Lecture 3: Radiometric Dating – Simple Decay


Terminology

Radioactive: unstable nuclide, decays to a daughter nuclide (stable or unstable)

Radiogenic: a nuclide that is the product of decay

Cosmogenic: produced by interaction of cosmic rays with matter

Anthropogenic: produced artificially

Primordial: existed at the beginning of the Solar System

Activity (A): $A = \lambda N$, the activity of a nuclide is shown in round brackets $(A)$

Secular equilibrium: $(A)_1 = (A)_2 = (A)_3$ or $\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3$

Closed system: system with walls impermeable to matter

Simple Radioactive Decay

Radioactive decay is a stochastic process linked to the stability of nuclei. The rate of change in the number of radioactive nuclei is a function of the total number of nuclei present and the decay constant $\lambda$.

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

The sign on the left hand is negative because the number of nuclei is decreasing. Rearranging this equation yields

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

and integrating yields

$$\ln N = -\lambda t + C$$

C is the integration constant. We solve for C by setting $N = N_0$ and $t = t_0$. Then

$$C = \ln N_0$$

Substituting for C gives

$$\ln N = -\lambda t + \ln N_0$$

We rearrange

$$\ln N - \ln N_0 = -\lambda t$$

Rearrange again

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

Eliminate the natural log

$$N N_0 = e^{-\lambda t}$$

And rearrange

$$N = N_0 e^{-\lambda t}$$

Simple Decay: Radioactive Parent $\Rightarrow$ Stable Daughter

$$D^* = N_0 (1 - e^{-\frac{t}{T}})$$

$$N = N_0 e^{-\frac{t}{T}}$$

Number of Atoms (N or D)

Half-lives

0 1 2 3 4 5 6 7 8 9 10

0 100 200 300 400 500 600 700 800 900 1000

ingrowth of daughter
decay of parent
Unfortunately, we don’t know \( N_0 \) a priori, but decayed \( N \) have produced radiogenic daughters \( D^* \).

Therefore

\[ D^* = N_{0} - N \]

Replacing \( N_0 \) with \( N \)

\[ D^* = N \, e^{-t} - N \]

Rearranged

\[ D^* = N (e^{-t} - 1) \quad \text{or}, \quad D^* = N \, k \, t, \]

The number of daughter isotopes is the sum of those initially present plus those radiogenically produced.

\[ D = D_0 + D^* \]

Therefore

\[ D = D_0 + N \, e^{-t} - N \]

This is the basic radioactive decay equation used for determining ages of rocks, minerals and the isotopes themselves. \( D \) and \( N \) can be measured and \( k \) has been experimentally determined for nearly all known unstable nuclides. The value \( D_0 \) can be either assumed or determined by the isochron method.

For small \( t \) we can simplify with a Taylor series expansion

\[ e^t = 1 + t + (t^2/2!) + (t^3/3!) + \ldots, \quad \text{simplifies to} \quad e^t = 1 + t, \quad \text{for small} \ t \]

The half-life, that is the time after which half of the initially present radioactive atoms have decayed (\( N = 1/2 \) \( N_0 \) at \( t = T_{1/2} \)) is

\[ T_{1/2} = \ln 2 / k \]

Sometimes you will also find reference to the mean life \( \tau \), that is the average live expectancy of a radioactive isotope

\[ \tau = 1 / k \]

The mean life is longer than the half-life by a factor of \( \ln 2 (1.443) \). For the derivation of \( \tau \) see page 39 of Gunter Faure’s book *Principles of Isotope Geology*.

