

Geol. 655 Isotope Geochemistry

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BASICS OF RADIOACTIVE ISOTOPE GEOCHEMISTRY

INTRODUCTION

We can broadly define two principal applications of radiogenic isotope geochemistry. The first is *geochronology*. Geochronology makes use of the constancy of the rate of radioactive decay. Since a radioactive nuclide decays at a rate to its daughter independent of everything, we can determine a *time* simply by determining how much of the nuclide has decayed. We will discuss the significance of this *time* at a later point. The other application is *tracer studies*. These studies make use of the differences in the ratio of the radiogenic daughter isotope to other isotopes of the element. We can understand the utility of such studies without, for the moment, understanding why such differences in isotope ratios arise. These sorts of studies are analogous to tracer studies performed in biology. For example, biologists will inject an organism with a radioactive nuclide, such as one of carbon or phosphorus, to investigate the organism's metabolism and physiology. Unfortunately, the time scales of geology are too long for us to inject the Earth with a radioactive tracer to study its physiology. But we can make use of natural tracers, the radiogenic isotopes, to investigate fundamental Earth processes. For example, Nd isotope ratios have been used to distinguish different ocean water masses. Radiogenic isotope ratios are also used in a more sophisticated way, namely to understand evolutionary histories. Table 4.1 lists the principal decay systems used in geology; these are also illustrated in Figure 4.1.

TABLE 4.1: Geologically Useful Long-Lived Radioactive Decay Schemes

Parent	Decay Mode	λ	Half-life	Daughter Ratio
^{40}K	β^+ , e.c, β^-	$5.543 \times 10^{-10} \text{y}^{-1}$	$1.28 \times 10^9 \text{yr}$	^{40}Ar , ^{40}Ca $^{40}\text{Ar}/^{36}\text{Ar}$
^{87}Rb	β^-	$1.42 \times 10^{-11} \text{y}^{-1}$	$4.8 \times 10^{10} \text{yr}$	^{87}Sr $^{87}\text{Sr}/^{86}\text{Sr}$
^{138}La	β^-	$2.67 \times 10^{-12} \text{y}^{-1}$	$2.59 \times 10^{11} \text{yr}$	^{138}Ce , ^{138}Ba $^{138}\text{Ce}/^{142}\text{Ce}$, $^{138}\text{Ce}/^{136}\text{Ce}$
^{147}Sm	α	$6.54 \times 10^{-12} \text{y}^{-1}$	$1.06 \times 10^{11} \text{yr}$	^{143}Nd $^{143}\text{Nd}/^{144}\text{Nd}$
^{176}Lu	β^-	$1.94 \times 10^{-11} \text{y}^{-1}$	$3.6 \times 10^{10} \text{yr}$	^{176}Hf $^{176}\text{Hf}/^{177}\text{Hf}$
^{187}Re	β^-	$1.64 \times 10^{-11} \text{y}^{-1}$	$4.23 \times 10^{10} \text{yr}$	^{187}Os $^{187}\text{Os}/^{188}\text{Os}$, $^{187}\text{Os}/^{186}\text{Os}$
^{190}Os	α	$1.54 \times 10^{-12} \text{y}^{-1}$	$4.50 \times 10^{11} \text{yr}$	^{186}Os $^{186}\text{Os}/^{188}\text{Os}$
^{232}Th	α	$4.948 \times 10^{-11} \text{y}^{-1}$	$1.4 \times 10^{10} \text{yr}$	^{208}Pb , ^4He $^{208}\text{Pb}/^{204}\text{Pb}$, $^3\text{He}/^4\text{He}$
^{235}U	α	$9.849 \times 10^{-10} \text{y}^{-1}$	$7.07 \times 10^8 \text{yr}$	^{207}Pb , ^4He $^{207}\text{Pb}/^{204}\text{Pb}$, $^3\text{He}/^4\text{He}$
^{238}U	α	$1.551 \times 10^{-10} \text{y}^{-1}$	$4.47 \times 10^9 \text{yr}$	^{206}Pb , ^4He $^{206}\text{Pb}/^{204}\text{Pb}$, $^3\text{He}/^4\text{He}$

Note: the branching ratio, i.e. ratios of decays to ^{40}Ar to total decays of ^{40}K is 0.117. The production of ^3He from ^{147}Sm decay is insignificant compared to that produced by decay of U and Th. ^{147}Sm and ^{190}Pt also produces ^4He , but a trivial amount compared to U and Th.

