

Lecture 3: Radiometric Dating – Simple Decay

The oldest known rocks on Earth: 4.28 billion years - Nuvvuagittuq belt region, N' Quebec on the shores of Hudson Bay. *O'Neil et al., Science 321 (2008) 1828-1831.*



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 λ .

$$-dN / dt = \lambda N$$

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

$$-dN / N = \lambda dt$$

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

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

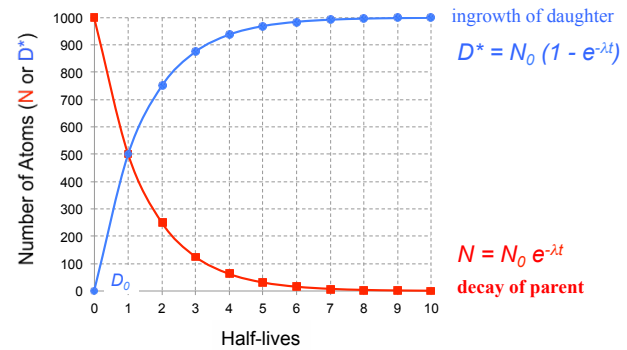
Eliminate the natural log

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

And rearrange

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

Simple Decay: Radioactive Parent \Rightarrow Stable Daughter



...continue...

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 $N e^{\lambda t}$ yields $D^* = N e^{\lambda t} - N$

Rearranged $D^* = N (e^{\lambda t} - 1)$ or, for small λt , $D^* = N \lambda t$.

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

$D = D_0 + D^*$

Therefore, $D = D_0 + N (e^{\lambda t} - 1)$ or, for small λt , $D = D_0 + N \lambda t$.

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 λ 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 λt we can simplify with a Taylor series expansion

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

simplifies to $e^{\lambda t} = 1 + \lambda t$, for small λt

...continue...

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

$$T_{1/2} = \ln 2 / \lambda$$

Sometimes you will also find reference to the **mean life** τ , that is the average live expectancy of a radioactive isotope

$$\tau = 1 / \lambda$$

The mean life is longer than the half-life by a factor of $1/\ln 2$ (1.443). For the derivation of τ see page 39 of Gunter Faure's book *Principles of Isotope Geology*.

The Isochron Method

Consider the decay of ^{87}Rb to ^{87}Sr

$$^{87}_{37}\text{Rb} \Rightarrow ^{87}_{38}\text{Sr} + \text{ } + \text{ }$$

Substituting into the decay equation

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

Dividing by a stable Sr isotope, ^{86}Sr

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

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

$$m = (e^{\lambda t} - 1)$$

and constant b , the **initial ratio**

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

Prerequisites:

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

(1) $f = A / (A + B)$

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

(2) $C_M = C_A f + C_B (1 - f)$

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

(3) $C_M = f(C_A - C_B) + C_B$

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 homogenous 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

$$(4) \quad C_{M2} = C_{M1} [(C_{A2} - C_{B2}) / (C_{A1} - C_{B1})] + [(C_{B2} C_{A1} - C_{A2} C_{B1}) / (C_{A1} - C_{B1})]$$

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

$$(5) \quad I_{EM} = (C_{EA} Ab_{1IEA} N f / AW_{EA}) + [C_{EB} Ab_{1IEB} N (1 - f) / AW_{EB}]$$

- with
- I_{EM} = 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
 - Ab_{1IEA} = atomic abundance of isotope 1 of element E in component A
 - Ab_{1IEB} = atomic abundance of isotope 1 of element E in component B
 - N = number of atoms per mole (Avogadro number 6.022045×10^{23})
 - AW_{EA} = 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

$$(6) \quad \frac{I_{1E}}{I_{2E}} = \frac{C_{EA} Ab_{1IEA} f AW_{EB} + C_{EB} Ab_{1IEB} (1 - f) AW_{EA}}{C_{EA} Ab_{2IEA} f AW_{EB} + C_{EB} Ab_{2IEB} (1 - f) AW_{EA}}$$

