initial Sr ratio. This can be overcome in theory by using a number of measurements from separates that would have shared the same age and initial Sr ratio. By doing this we define isochrons (which are the lines on the ^{87}Sr/^{86}Sr vs ^{87}Rb/^{86}Sr plot). This requires all the separates to have crystallized at the same time, that the initial Sr isotopic ratios were the same, and that each separate remained closed since then. These assumptions can cause trouble and are a common problem in isotopic systems—things like magma mixing, fractionation effecting isotopes, variable absorption of surrounding rock, etc., will mess this up. The U-Pb system has the elegance that it can reveal the presence of these problems.

A different problem is the accuracy of decay constants (λ, above). Both K-Ar and Rb-Sr have had their constants redefined and so older dates need to be recalculated to newer constants to be compared with more recent work.

U-Pb:

Radioactive uranium will, in general, decay to lead (as does ^{232}Th). It is important to note that there are a number of intermediate products along the way with their own half lives in the tens to low hundreds of thousands of years. When dating young rocks, those intermediate products can become important (indeed, can be exploited as well: estimates of the time melts take from arising in the mantle to erupting in a volcano are often based on these disequilibrium products). For most of our purposes, though, we can just worry about the full decay to a stable isotope of lead.

Let us begin with the direct relation between the number of atoms of the 206 isotope of lead, ^{206}Pb, in some volume of rock at a time *t* after the system has been closed to loss or gain of lead or uranium:

$$^{206}\mathrm{Pb} = {}^{206}\mathrm{Pb_i} + {}^{238}\mathrm{U}\left(e^{\lambda t}-1\right) \tag{5}$$

where the initial amount of ^{206}Pb is denoted ^{206}Pb$_i$. (As before, you can see this last term most easily from $^{238}\mathrm{U} = {}^{238}\mathrm{U_i}\, e^{-\lambda t}$ and that $^{206}\mathrm{Pb_r} = {}^{238}\mathrm{U_I} - {}^{238}\mathrm{U}$ and substituting away). Again, we divide by the number of atoms of a non-radiogenic isotope of lead, ^{204}Pb to get:

$$\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}} = \left(\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_{\mathrm{i}} + \frac{^{238}\mathrm{U}}{^{204}\mathrm{Pb}}\left(e^{\lambda t}-1\right) \tag{6}$$

We can solve for the time since the system was closed to get

$$t = \frac{1}{\lambda}\ln\left[\frac{\dfrac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}} - \left(\dfrac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_{\mathrm{i}}}{\dfrac{^{238}\mathrm{U}}{^{204}\mathrm{Pb}}} + 1\right] \tag{7}$$

The same set of equations can be derived for ^{207}Pb and ^{235}U. We may rewrite this as

$$\frac{^{206}\mathrm{Pb}*}{^{238}\mathrm{U}} = e^{\lambda t} - 1 = \frac{\dfrac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}} - \left(\dfrac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_{\mathrm{i}}}{\dfrac{^{238}\mathrm{U}}{^{204}\mathrm{Pb}}} \tag{8}$$