THE BASIC EQUATIONS

The basic equation of radioactive decay is:

$$\frac{dN}{dt} = -\lambda N \quad 4.1$$

λ is the decay constant, which we define as the probability that a given atom would decay in some time dt . It has units of time^{-1} . Let's rearrange equation 4.1 and integrate:

$$\int_{N_0}^N \frac{dN}{N} = \int_0^t -\lambda dt \quad 4.2$$

where N_0 is the number of atoms of the radioactive, or parent, isotope present at time $t=0$. Integrating, we obtain:

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<div><div><div>Sm</div><div>Radioactive (Parent)</div></div><div><div>Os</div><div>Radiogenic (Daughter)</div></div><div><div>Rd</div><div>Radiogenic and Radioactive</div></div></div>																								He
H																								
Li	Be																							
Na	Mg																							
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr							
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe							
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rd							
Fr	Ra	Ac																						
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu							
			Ac	Th	Pa	U																		

Figure 4.1. Periodic Table showing the elements having naturally occurring radioactive isotopes and the elements produced by their decay.

$$\ln \frac{N}{N_0} = -\lambda t \quad 4.3$$

This can be expressed as: $\frac{N}{N_0} = e^{-\lambda t}$ or $N = N_0 e^{-\lambda t}$ 4.4

Suppose we want to know the amount of time for the number of parent atoms to decrease to half the original number, i.e., t when $N/N_0 = 1/2$. Setting N/N_0 to $1/2$, we can rearrange 4.3 to get:

$$\ln \frac{1}{2} = -\lambda t_{1/2} \quad \text{or} \quad \ln 2 = \lambda t_{1/2}$$

and finally: $t_{1/2} = \frac{\ln 2}{\lambda}$ 4.5

This is the definition of the *half-life*, $t_{1/2}$.

Now the decay of the parent produces some daughter, or *radiogenic*, nuclides. The number of daughters produced is simply the difference between the initial number of parents and the number remaining after time t :

$$D = N_0 - N \quad 4.6$$

Rearranging 4.4 to isolate N_0 and substituting that into 4.6, we obtain:

$$D = N_0 e^{\lambda t} - N = N(e^{\lambda t} - 1) \quad 4.7$$

This tells us that the number of daughters produced is a function of the number of parents present and time. Since in general there will be some atoms of the daughter nuclide around to begin with, i.e., when $t = 0$, a more general expression is:

$$D = D_0 + N(e^{\lambda t} - 1) \quad 4.8$$

where D_0 is the number of daughters originally present.

An exponential function can be expressed as a Taylor Series expansion:

$$e^{\lambda t} = 1 + \lambda t + \frac{(\lambda t)^2}{2!} + \frac{(\lambda t)^3}{3!} + \dots \quad 4.9$$

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Provided $\lambda t \ll 1$, the higher order terms become very small and can be ignored; hence for times that are short compared to the decay constant (i.e., for $t \ll 1/\lambda$), equation 4.8 can be written as:

$$D \cong D_0 + N \lambda t \quad 4.10$$

Let's now write equation 4.8 using a concrete example, such as the decay of ^{87}Rb to ^{87}Sr :

$$^{87}\text{Sr} = ^{87}\text{Sr}_0 + ^{87}\text{Rb}(e^{\lambda t} - 1) \quad 4.11$$

As it turns out, it is generally much easier, and usually more meaningful, to measure the ratio of two isotopes than the absolute abundance of one. We therefore measure the ratio of ^{87}Sr to a non-radio-genic isotope, which by convention is ^{86}Sr . Thus the useful form of 4.11 is:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_0 + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} (e^{\lambda t} - 1) \quad 4.12$$

Similar expressions can be written for other decay systems.