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 this approximation introduces only small errors (e.g., if the Sr-isotopic composition of component A = 0.700 and that of component B = 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 $AW_{EA} = AW_{EB}$ (i.e., $Ab_{1IEA} = Ab_{1IEB}$ and $Ab_{2IEA} = Ab_{2IEB}$) the mixing equation becomes

$$(7) \quad \frac{I_{1E}}{I_{2E}} = \frac{C_{EA} Ab_{1IEA} f + C_{EB} Ab_{1IEB} (1 - f)}{Ab_{2IEA} [C_{EA} f + C_{EB} (1 - f)]}$$

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

$$\begin{aligned} (I_{1E} / I_{2E})_M &= R_M \\ (Ab_{1IEA} / Ab_{2IEA})_A &= R_A \\ (Ab_{1IEB} / Ab_{2IEB})_B &= R_B \end{aligned}$$

Then

$$(8) \quad R_M = R_A (C_{EA} f / C_{EM}) + R_B [C_{EB} (1 - f) / C_{EM}]$$

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

$$(9) \quad R_M = \{ [C_{EA} C_{EB} (R_B - R_A)] / [C_{EM} (C_{EA} - C_{EB})] + [C_{EA} R_A - C_{EB} R_A] / [C_{EA} - C_{EB}] \}$$

and can be further simplified to

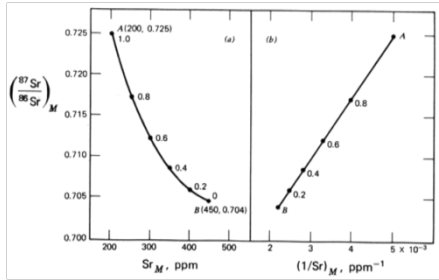
$$(10) \quad R_M = x / C_{EM} + y$$

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_M versus $1/C_{EM}$, i.e., 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_M versus $1/C_{EM}$ if the assumption $AW_{EA} = AW_{EB}$ is justified. In all other cases, differences in the isotope abundance 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 represent 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.

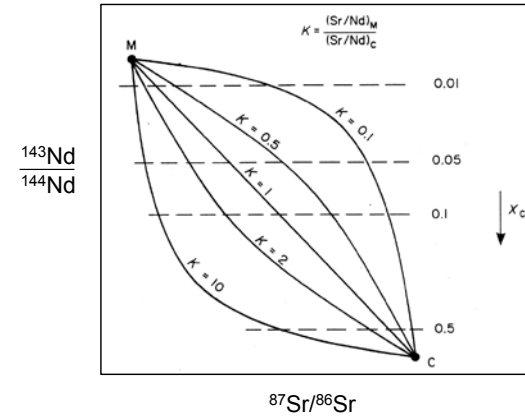
Linearized mixing hyperbola



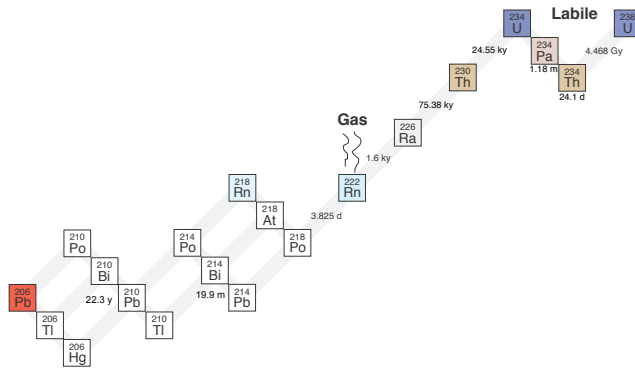
Mixing of two components with two elements (1 and 2) of different isotopic composition (R) in coordinates R_1 and R_2 are generally hyperbolic. This is shown in the next figure, using Sr and Nd as an example (from Dickin, 1995, in this example: c = crust, m = mantle, x_c = fraction crust).

Only in the special case when the ratios of the concentration of the two elements in the two components are equal (e.g., $[C_{Nd} / C_{Sr}]_A = [C_{Nd} / C_{Sr}]_B$), 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 Albaredo (1995).