The Isochron Method

Consider the decay of \(^{87}\text{Rb} \) to \(^{87}\text{Sr} \)

\[ ^{87}\text{Rb} \rightarrow ^{87}\text{Sr} + \gamma + \]

Substituting into the decay equation

\[ ^{87}\text{Sr} = ^{87}\text{Sr}_0 + ^{87}\text{Rb} (e^{-t} - 1) \]

Dividing by a stable Sr isotope, \(^{86}\text{Sr} \)

\[ ^{87}\text{Sr} / ^{86}\text{Sr} = ^{87}\text{Sr}_0 / ^{86}\text{Sr} + ^{87}\text{Rb} / ^{86}\text{Sr} (e^{-t} - 1) \]

In a diagram with axes \( x = ^{87}\text{Rb} / ^{86}\text{Sr} \) and \( y = ^{87}\text{Sr} / ^{86}\text{Sr} \) this equation defines a line, \( y = mx + b \)

With the slope

\[ m = (e^{-t} - 1) \]

and constant \( b \), the initial ratio

\[ b = (^{87}\text{Sr}_0 / ^{86}\text{Sr}) \]

Prequisites:
1. Isotopic homogeneity at start (identical \(^{87}\text{Sr} / ^{86}\text{Sr} \))
2. Chemical variability at start (variable Rb/Sr)
3. Closed system from \( t=0 \) to \( t=T \)

Mixing

The mass balance of any element is determined by input (usually from a number of sources) and removal (usually a number of sinks). Mixing is thus a fundamental process in quantifying the elemental and isotopic composition of a reservoir. If we mix two components (A and B) in different proportions, a mixing parameter (\( f \)) can be defined as

\[ f = A / (A + B) \]

The concentration (C) of any element in the mixture (M) is then

\[ C_M = C_A f + C_B (1 - f) \]

If A and B are mixed in various proportions (\( f \)), the concentration in the mixture (\( C_M \)) is a linear function of \( f \).

\[ C_M = f (C_A - C_B) + C_B \]

The mixing parameter \( f \) can be calculated from the concentration of an element in the mixture if the end-member concentrations are known. It is important to understand that mixing is considered an instantaneous process in these models. It therefore does not matter whether the input is spatially homogeneous along the ocean shores or concentrated in one spot. This is, obviously, a simplification - in reality the distribution of sources does matter and point sources can lead to local deviations from “average” values.
Two components with two elements

In the next step we consider mixing two components (A and B) with two elements (1 and 2). The concentrations of element 1 and 2 in A and B are then \( C_A1, C_A2, C_B1 \) and \( C_B2 \), respectively. The concentration of element 2 in a mixture (\( C_M2 \)) of A and B is related to the concentration of element 1 in the mixture (\( C_M1 \)) according to

\[
C_M2 = C_M1 \left[ \frac{(C_A2 - C_B2)}{(C_A1 - C_B1)} \right] + \left[ \frac{(C_B2 C_A1 - C_A2 C_B1)}{(C_A1 - C_B1)} \right]
\]

This equation represents a straight line in coordinates \( C_M1 \) and \( C_M2 \). All mixtures of component A and B, including the end-member compositions, lie on this line. Therefore, an array of data points representing mixing of two components can be fitted with a mixing line. If the concentration of one of the two elements in the end-members is known, above equation can be used to calculate the concentration of the other element. In addition, the mixing parameter \( f \) can be calculated.

Two components with different isotopic composition (e.g., Isotope Dilution)

We can expand the above equation even further and include mixing of two components with different isotopic compositions. The most convenient way of setting up mass balances for isotopes is to start with only one isotope. The number of atoms of isotope 1 of element E in a weight unit of the mixture is given by

\[
I_{1EM} = (C_{EA} \text{Ab}_{I1EA} N f / A_{WEA}) + (C_{EB} \text{Ab}_{I1EB} (1 - f) / A_{WEB})
\]

with
- \( I_{1EM} \) = number of atoms of isotope 1 of element E per unit weight in the mixture
- \( C_{EA} \) = concentration of element E containing isotope 1 in component A
- \( C_{EB} \) = concentration of element E containing isotope 1 in component B
- \( \text{Ab}_{I1EA} \) = atomic abundance of isotope 1 of element E in component A
- \( \text{Ab}_{I1EB} \) = atomic abundance of isotope 1 of element E in component B
- \( N \) = number of atoms per mole (Avogadro number \( 6.022045 \times 10^{23} \))
- \( A_{WEA} \) = atomic weight of element E in component A
- \( f \) = mixing parameter (see above)