A SPECIAL CASE: THE U-TH-PB SYSTEM

The U-Th-Pb system is somewhat of a special case as there are 3 decay schemes producing isotopes of Pb. In particular two U isotopes decay to two Pb isotopes, and since the two parents and two daughters are chemically identical, combining the two provides a particularly powerful tool.

Let's explore the mathematics of this. First some terminology. The $^{238}\text{U}/^{204}\text{Pb}$ ratio is called μ , the $^{232}\text{Th}/^{238}\text{U}$ is called κ . The ratio $^{238}\text{U}/^{235}\text{U}$ is constant in the Earth at 137.88 (except in nuclear reactors and Oklo!). Now, we can write two versions of equation 4.8

$$^{207}\text{Pb}/^{204}\text{Pb} = ^{207}\text{Pb}/^{204}\text{Pb}_0 + \frac{\mu}{137.88} (e^{\lambda_{235} t} - 1) \quad 4.13$$

and

$$^{206}\text{Pb}/^{204}\text{Pb} = ^{206}\text{Pb}/^{204}\text{Pb}_0 + \mu (e^{\lambda_{238} t} - 1) \quad 4.14$$

These can be rearranged by subtracting the initial ratio from both sides and calling the difference between the initial and the present ratio Δ . For example, equation 4.13 becomes

$$^{207}\text{Pb}/^{204}\text{Pb} - ^{207}\text{Pb}/^{204}\text{Pb}_0 = \frac{\mu}{137.88} (e^{\lambda_{235} t} - 1) \quad 4.15$$

Dividing the equivalent equation for ^{235}U - ^{207}Pb by equation 4.15 yields:

$$\frac{^{207}\text{Pb}/^{204}\text{Pb} - ^{207}\text{Pb}/^{204}\text{Pb}_0}{^{206}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}_0} = \frac{(e^{\lambda_{235} t} - 1)}{137.88 (e^{\lambda_{238} t} - 1)} \quad 4.16$$

Notice the absence of the μ term. The equation holds for any present-day ratio of $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ we measure and thus for all pairs of ratios. The left-hand side is thus simply the slope of a series of data points from rocks or minerals formed at the same time (and remaining closed systems since time t) on a plot of $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$. This means we can determine the age of a system without knowing the parent-daughter ratio. The bad news is that equation 4.16 cannot be solved for t . However, we can guess a value of t , plug it into the equation, calculate the slope, compare the calculated slope with the observed one, revise our guess of t , calculate again, etc. Pretty laborious, but making 'educated guesses' of t and using a computer, this is pretty easy. In fact, using simple minimization algorithms we can generally converge to a high degree of accuracy after a few iterations.

Geochronology

Geochronology is one of the most important applications of isotope geochemistry. Let's rewrite equation 4.12 in more general terms

$$R = R_0 + R_{P/D} (e^{\lambda t} - 1) \quad 4.17$$

where R_0 is the initial ratio and $R_{P/D}$ is the parent/daughter ratio. Measurement of geologic time is based this equation, or various derivatives of it. First let's consider the general case. Given a measurement of an isotope ratio, R , and a parent-daughter ratio, $R_{P/D}$, two unknowns remain in equation 4.17: t and the initial ratio. In general, we can calculate neither from a single pair of measurements.

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In the special case where the initial concentration of the daughter is very small, we can neglect R_0 or, if $R \gg R_0$, simple assumptions about R_0 may suffice. But in the general case, we must measure R and $R_{P/D}$ on a second system for which we believe t and R_0 are the same. Then we have two equations and two unknowns and subtracting the two equations yields

$$R = R_{P/D} (e^{\lambda t} - 1) \quad 4.18$$

which eliminates $R_{P/D}$ from the equation and allows us to solve for t . This can be rearranged as:

$$\frac{R}{R_{P/D}} = e^{\lambda t} - 1 \quad 4.19$$

In practice, one measures many pairs and solving for $\Delta R / \Delta R_{P/D}$ by regression (indeed, geochronologists would not generally accept an age based on only two measurements). t may then be solved for as

$$t = \frac{\ln\left(\frac{R}{R_{P/D}} + 1\right)}{\lambda} \quad 4.20$$

For a given value of t , equation 4.17 has the form $y = a + bx$, where y is R , a is R_0 , b is $e^{\lambda t} - 1$, and x is $R_{P/D}$. This is, of course, an equation for a straight line on a plot of R vs. $R_{P/D}$ with slope $b = e^{\lambda t} - 1$, and intercept $a = R_0$. Thus on such a plot, the slope of the line depends only on t (since λ is a constant for any given decay system). A line whose slope depends only on t is known as an *isochron*. Note that on a plot of $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$, a line may also be an isochron, since its slope depends only on t .