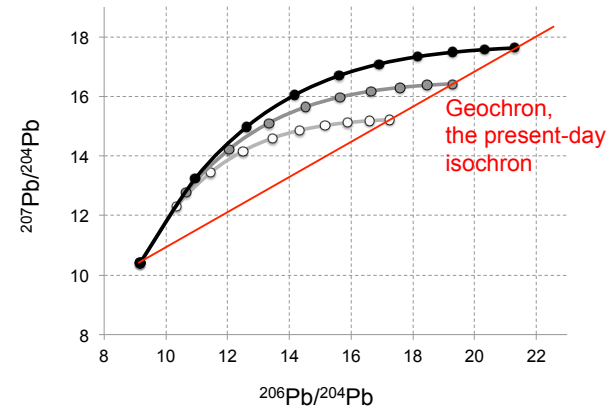
Mixing hyperbola

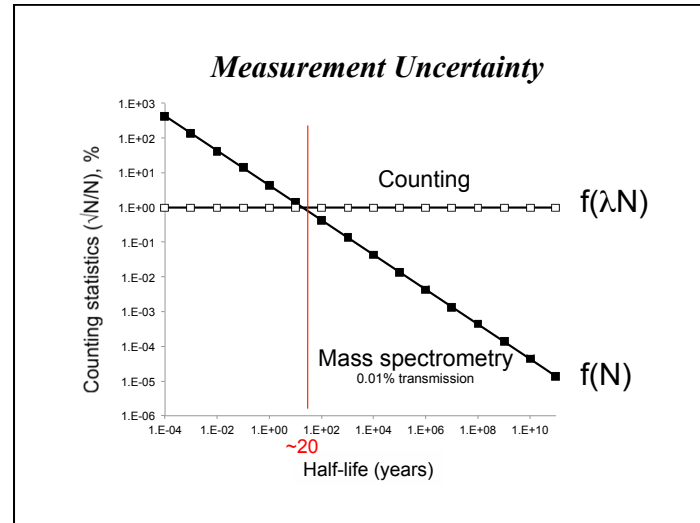
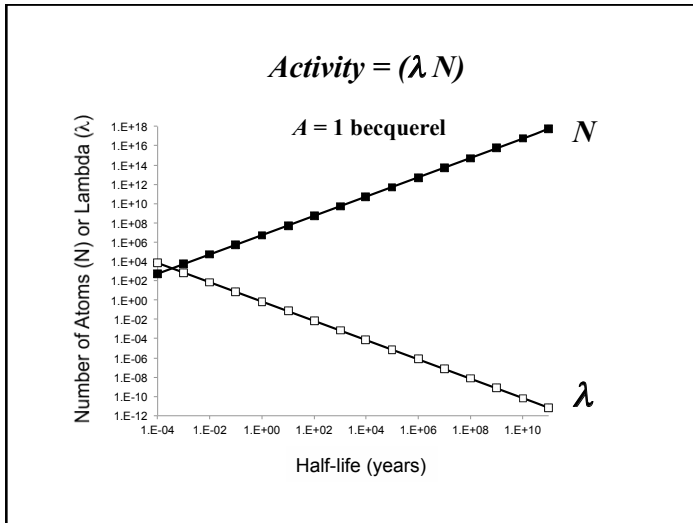


238-U Decay Series



The Pb-Pb method of dating





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 $\sqrt{N/N}$, 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. $= \sqrt{1/2} * 1/\sqrt{N}$

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. $m_2 = m_1$, if m_1 and m_2 are isotopes in the numerator). This trend is often distinct from an instrumental fractionation trend and helps to assess what process dominates the uncertainty of your analysis.

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mean concentration = $\bar{C} = \frac{\sum C_i}{N}$

r.m.s. deviation from average = $\sigma = \left[\frac{\sum (C_i - \bar{C})^2}{N} \right]^{1/2}$ (4.21)

For this particular data set, \bar{C} turns out to be 99.944 mM, but one glance at Figure 4.2 shows that not all of those digits are significant. σ turns out to be 0.66 mM, so we would calculate that the concentration of a typical bottle is 99.944 ± (1.96 · 0.66) mM = 99.944 ± 1.29 mM. In practice, we would not report so many digits; the usual convention is that the last reported digit should be uncertain by an amount between 3 and 30 units. So we would write 99.9 ± 1.3 mM (the last digit, in the tenth-millimolar position, is uncertain by 13 units) in writing confidence limits for the distribution. This implies that 95% of the time a bottle selected at random would have a concentration between 98.6 and 101.2 mM.