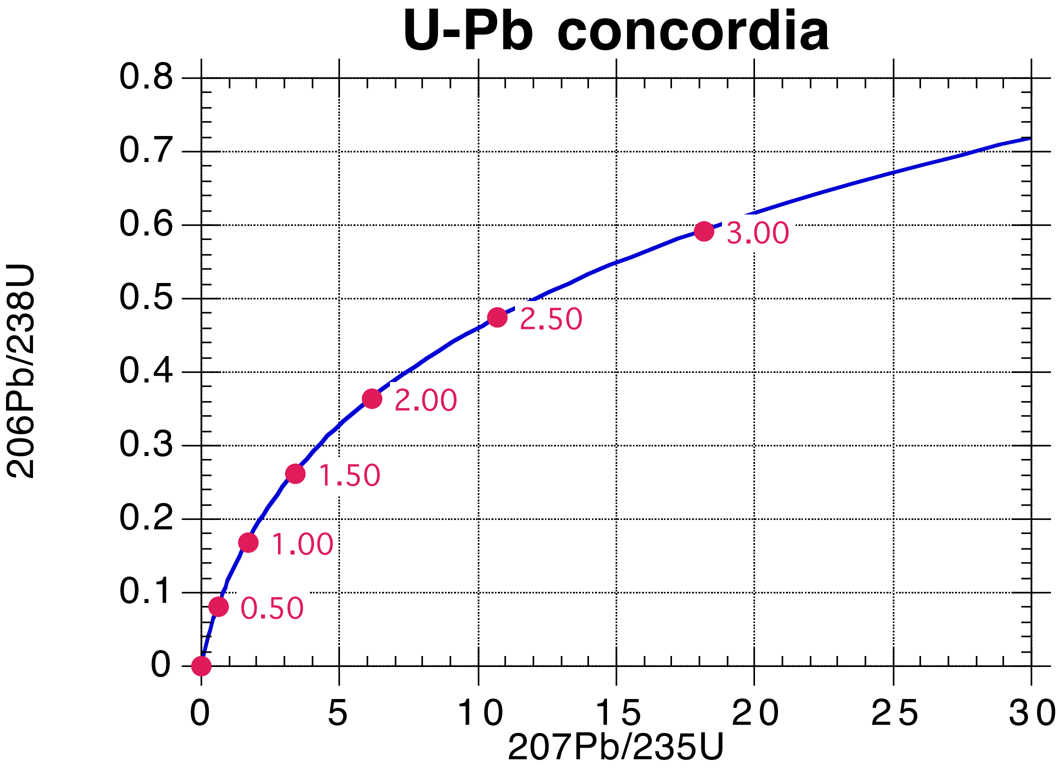
where $^{206}Pb^*$ is the radiogenic lead ($^{206}Pb - {}^{206}Pb_i$). Or, once again in terms of the age of the mineral,

$$t = \frac{1}{\lambda}\ln\left(\frac{^{206}Pb^*}{^{238}U} + 1\right) \tag{9}$$

Now if a mineral has been a closed system, we should get the same age from the ^{206}Pb-^{238}U system as the ^{207}Pb-^{235}U system. If we designate the decay constants for these as $\lambda_{206}$and λ_{207}, respectively, we can set the equivalent versions of (9) equal to one another:

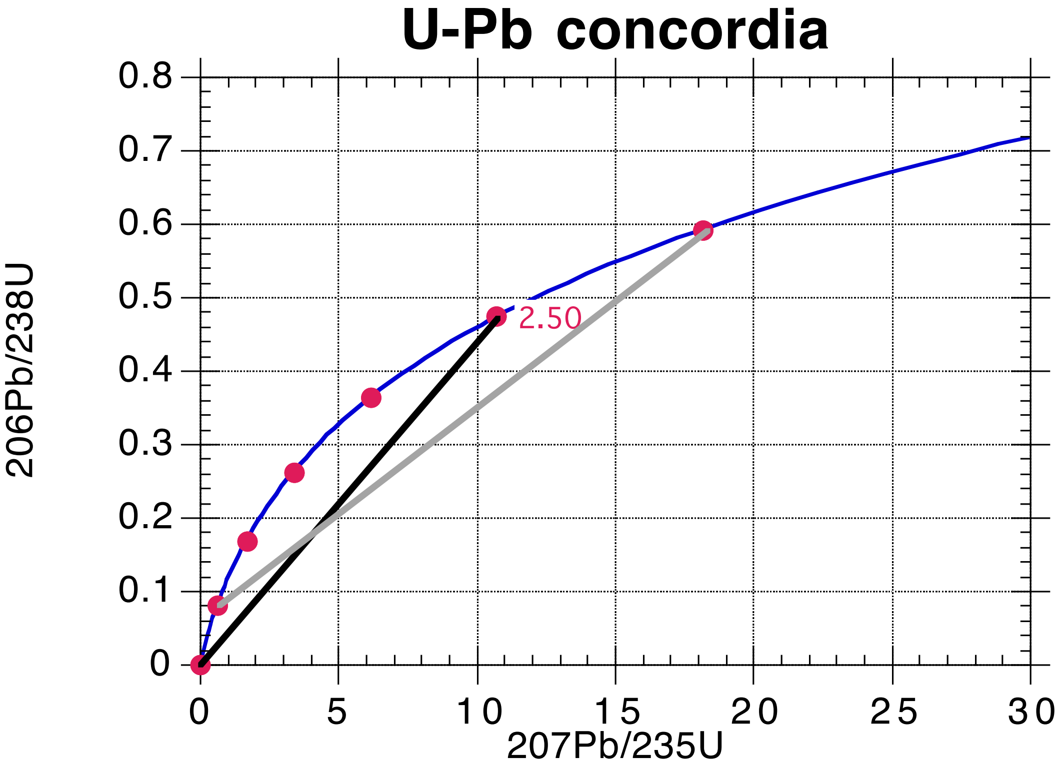
$$\begin{gathered} t = \frac{1}{\lambda_{206}}\ln\left(\frac{^{206}Pb^*}{^{238}U} + 1\right) = \frac{1}{\lambda_{207}}\ln\left(\frac{^{207}Pb^*}{^{235}U} + 1\right) \\ \frac{^{206}Pb^*}{^{238}U} = \left(\frac{^{207}Pb^*}{^{235}U} + 1\right)^{\frac{\lambda_{206}}{\lambda_{207}}} - 1 \end{gathered} \tag{10}$$