Regression is simply a statistical method of calculating the slope of a line. Regression treatment yields both a slope and an intercept. The latter is simply the initial ratio since, as may be seen from 4.17, $R = R_0$ when $R_{P/D} = 0$. The geochronological information is contained in the slope, since it depends on t , but important geochemical information can also be obtained from the value of the intercept, the initial ratio, since it gives some information about the history prior to time t of the system being dated.

There are two important assumptions built into the use of equation 4.20.

- (1) that the system of interest was at isotopic equilibrium at time $t = 0$. Isotopic equilibrium in this case means the system had a homogeneous, uniform value of R_0 .
- (2) that the system as a whole and each analyzed part of it was closed between $t = 0$ and time t (usually the present time). By 'closed system' we mean there has been no transfer of the parent or the daughter element into or out of the system.

Violation of these conditions is the principal source of error in geochronology. Other errors arise from errors or uncertainties associated with the analysis. If the range in variation in isotope ratios is small, the analytical errors can be the limiting factor in the determination of an age. Note that both R and $R_{P/D}$ must be known accurately. Finally, of course, we must also know λ accurately. This is generally only a problem when working with a new (one with which little previous work has been done) decay system, in which case the first task is to determine λ accurately.

The requirement of a closed system and an initially homogeneous system above, suggests a meaning for the nature of the event dated by radiogenic isotope geochemistry, and a meaning for *time* in the first paragraph. In general, the *event* is the last time the system was open to complete exchange of the parent and daughter elements between the various subsystems we sample and analyze, i.e., the last point in time that the system had a homogeneous, uniform value of R . Since the rate at which chemical reactions occur increases exponentially with temperature, this event is generally a thermal one: i.e., the last time the system was hot enough for such exchange between subsystems to occur. Exactly what temperature is implied can vary widely, depending on the nature of our samples and the particular decay system we are using. Minerals such as biotite and hornblende will lose Ar at temperatures of a few hundred degrees. On the other hand, minerals such as pyroxene can remain closed to Sm and Nd exchange up to nearly 1000° C. The 'closure' temperatures of various isotope sys-

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tems in various minerals can be used to advantage: in some cases, an analysis of a variety of decay systems on a variety of sample types has recorded entire cooling histories.

The agent accomplishing isotopic homogenization of a 'system' is usually diffusion, the rate of which, like other reaction rates, increases exponentially with temperature. Diffusion rates will vary depending on the element and the properties of the material through which the element diffuses. We can nevertheless make the general observation that the greater the length scale the greater will be the time (or the higher the temperature required) for isotopic homogenization to be achieved. For the same temperature and duration of a thermal event, diffusion will more readily achieve isotopic homogenization on a small scale than on a large one. Thus, if our samples or subsystems are 'whole rocks' collected meters or perhaps kilometers apart, the event dated will generally be a higher temperature one than an event dated by analysis of individual minerals from a rock specimen whose scale is only a few centimeters.

Calculating an Isochron

Statistics books generally give an equation for linear *least squares* regression assuming one dependent and one independent variable. The independent variable is assumed to be known absolutely. The idea of least squares regression is to minimize the *squares* of the deviations from the regression line. The quantity to be minimized is the sum of the squares of deviations:

$$\sum_{i=1}^n e^2 = \sum_{i=1}^n (y_i - a - bx_i)^2 \quad 4.21$$

The use of the squares of the deviations mean that large deviations will affect the calculated slope more than small deviations. By differentiating equation 4.21, it can be shown that the minimum value for the left side occurs when the slope is:

$$b = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sum (x_i - \bar{x})^2} \quad 4.22$$

where \bar{x} and \bar{y} are the means of x and y respectively, and x_i and y_i are the i^{th} pair of observations of x and y respectively. When can see from 4.22 that the regression slope is the cross product of the deviations of x and y from the means divided by the square of the deviations of x from the mean of x . A more convenient computational form of 4.22 is:

$$b = \frac{\sum_i (x_i y_i) - \bar{y} \bar{x} n}{\sum_i x_i^2 - \bar{x}^2 n} = \frac{\sum_i (x_i y_i) - (\sum_i y_i \sum_i x_i)/n}{\sum_i x_i^2 - \bar{x}^2 n} \quad 4.23$$