A similar equation can be set up for the number of atoms of isotope 2 of element E and the two equations can be combined. This manipulation eliminates the Avogadro number and allows us to deal with isotope ratios

\[
\frac{I_{1E}}{I_{2E}} = \frac{C_{EA} \text{Ab}_{I1EA} f / C_{EM}}{C_{EB} \text{Ab}_{I2EB} (1 - f) / C_{EM}}
\]

To make life (and math) easier it is generally assumed that the atomic weights (and thus the isotopic abundance) of element E are identical in the two components A and B. This approximation simplifies the above equation. WARNING: This approximation is justified only if the isotopic composition of element E is very similar in A and B. For many isotope systems (e.g., Sr isotopes) this approximation introduces only small errors (e.g., 0.700 and 0.800, the corresponding atomic weights vary by less than 1%). For some isotope systems with large dynamic range in isotope compositions this assumption is not valid and the full mixing equation has to be used.

Assuming that \( A_{WEA} = A_{WEB} \), the mixing equation becomes

\[
I_{1M} = \frac{C_{EA} \text{Ab}_{I1EA} f + C_{EB} \text{Ab}_{I1EB}}{\text{Ab}_{I1E} (f + 1 - f)}
\]

This equation can be rearranged using equation (2) and substituting

\[
\frac{\Delta I_1}{\Delta I_2} = R_M
\]

Then

\[
R_M = R_A \left[ \frac{(C_A1 f)}{C_{EM}} \right] + R_B \left[ \frac{(1 - f)}{C_{EM}} \right]
\]

After eliminating \( f \) from the equation and rearranging again, the equation becomes

\[
R_M = \frac{\left[ C_{EA} R_B (C_{EA} - C_{EM}) + C_{EB} R_A (1 - f) \right]}{\left[ C_{EA} f + C_{EB} (1 - f) \right]}
\]

where the constants \( x \) and \( y \) replace the appropriate portions of the above equation. This is the equation of a hyperbola in coordinates of \( R_M \) and \( C_{EM} \) that can be linearized by plotting \( R \) versus \( \frac{1}{C_{EM}} \), the isotope ratio of the mixture versus its inverse concentration.

It is important to understand that this line will only be a straight line in a plot \( R \) versus \( \frac{1}{C_{EM}} \) if the assumption \( A_{WEA} = A_{WEB} \) is justified. In all other cases, differences in the isotopic abundances of each component cannot be neglected and \( R_M \) has to be plotted against the concentration of an isotope of element E rather than the concentration of element E itself. One example is a plot of \( ^{87}\text{Sr} / ^{86}\text{Sr} \) versus \( ^{87}\text{Rb} / ^{86}\text{Sr} \), also known as an isochron diagram. In such a diagram a linear array of data points either represents mixture of two components, or has age significance (slope being equal to \( e^{\lambda t} - 1 \)).

The ambiguity in the interpretation of mixing lines and isochrons in such diagrams haunts isotope geochemists.
Mixing of two components with two elements (1 and 2) of different isotopic composition (R) in coordinates $R_1$ and $R_2$ are generally hyperbolic. This is shown in the next figure, using Sr and Nd as an example (from Dickin, 1995, in this example: $c$ = crust, $m$ = mantle, $x_c$ = fraction crust).

Only in the special case when the ratios of the concentration of the two elements in the two components are equal (e.g., $[\text{Nd}/\text{Sr}]_A = [\text{Nd}/\text{Sr}]_B$), mixing lines will be straight lines. A more detailed treatment of this problem can be found in chapter 9 in Faure (1986) and chapter 1 in Albarede (1995).