Armed with the values of the decay constants, $\lambda_{206} = 1.55125\ 10^{-10}\ yr^{-1}$ and $\lambda_{207} = 9.8485\ 10^{-10}\ yr^{-1}$, we can plot the two ratios of lead and uranium isotopes against one another. The curve so plotted represents the locus of possible measurements where the dates from the two radiogenic systems are identical, or concordant. Hence this curve is called the concordia, shown below with points marked in billions of years of age:



The neat thing about this system is the series of checks it can provide. Frequently the only checks on a radiogenic age are ones of consistency with external estimates, such as paleontological control or crosscutting relations with other dated materials. In this case, however, we have two separate geochronometers using the same elements and thus most of the chemical effects we could envision will affect both geochronometers the same.

For instance, a problem common to all geochronometers is the loss of a parent or daughter product (i.e., the system is not perfectly closed). In such a case, the estimate from a single geochronometer will be in error. Here, however, some help is available. Consider the loss of lead at some time, perhaps by diffusion out of the crystal. Complete loss of lead will result in a return to the lower left corner of the plot; a partial loss will be along the line from the age of the crystal to the lower left corner, as is shown below for a 2.5 billion year old crystal:



Now obviously any individual grain will only have one point along that line, but within a rock we might expect several different grains to lose different amounts of lead due to differences in grain size or crystal defects, etc. Thus we can observe from a single rock this line, termed a discordia. Now the fun part is that if you close the system again and let it evolve for 500 million years, you will get to the gray line above. Now the mineral was originally crystallized at 3.0 Ga and its isotopic system was opened at 500 Ma--and these two dates are the end points of the line. So we can see that the isotopic system was disturbed **and** still infer the original crystallization age. It turns out that addition of U at a specific time will produce the same result; removal of U or addition of lead (a less frequent occurrence) will push the measurement along the discordia but away from the origin.

Because of these properties, U-Pb dates on igneous rocks are often the standard of choice in determining crystallization ages, especially when the mineral used is zircon, which forms and closes at high temperatures. Thus some isotopic ages from Precambrian sediments are suspect because of possible loss of parent or daughter, but U-Pb dates on igneous rocks are viewed as very solid constraints.

Several minerals are capable of holding Pb and U, but the mineral of preference is zircon (others like monazite and allenite are useful in particular circumstances). Zircons are pretty good at holding on to their Pb and U once formed, to the point where some zircons from metamorphic melts retain the age of the parent rock rather than the new magma. Zircons are pretty tough and can travel a long ways, so that makes them a good target for sedimentary rocks where we want to see what the parent rock might have been (consider in contrast K in feldspars or micas--how far would that travel?).

There are three main approaches used for measuring uranium-lead ratios. The oldest uses a thermal ionization mass spectrometer (TIMS) with isotope dilution (so ID-TIMS). Samples are prepared chemically through dissolution. This technique generally requires samples on the order of 10 μg or larger but can produce estimates of both $^{238}U/^{206}Pb$ and $^{235}U/^{207}Pb$. It is the most precise, getting precision values as low as 0.2%. Secondary ion mass spectrometry (SIMS) spalls off ions by shooting an ion beam at the sample; sample weights can be as low as 5 ng, but ratios have to calculated by making measurements on standards alternating with the samples being measured. Precisions of ~3% are generally reported. Most popular of late is laser-ablation inductively coupled plasma mass spectrometry (LA-ICPMS) where the ions are created by a laser beam. Sample sizes and precisions are fairly comparable to SIMS, but the analysis times are far shorter and cheaper, allowing for far more measurements to be made. Both SIMS and LA-ICPMS approaches require the use of a standard to obtain accurate ages (rather like Ar-Ar dating). In general, LA- ICPMS produces age estimates for zircons under ~1.2 Ga from $^{238}U/^{206}Pb$ ages; $^{207}Pb/^{206}Pb$ ages are preferred beyond that. Precisions of perhaps 2% are possible with this instrument. Greater details on U-Pb geochronology can be found in Schoene, 4.10 U–Th–Pb Geochronology, *in Treatise on Geochemistry* (2nd edition), vol. 4 *The Crust*, p. 341-378, doi: 10.1016/B978-0-08- 095975-7.00310-7, 2014 and in Gehrels et al., Enhanced precision, accuracy, efficiency, and spatial resolution of U-Pb ages by laser ablation–multicollector–inductively coupled plasma– mass spectrometry, *G^3*, 9 (3), Q03017, doi:10.1029/2007GC001805, 2008.