The intercept is then given by: $a = \bar{y} - b\bar{x}$ 4.24

The error on the slope is:

$$\sigma_b = \sqrt{\left[\sum y_i^2 - \bar{y}^2 n - \frac{(\sum x_i y_i - \bar{y} \bar{x} n)^2}{\sum x_i^2 - \bar{x}^2 n} \right] \left[\frac{1}{(n-2)(\sum x_i^2 - \bar{x}^2 n)} \right]} \quad 4.25$$

The error on the intercept is:

$$\sigma_a = \sqrt{\left[\sum y_i^2 - \bar{y}^2 n - \frac{(\sum x_i y_i - \bar{y} \bar{x} n)^2}{\sum x_i^2 - \bar{x}^2 n} \right] \left[\frac{1}{n} + \frac{\bar{x}^2}{(\sum x_i^2 - \bar{x}^2 n)} \right] \left[\frac{1}{n-2} \right]} \quad 4.26$$

While it is true that R is a function of $R_{p/D}$ in a geologic sense and hence may be considered the dependent variable, in practice both R and $R_{p/D}$ are measured quantities and neither is known absolutely: both have errors of measurement associated with them. These must be taken into account for a proper estimate of the slope and the errors associated with it. In some cases, the errors in measurement of x and y can be correlated, and this must also be taken into account. The so-called *two-error re-*

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gression algorithm takes account of these errors. This is, however, considerably less straight-forward than the above. The approach is to weight each observation according to the measurement error (the weighting factor will be inversely proportional to the analytical error). A solution has been published by York (1969). The regression slope is:

$$b = \frac{\sum_i Z_i^2 (y_i - \bar{y}) \left[\frac{x_i - \bar{x}}{\omega(y_i)} + \frac{b(y_i - \bar{y})}{\omega(x_i)} - \frac{r_i(y_i - \bar{y})}{\alpha_i} \right]}{\sum_i Z_i^2 (x_i - \bar{x}) \left[\frac{x_i - \bar{x}}{\omega(y_i)} + \frac{b(y_i - \bar{y})}{\omega(x_i)} - \frac{br_i(y_i - \bar{y})}{\alpha_i} \right]} \quad 4.27$$

where $\omega(x_i)$ is the weighting factor for x_i (generally taken as the inverse of the square of the error), $\omega(y_i)$ is the weighting factor for y_i , r_i is the correlation between the error of measurement of x_i and y_i , $\alpha = \sqrt{\omega(x_i)\omega(y_i)}$, $\bar{x} = \sum Z_i x_i / \sum Z_i$, $\bar{y} = \sum Z_i y_i / \sum Z_i$ (weighted means), and Z is:

$$b = \frac{\alpha_i^2}{\omega(y_i) + \omega(x_i) - 2br_i\alpha_i}$$

Note that the expression for b contains b . This requires an iterative solution: not something you want to do in your head, but reasonably easy with a computer. For example, the first estimate of b could be made using equation 4.23. The difference between this method and the standard one is not great, so convergence is generally quick. The intercept is calculated as in equation 4.24. Calculating the errors associated with a and b is reasonably hairy, but approximate solutions are given by:

$$\sigma_b = \sqrt{\frac{1}{\sum_i Z_i (x_i - \bar{x})^2}} \quad 4.28$$

$$\sigma_a = \sqrt{\frac{\sigma_b}{\sum_i Z_i}} \quad 4.29$$

REFERENCES AND SUGGESTIONS FOR FURTHER READING

York, D., Least squares fitting of a straight line with correlated errors, *Earth Planet. Sci. Lett.*, 5, 320-324, 1969.