**238-U Decay Series**

- $^{238}$U (Decay Series)
- $^{238}$U: $\frac{1}{2}T = 2.455 \times 10^9$ years
- $^{234}$Th: $\frac{1}{2}T = 24.1\text{ days}$
- $^{222}$Rn: $\frac{1}{2}T = 3.825 \text{ days}$
- $^{218}$Pb: $\frac{1}{2}T = 24.55 \text{ ky}$
- $^{206}$Pb: $\frac{1}{2}T = 75.38 \text{ ky}$

**The Pb-Pb method of dating**

- $^{207}$Pb/$^{204}$Pb
- $^{206}$Pb/$^{204}$Pb
- Geochron, the present-day isochron
Measurement Uncertainties

All measurements are afflicted with uncertainties. For large number of events, binomial distributions asymptotically approach Gaussian (or normal) distributions. The spread in events (here numerical values of isotope ratios, count rates or ion currents) is equal to \( \sqrt{N} \). According to Gaussian statistics about 2/3 of the results lie within the range \( N \pm \sqrt{N} \) (one standard deviation), about 95% lie within the range \( N \pm 2\sqrt{N} \) (two standard deviations), and ~99% lie within the range \( N \pm 3\sqrt{N} \). The fractional uncertainty is thus \( \frac{\sqrt{N}}{N} \), or \( 1/\sqrt{N} \). If you measure twice as long (\( N^{*} \)) you get twice as many events

\[ N^{*} = 2N \]

the fractional uncertainty is

\[ \sqrt{2N}/2N = 1/\sqrt{2N} \]

i.e.

\[ = \sqrt{1/2} \times 1/\sqrt{N} \]

reducing the fractional uncertainty only by ~30%. The fractional uncertainty improves only as the square root of time (or ion current). If you attempt to improve the uncertainty by a factor of two, you need to measure four times as long, or measure a four-times stronger ion current.

In order to evaluate if uncertainties associated with small ion beam intensities significantly affect the measured ratios it is often helpful to assume that all uncertainties are associated with uncertainties in the smallest ion current (least abundant isotope). By assuming an arbitrary uncertainty in the measurement of this ion current you can plot an error trend on plots of isotope ratio versus another isotope ratio (same isotope in the denominator, i.e. \( m_3 = m_4 \), if \( m_1 \) and \( m_3 \) are isotopes in the numerator). This trend is often distinct from a instrumental fractionation trend and helps to assess what process dominates the uncertainty of your analysis.
User's Manual for

Isoplot
3.00

A Geochronological Toolkit for Microsoft Excel

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Subject: Re: mathematical correction
From: "Warren S. Wasser" <wasser@ncsu.edu>
Date: Wed, 12 Sep 2012 23:46:28 -0400

Sorry about the delay in responding - it occurred because I have moved from Princeton, and my books just got unpacked.

The first source I can give you is the latest (seventh edition) of General, Miller and Shaw. Section 5-23(d) of the Handbook gives the formula in a slightly different but equivalent form:

\[ R = \left( \frac{x}{y} \right)^p \]

You can round to the nearest 0.1% or 0.001% and perhaps slightly understate the true uncertainty if you prefer.

Another source is a colleague of mine in the next building who saw in a paper I wrote: "Generally the uncertainty of a measurement can be estimated by more than plus or minus 2%".

Also, your inquiry, I found that some methods are much more certain about assigning half-lives, only 10% of the time do I assign half-lives 10% (or less) uncertainty. The 7.7 ± 0.7% is the best estimate I can give you for the uncertainty in the half-life.

Dear Prof. Wasser,

Your updated book on the physical basis of chronology contains a statement (page 76, lines 4-6 below) that is very similar to the statement in equal 100% interval.

I am looking for a method of assigning the uncertainty of the measured half-life in a way that is consistent with the physical basis of chronology and the accuracy of the model.

A method that is consistent with the accuracy of the model in assigning the uncertainty of the measured half-life.

With kind regards and thanks,

Bruno P.E.

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