Geochronology using radiogenic isotopes

Isotope geochemistry is a branch of the Earth Sciences that uses the isotopic signatures of rocks and minerals to study Earth processes. Recall from basic chemistry that elements are defined by their atomic number, which is the numbers of protons in an atom's nucleus. For example, uranium (symbol U) has 92 protons and thus has the atomic number 92, whereas lead (symbol Pb) has atomic number 82. *Isotopes* are atoms that have the same atomic number (and thus the same element name) but have different numbers of neutrons. Isotope geochemistry studies the variations in the abundances of different isotopes in the rocks that comprise Earth, since these hold clues to the different physical and chemical process occurring inside the Earth.

Two subclasses of isotope geochemistry are stable isotopes and radiogenic isotopes. The study of radiogenic isotopes examines how radioactive isotopes actively decay from a parent isotope into a daughter isotope. The decay rate of radioactive isotopes can vary from fractions of a second to billions of years, depending on the particular isotope.

We can use the relative abundance of certain parent and daughter isotopes in a given rock sample as a clock that records the amount of time since a rock formed. You may have already heard about *radiocarbon* dating, which measures the relative abundance of carbon isotopes to determine the age of objects containing organic carbon (for example wooden objects found at archaeological sites).

In radioactive decay, the time rate of decay of the parent isotope is proportional to its concentration. Thus, if P is a measure of the concentration of the parent isotope, we can state this mathematically as:

$$\frac{dP(t)}{dt} = -\lambda P(t), \tag{1}$$

λ is the *decay constant*. We can integrate this differential equation over time to obtain the radioactive decay equation:

$$P(t) = P_0 e^{-\lambda t}, \tag{2}$$

where P_0 is the initial concentration when $t = 0$. This shows that radioactive decay is an exponential process.

The *half-life*, $t_{1/2}$, is the time it takes for $P = P_0/2$, meaning the time it takes for half of the parent isotope to decay into the daughter isotope. Inserting this into the decay equation and rearranging gives

$$\frac{P}{P_0} = \frac{1}{2} = e^{-\lambda t_{1/2}}. \tag{3}$$

From this it is clear that if time $t_{1/2}$ is know, λ can be solved for. Conversely, if λ is known, $t_{1/2}$ can be solved for.

Rearranging the decay equation (2) we can write an expression for P_0:

$$P_0 = P(t)e^{\lambda t} \tag{4}$$

The amount of daughter nuclides D^* produced by the radioactive decay is the difference between the initial concentration and the present day concentration of the parent isotope:

$$D^*(t) = P_0 - P(t) \tag{5}$$

Inserting P_0 from equation 4 gives:

$$D^*(t) = P(t)(e^{\lambda t} - 1). \tag{6}$$

The total number of daughter nuclides D is then the sum of those produced by decay of the parent isotope as well as any initial concentration in the sample D_0:

$$D(t) = D_0 + D^*(t). \tag{7}$$

The full expression for the daughter isotope is then

$$D(t) = D_0 + P(t)(e^{\lambda t} - 1). \tag{8}$$

$D(t)$ and $P(t)$ can be measured in the lab, but we can't extract the age of the rock t without also knowing the initial concentration of the daughter isotope D_0. We will explore this issue more below.

Now let's consider the decay of uranium to lead. There are two radioactive uranium isotopes that decay:

$$^{238}\mathrm{U} \longrightarrow {}^{206}\mathrm{Pb} \tag{9}$$
$$^{235}\mathrm{U} \longrightarrow {}^{207}\mathrm{Pb} \tag{10}$$

^{238}U has a half-life of 4.47 billion years and ^{235}U has a half-life of 704 million years. The full expressions are then:

$$^{206}\mathrm{Pb} = {}^{206}\mathrm{Pb}_0 + {}^{238}\mathrm{U}(e^{\lambda_{238} t} - 1) \tag{11}$$
$$^{207}\mathrm{Pb} = {}^{207}\mathrm{Pb}_0 + {}^{235}\mathrm{U}(e^{\lambda_{235} t} - 1) \tag{12}$$

where λ_{238} is the decay constant for ^{238}U and λ_{235} is the decay constant for ^{235}U.

Measuring the absolute abundances of isotopes in a rock sample can be done in the lab; however, it is much more accurate to measure the *relative* abundance of isotopes, which can be done with a high level of precision using a mass spectrometer. Thus, it is more common to normalize the decay equations using a stable (i.e., non-radiogenic) isotope.

For U-Pb decay, usually the non-radiogenic isotope ^{204}Pb is used. The above equations can be normalized by this stable isotope by dividing by its concentration, giving:

$$\left(\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right) = \left(\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_0 + \left(\frac{^{238}\mathrm{U}}{^{204}\mathrm{Pb}}\right)(e^{\lambda_{238}t} - 1) \tag{13}$$

$$\left(\frac{^{207}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right) = \left(\frac{^{207}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_0 + \left(\frac{^{235}\mathrm{U}}{^{204}\mathrm{Pb}}\right)(e^{\lambda_{235}t} - 1) \tag{14}$$

Note that both of these formulas are basically the equation for a line, $y = mx + b$:

$$\underbrace{\left(\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)}_{\mathrm{y}} = \underbrace{(e^{\lambda_{238}t} - 1)}_{\mathrm{m}}\underbrace{\left(\frac{^{238}\mathrm{U}}{^{204}\mathrm{Pb}}\right)}_{\mathrm{x}} + \underbrace{\left(\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_0}_{\mathrm{b}}. \tag{15}$$

A line can be fit to a plot of $\left(\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)$ versus $\left(\frac{^{238}\mathrm{U}}{^{204}\mathrm{Pb}}\right)$ and the age t is found from the slope of the line m. The intercept of the line b is the initial ratio $\left(\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_0$. A similar analysis can be carried out for the ^{235}U system.

In certain minerals such as zircons that form during cooling in a magma body, lead atoms are excluded from the developing crystal structure and thus $\mathrm{Pb}_0 = 0$ in the above expressions. Equations 11 and 12 simplify to

$$\left(\frac{^{206}\mathrm{Pb}}{^{238}\mathrm{U}}\right) = (e^{\lambda_{238}t} - 1) \tag{16}$$

$$\left(\frac{^{207}\mathrm{Pb}}{^{235}\mathrm{U}}\right) = (e^{\lambda_{235}t} - 1) \tag{17}$$

Taking the ratio of these equations gives:

$$\left(\frac{^{206}\mathrm{Pb}}{^{238}\mathrm{U}}\right) = \frac{(e^{\lambda_{238}t} - 1)}{(e^{\lambda_{235}t} - 1)}\left(\frac{^{207}\mathrm{Pb}}{^{235}\mathrm{U}}\right). \tag{18}$$

Plotting these two ratios against each other results in a *concordia* curve that depends non-linearly on the time t. The age t for a given sample can be determined by comparing plots of the sample's $\left(\frac{^{206}\mathrm{Pb}}{^{238}\mathrm{U}}\right)$ versus $\left(\frac{^{207}\mathrm{Pb}}{^{235}\mathrm{U}}\right)$ with predictions for times t computed using equations 16 and 17.

We will explore these equations in this week's homework assignment and will use them to date the age of rock samples from the Moon.