We can also generalize result (3) at the beginning of Section 4.3 to say that the average of N measurements is expected to be in error by an amount which is proportional to $1/\sqrt{N}$. This is the principle behind **signal averaging**. The average of 1000 trials is expected to be ~1000 times more accurate than the result of a single trial. So we would report 99.974 ± (1.96 · 0.66)/√1000 mM = 99.94 ± 0.04 mM (again to the correct number of significant digits) in writing confidence limits for the mean.

Note now that the labeled mean concentration is outside of the error bars, which as we noted before were based on 95% confidence limits. This means that, if the mean concentration were really 100 mM, there would be less than one chance in 20 that 1000 bottles, chosen at random, would give a deviation from the average which was this large. Based on these statements, we can conclude (again at the 95% confidence level) that the actual mean concentration, which we could approach in principle by measuring an extremely large number of bottles, is less than 100.00 mM.

Which is more important: confidence limits for the mean or confidence limits for the distribution? It depends on the application. The vendor of the standardized solutions above should report confidence limits for the distribution to its customers, who will use one bottle at a time (for example, in preparing a saline solution to be injected into a patient). In other cases, however, the error is in the measurement process itself. We believe that all electrons have the same mass, but 1000 measurements of electron mass will likely all give slightly different answers. Then we want to know confidence limits for the mean. In addition, 95% confidence limits for the mean are used by pollsters to predict the results of an election. The fact that individual preferences vary is not interesting; what is interesting is whether, on average, more than 50% of the voters prefer one specific candidate.

The approach described above only gives correct confidence for a very large number of observations, say $N > 50$. It is possible to generalize these formulas to assign

HAROLD D. SWEENEY, JR., THE PHYSICAL BASIS OF CHEMISTRY, 2ND EDITION, PRENTICE-HALL AND JOHN WILEY & SONS, 1977, page 70

Re: usual convention

Subject: Re: usual convention
 From: "Warren S. Warren" <warren.warren@duke.edu>
 Date: Thu, 06 Oct 2005 14:27:59 -0400
 To: behrenbrink@whoi.edu

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

The best source I can give you is the latest (seventh) edition of Garland, Nibler and Shoemaker, Experiments in Physical Chemistry (McGraw-Hill, New York, 2003). Shoemaker was the lead author on the early editions, and this is a standard reference textbook. You will find this convention on page 30, in the slightly different but equivalent form:

"Numerical values are considered to be uncertain in the last digit by plus or minus 3 or more, and perhaps slightly uncertain in the next-to-last digit. Ordinarily the next-to-last digit should not be uncertain by more than plus or minus 2."

After your inquiry, I found that most textbooks are much more vague about assigning specific rules, perhaps because statisticians do not like significant digits (for obvious reasons). The "3 to 30" rule is the one I remembered when I began experimental science.

At 05:50 PM 9/14/2005, you wrote:

Dear Prof. Warren:

Your splendid book on the physical basis of chemistry contains a statement (page 70, lines 4-6 below equation 4.21) that is very sensible and that I would like to trace to its source. My local experts here at WHOI had not seen this convention expressed in this form and could not help me locating its origin. Would you be kind enough to point me to the source of this "usual convention"?

With kind regards and thanks,
 Bernhard P.E.

Bernhard Peucker-Ehrenbrink
 Dept. Marine Chemistry & Geochemistry
 Woods Hole Oceanographic Institution
 360 Woods Hole Road, MS 25
 Woods Hole, MA 02543-1541, USA
 Ph: (01) 508 289 2518
 Fax: (01) 508 457 2193
 URL: www.whoi.edu/people/bpeucker
 NENIMP URL: www.whoi.edu/nenimp

Warren S. Warren, Professor of Chemistry and Radiology, Duke University
 Director, Center for Molecular and Biomolecular Imaging
 Gross Chemical Building, 135 Science Drive, Box 90346, Durham, NC 27708
 phone: (919)660-1604, fax: (919)287-2454

User's Manual for

Isoplot

3.00

A Geochronological Toolkit for Microsoft Excel

Berkeley Geochronology Center
 Special Publication No. 4

Kenneth R. Ludwig
 Revised May 30, 2003

2455 Ridge Road, Berkeley CA 94709
kludwig@bgc.org