Lecture 3: Radiometric Dating – Simple Decay


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**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

\[
\ln N/N_0 = - \lambda \, t
\]

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

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Simple Decay: Radioactive Parent $\Rightarrow$ Stable Daughter

\[ N = N_0 e^{-\lambda t} \]

decay of parent

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Simple Decay: Radioactive Parent $\Rightarrow$ Stable Daughter

\[ \begin{align*}
D^* &= N_0 \left(1 - e^{-\lambda t}\right) \\
N &= N_0 e^{-\lambda t}
\end{align*} \]
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

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

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

$$D = D_0 + D^*$$

Therefore,

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

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 $\lambda$ 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 $\lambda t$ we can simplify with a Taylor series expansion

$$e^{\lambda t} = 1 + \lambda t + (\lambda t)^2/2! + (\lambda t)^3/3! + \ldots \quad \text{simplifies to } e^{\lambda t} = 1 + \lambda t, \text{ for small } \lambda t$$
The **half-life**, that is the time after which half of the initially present radioactive atoms have decayed ($N = \frac{1}{2} N_0$ at $t = T_{1/2}$) is

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

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

$$\tau = \frac{1}{\lambda}$$

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

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

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

Conservation rules

Reaction:

Charge
Baryon #
Lepton #

Courtesy Brookhaven National Lab.
The Isochron Method

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

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

Conservation rules

Reaction: $n \rightarrow p + e^- + \overline{v}_e$

Charge

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>+1</th>
<th>-1</th>
<th>0</th>
</tr>
</thead>
</table>

Baryon #

|        | +1 | +1 | 0  | 0 |

Lepton #

|        | 0  | 0  | +1 | -1 |

Courtesy Brookhaven National Lab.
TheIsochron Method

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

$$^{87}_{37}\text{Rb} \Rightarrow ^{87}_{38}\text{Sr} + e^- + \bar{\nu}_e + E$$

Substituting into the decay equation

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

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

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

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

With the slope

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

and constant $b$, the initial ratio

$$b = \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_0$$

Prerequisites:

1. Isotopic homogeneity at start (identical $^{87}\text{Sr}/^{86}\text{Sr}$)

2. Chemical variability at start (variable Rb/Sr)

3. Closed system for parent/daughter isotopes from t=0 to t=T

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**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) \[ f = \frac{A}{A + B} \]

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

\[
C_{M2} = C_{M1} \left[ \frac{(C_{A2} - C_{B2})}{(C_{A1} - C_{B1})} \right] + \left[ \frac{(C_{B2} C_{A1} - C_{A2} C_{B1})}{(C_{A1} - C_{B1})} \right]
\]

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.

For the number of atoms of an element (N, units of numbers of atoms, n), the accounting involves the concentration of the element (C, units of g/g), the weight of the sample that is being processed (wt, units of gram), the atomic weight of the element with a specific isotope composition (AW, g/mole), the abundance of the isotope (Ab, unitless, expressed as fraction) of the element, and Avogadro’s number (#, $6.022 \times 10^{23}$ atoms per mole):

\[
N = \frac{(C \cdot wt \cdot # \cdot Ab)}{AW} \quad \text{dimensional analysis: (g/g g n/mole) / (g/mol) = n}
\]
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

\[
I_{1EM} = (C_{EA} A_{1EA} N f / AW_{EA}) + [C_{EB} A_{1EB} N (1 - f) / AW_{EB}]
\]

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
- \(A_{1EA}\) = atomic abundance of isotope 1 of element E in component A
- \(A_{1EB}\) = atomic abundance of isotope 1 of element E in component B
- \(N\) = number of atoms per mole (Avogadro number 6.022045 \times 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

\[
\frac{I_{1E}}{M} = \frac{C_{EA} A_{1EA} f AW_{EB} + C_{EB} A_{1EB} (1 - f) AW_{EA}}{C_{EA} A_{2EA} f AW_{EB} + C_{EB} A_{2EB} (1 - f) AW_{EA}}
\]
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., \( Ab_{I1EA} = Ab_{I1EB} \) and \( Ab_{I2EA} = Ab_{I2EB} \)) the mixing equation becomes

\[
\begin{align*}
I_1E \quad & \quad C_{EA} \, Ab_{I1EA} \, f + C_{EB} \, Ab_{I1EB} \, (1 - f) \\
M \quad & \quad \frac{C_{EA} \, f + C_{EB} \, (1 - f)}{C_{EA} \, f + C_{EB} \, (1 - f)} \\
I_2E \quad & \quad Ab_{I2EA} \, [C_{EA} \, f + C_{EB} \, (1 - f)]
\end{align*}
\]

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

\[
\begin{align*}
(I_1E / I_2E)_M & = R_M \\
(Ab_{I1EA} / Ab_{I2EA})_A & = R_A \\
(Ab_{I1EB} / Ab_{I2EB})_B & = R_B
\end{align*}
\]

Then

\[
R_M = R_A \, \left( \frac{C_{EA} \, f}{C_{EM}} \right) + R_B \, \left[ C_{EB} \, (1 - f) / C_{EM} \right]
\]
After eliminating (f) from the equation and rearranging again, the equation becomes

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

and can be further simplified to

\[
R_M = \frac{x}{C_{EM}} + y
\]

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 \(e^{\lambda \tau} - 1\)).

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., $[C_{Nd} / C_{Sr}]_A = [C_{Nd} / C_{Sr}]_B$), 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 Albarede (1995).
Mixing hyperbola

\[ K = \frac{(\text{Sr/Nd})_M}{(\text{Sr/Nd})_C} \]

Image by MIT OpenCourseWare.
238-U Decay Series

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The Pb-Pb method of dating
The Pb-Pb method of dating

$\frac{^{207}\text{Pb}}{^{204}\text{Pb}}$ 

$\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$

bya = billion years ago
The Pb-Pb method of dating

\[
\frac{^{207}\text{Pb}}{^{204}\text{Pb}} \quad \text{vs} \quad \frac{^{206}\text{Pb}}{^{204}\text{Pb}}
\]

\(\mu=8\) \hspace{1cm} \(\mu=10\) \hspace{1cm} \(\mu=12\)
The Pb-Pb method of dating

Geochron, the present-day isochron
12.744 Marine Isotope Chemistry
Fall 2012

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