This discussion of one particular isotopic system should have indicated some of the pitfalls and advantages of these techniques in general. Questions that should be in your mind in evaluating a radiometric age are what, if any, internal checks exist for loss or gain of isotopes important to the age date? What are the conditions under which the system is likely to be open in this manner? What assumptions that are geologically questionable have been made in making this age determination, and can we evaluate the possibility of these assumptions being violated? Similar questions can be asked of other geochronometers, as we shall see later in the course.

Closure temperatures

All geochronometers are actually measuring the point where a system becomes closed; thus a single rock can have many “ages”. The most obvious way a system is open is if the temperature is high enough for atoms to diffuse in and out of crystals. Here are some approximate closure temperatures (note that more exact numbers depend on the duration of heating, grain size, any pore fluids present, and the exact chemistry of the minerals involved):

U-Pb in zircon: excess of 900°C
U-Pb in titanite >~650°C
Sm-Nd in garnet ~600°C (variable)
U-Pb closure in apatite: 500°C
K-Ar in hornblende= 530°C (fast cooling) 500°C (slower)
Rb-Sr closure K-feldspar: ~520°C
Rb-Sr closure biotite: ~500°C
K-Ar in muscovite ~400°C
K-Ar in biotite=330°C (fast cooling) 300°C (slower)
Fission tracks-zircon 175°-250°C
Fission tracks-apatite 70-150°C (often abbreviated AFT)
U/Th-He – zircon (~130°-230°C?) (often abbreviated ZHe)
U/Th-He - apatite 30-90°C (often abbreviated AHe)

Note that certain approaches (e.g., Ar-Ar and ^{3}He-^{4}He) provide more information on the details of the cooling history rather than expand or contract a particular closure temperature. A considerable effort over the past 10-20 years has been to investigate the time rocks spend in and near a geochronometer's closure temperature (so-called partial retention or partial annealing zones).

Sm-Nd

Another geochronometer is more often used differently, and we shall encounter it occasionally when we talk about igneous rocks.

$$^{147}\mathrm{Sm} \rightarrow {}^{143}\mathrm{Nd} + \text{radioactive products} \tag{11}$$

where $t_{1/2}$ = 106 Gy or $\lambda = 6.54 \bullet 10^{-12}$ yr^{-1}. So much as for Rb-Sr, we can write

$$^{143}\mathrm{Nd} = {}^{143}\mathrm{Nd}_I + {}^{147}\mathrm{Sm}\,(e^{\lambda t} - 1) \tag{12}$$

Normalizing by nonradiogenic ^{144}Nd gets us

$$\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}} = \left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_I + \frac{^{147}\mathrm{Sm}}{^{144}\mathrm{Nd}}\left(e^{\lambda t} - 1\right) \tag{13}$$

or in Turcotte and Schubert as eqn 10-11, $\alpha = \alpha_0 + \mu\,(e^{\lambda t} - 1)$. Obviously we can take this and make it into a standard dating tool, but it turns out this is tricky to some degree because in many situations, Nd and Sm behave chemically very nearly the same. This actually is an advantage because the system only really resets when more striking changes occur to the rock.

You can turn this around to be

$$\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}} = \left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_I + \left(\frac{^{147}\mathrm{Sm}}{^{144}\mathrm{Nd}}\right)_I \left(1 - e^{-\lambda t}\right) \tag{14}$$

Now variations are small, so geochemists use $\varepsilon_{\mathrm{Nd}}$:

$$\varepsilon_{\mathrm{Nd}}(t) = \left[\frac{\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{sample}}(t)}{\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{CHUR}}(t)} - 1\right] \times 10^4 \tag{15}$$

CHUR is the **Ch**ondritic **U**niform **R**eference, and so it has $\varepsilon_{\mathrm{Nd}} = 0$. This is an estimate of the Nd ratio in chondritic meteorites thought to approximate what the bulk Earth should have. The basic idea is that if you took the entire Earth and measured its $\varepsilon_{\mathrm{Nd}}$, it would be zero.

