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.*

Courtesy of Jonathan O'Neil. Used with permission.

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
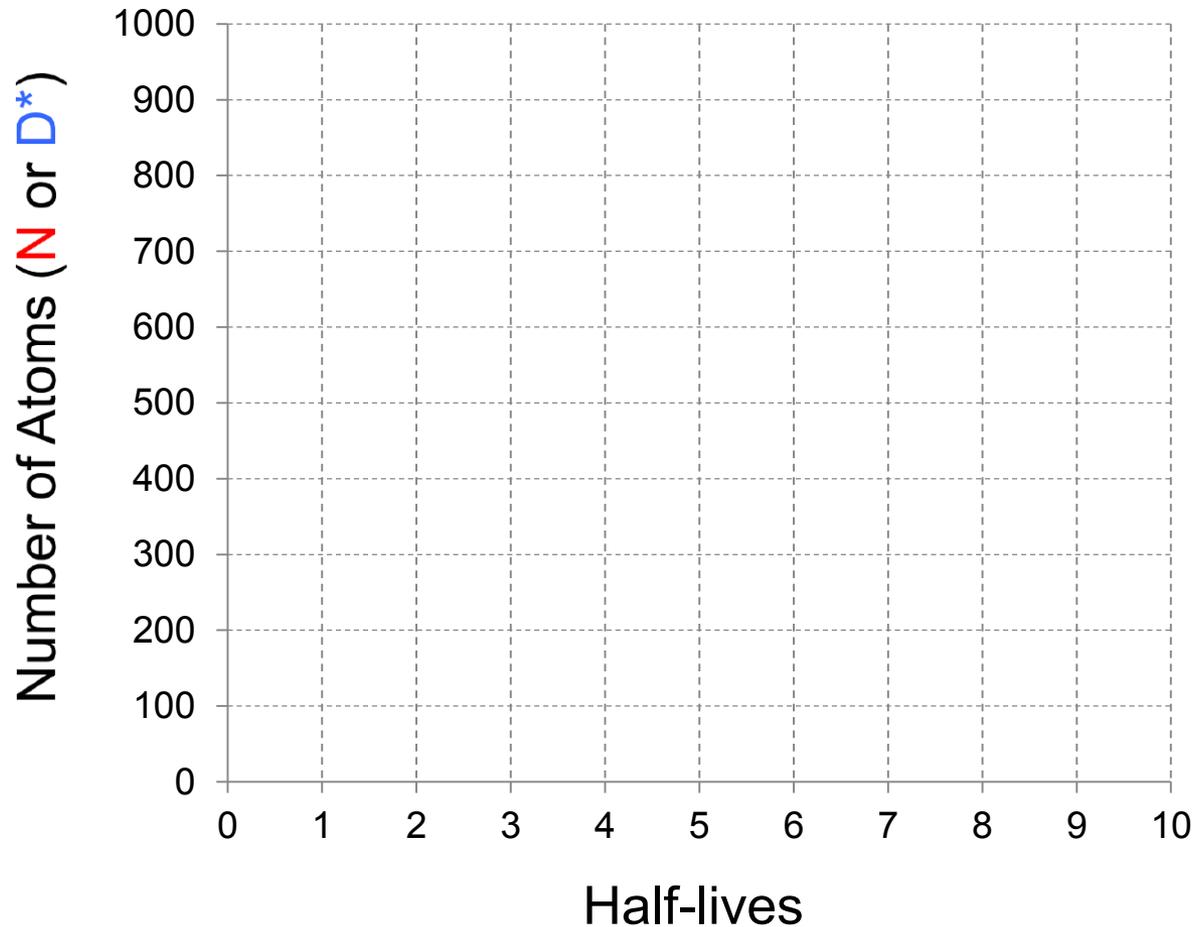
Simple Decay: Radioactive Parent ⇒ Stable Daughter
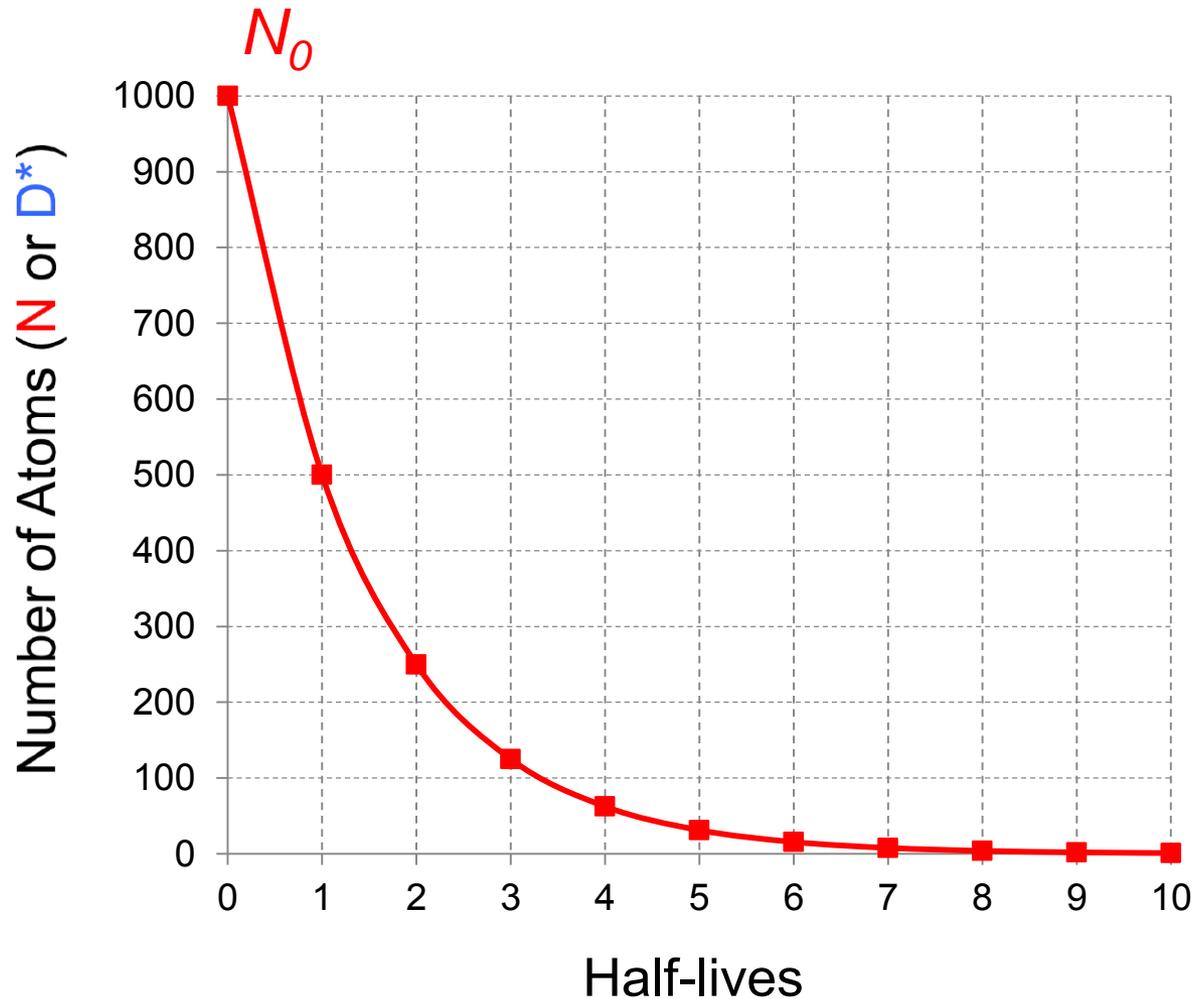
$$N = N_0 \, e^{-\lambda t}$$