Key to this is the fact that chemical differentiation will affect the different elements differently. For Sm-Nd, it turns out that Sm is more compatible than Nd, meaning it stays in the solid that is melting more than the Nd. So when you melt mantle to form crust, the initial Sm/Nd ratio declines in the melt (and the more silica rich the melt, in general the lower the Sm/Nd). So if we define a fractionation coefficient f as $\mu/\mu_s - 1$ (following Turcotte and Schubert, who use μ as the ratio of parent to stable element, here ^{147}Sm/^{144}Nd, and μ_s is the value for the silicate Earth), we see that $\mu = (1+f)\,\mu_s$, so then by substitution of (14) into (15) and then using our fractionation factor, we get

$$
\begin{aligned}
\varepsilon_{\mathrm{Nd}}(t) &= \left[\frac{\left(\frac{{}^{143}\mathrm{Nd}}{{}^{144}\mathrm{Nd}}\right)_{I\ SAMPLE} + \left(\frac{{}^{147}\mathrm{Sm}}{{}^{144}\mathrm{Nd}}\right)_{I\ SAMPLE} \left(1-e^{-\lambda t}\right)}{\left(\frac{{}^{143}\mathrm{Nd}}{{}^{144}\mathrm{Nd}}\right)_{I\ CHUR} + \left(\frac{{}^{147}\mathrm{Sm}}{{}^{144}\mathrm{Nd}}\right)_{I\ CHUR} \left(1-e^{-\lambda t}\right)} - 1 \right] \times 10^4 \\
&= \left[\frac{\left(\frac{{}^{143}\mathrm{Nd}}{{}^{144}\mathrm{Nd}}\right)_{I\ SAMPLE} + (1+f)\left(\frac{{}^{147}\mathrm{Sm}}{{}^{144}\mathrm{Nd}}\right)_{I\ CHUR} \left(1-e^{-\lambda t}\right)}{\left(\frac{{}^{143}\mathrm{Nd}}{{}^{144}\mathrm{Nd}}\right)_{I\ CHUR} + \left(\frac{{}^{147}\mathrm{Sm}}{{}^{144}\mathrm{Nd}}\right)_{I\ CHUR} \left(1-e^{-\lambda t}\right)} - 1 \right] \times 10^4
\end{aligned}
\qquad (16)
$$

Because of the very long half life of these materials, we actually get lines for these curves as the $e^{-\lambda t}$ term can be approximated as $(1-\lambda t)$.

This can be carried further as in the text, but for Sm-Nd, *f* is about –0.451 for the crust (Conversely, the mantle will have a positive value, and *f* of about 0.118 is derived from what is seen—note not just the converse because in differentiation most of the material stays behind in the depleted reservoir). (see Table 10-2 of the text). Observationally, $\varepsilon_{\mathrm{Nd}}(t) = 0.25\, t^2 - 3t + 8.5$, *t* is time in past in Ga and Nd values in the mantle. This can be used to try and estimate the extraction history of crust from mantle, but under what assumptions?

Now this happens as each chunk of crust is made. For awhile, scientists felt that this differentiation event dominated $\varepsilon_{\mathrm{Nd}}$ and so by drawing a line back from the observed $\varepsilon_{\mathrm{Nd}}$ value towards the mantle line (depleted mantle line), the intersection would yield the age at which the source material was extracted from the mantle; this was called the **Nd model age**. This age may or may not have meaning, because it requires that there be so subsequent mixing or differentiation.

Advantages of this technique are that Sm/Nd ratios are unaffected by processes below greenschist metamorphism (and you probably have to go higher to get much of an effect), so you can measure this on sediments. However, the earlier assumptions were too simplistic and model ages need not be the age at which that crust was extracted from the mantle. Nevertheless, the basic concept helps separate regions that have had profoundly different histories far back in the Precambrian.

Similar usage has been made of the Rb-Sr system (which will be the reason we will see the $({}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr})_I = 0.7060$ line used for the edge of the continent later on), Lu-Hf and Re-Os system. Lu-Hf is often measured now on zircons (expressed as $\varepsilon_{\mathrm{Hf}}$) as a form of double-dating that becomes more important when considering the source and history of detrital zircons.