decay of parent

Simple Decay: Radioactive Parent ⇒ Stable Daughter

ingrowth of daughter

$$D^* = N_0 \left(1 - e^{-\lambda t}\right)$$

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

decay of parent
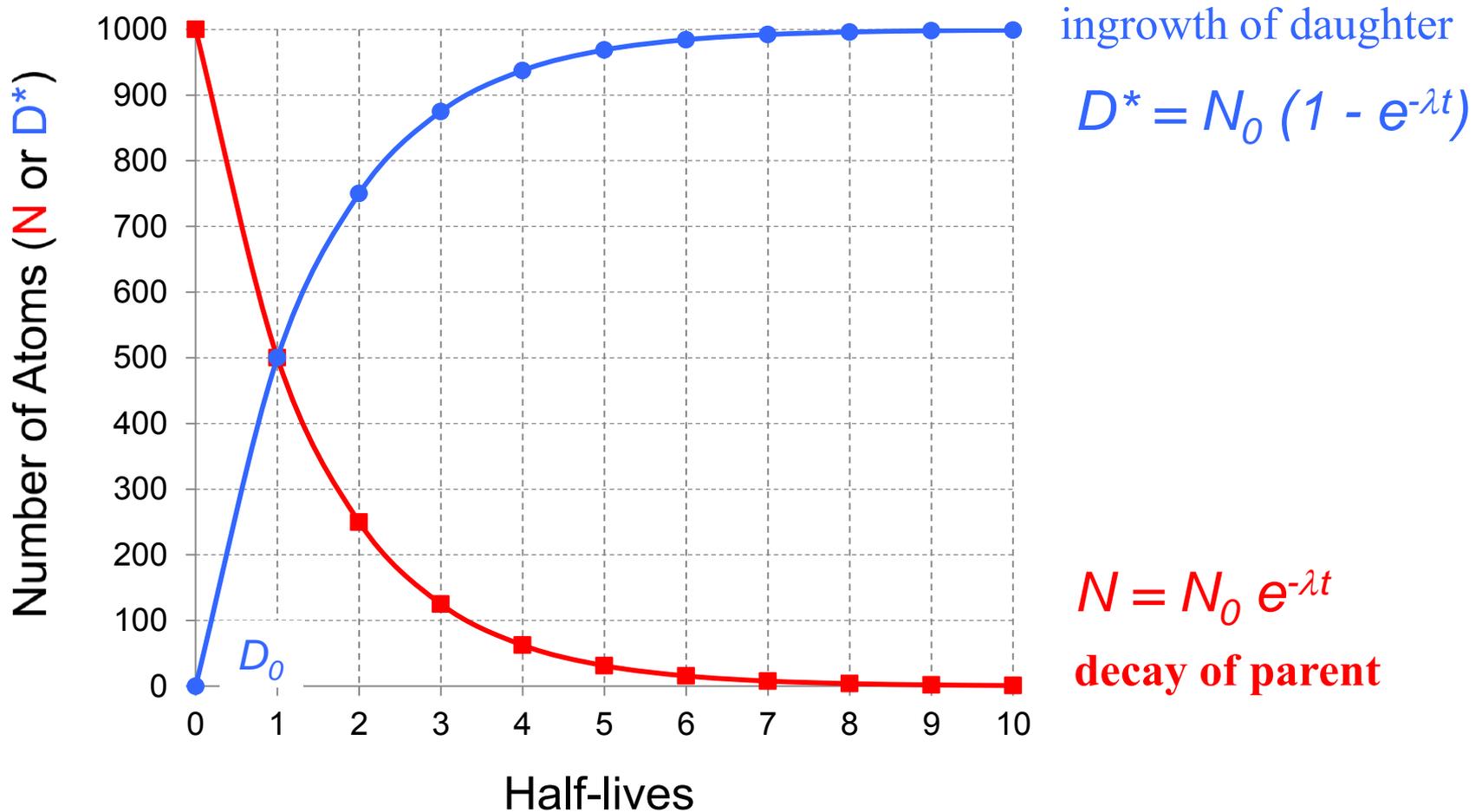
…continue…

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

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 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

$$e^{\lambda t} = 1 + \lambda t + (\lambda t)^2/2! + (\lambda t)^3/3! + \dots, \quad \text{simplifies to } e^{\lambda t} = 1 + \lambda t, \text{ for small } \lambda t$$

…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 (2nd edition)*.

The Isochron Method

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

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

Neutrons $\Rightarrow$

^{84}Sr		^{86}Sr	^{87}Sr	^{88}Sr
		^{85}Rb		^{87}Rb
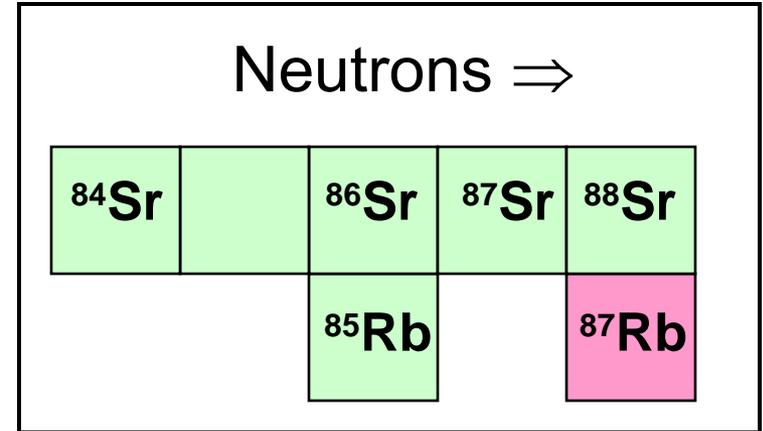
Conservation rules

Reaction:

Charge
Baryon #
Lepton #

The Isochron Method

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

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

Neutrons $\Rightarrow$

^{84}Sr		^{86}Sr	^{87}Sr	^{88}Sr
		^{85}Rb		^{87}Rb
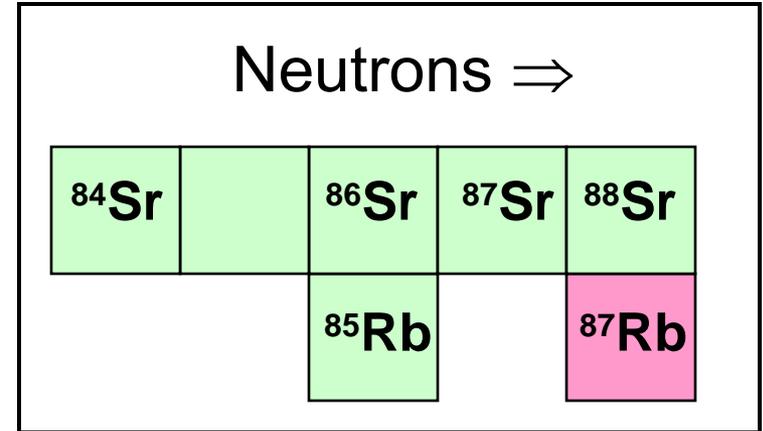
Conservation rules

Reaction:	n	$\longrightarrow$	p	+	e^-	+	$\overline{\nu}_e$
Charge	0		+1		-1		0
Baryon #	+1		+1		0		0
Lepton #	0		0		+1		-1

The Isochron Method

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

$$^{87}_{37}Rb \Rightarrow {}^{87}_{38}Sr + e^- + \overline{\nu_e} + E$$
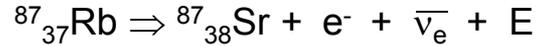
Substituting into the decay equation

$$^{87}Sr = {}^{87}Sr_0 + {}^{87}Rb\,(e^{\lambda t} - 1)$$

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

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

In a diagram with axes $x = {}^{87}Rb/^{86}Sr$ and $y = {}^{87}Sr/^{86}Sr$ this equation defines a line, $y = mx + b$
With the slope

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

and constant b, the **initial ratio**

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

Prerequisites:

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

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

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

Neutrons $\Rightarrow$

^{84}Sr	^{86}Sr	^{87}Sr	^{88}Sr
	^{85}Rb		^{87}Rb

http://www.nndc.bnl.gov/chart/
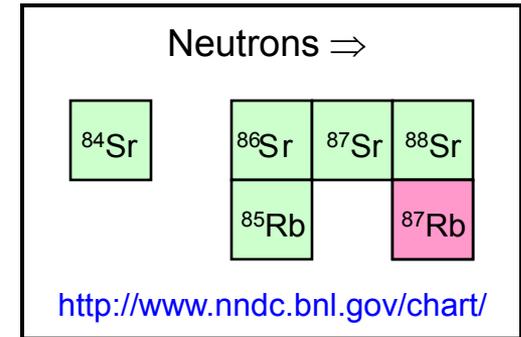
Courtesy Brookhaven National Lab.

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

$\dfrac{^{87}Sr}{^{86}Sr}$ slope -1

b

$^{87}Rb/^{86}Sr$

Peucker-Ehrenbrink, 2012
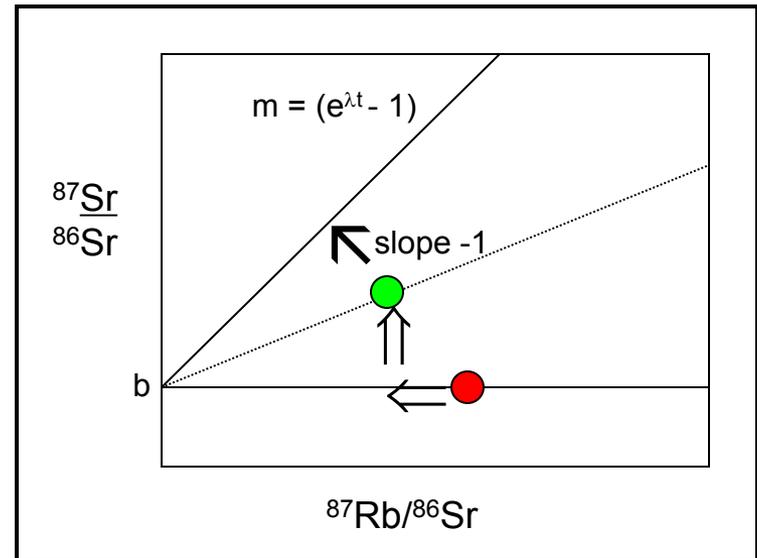
Mixing

The mass balance of any element is determined by input (usually from a number of sources) and removal (usually a number a 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

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

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.

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 (#, 6.022×10^{23} atoms per mole):

$$N = (C \ wt \ \# \ Ab) / AW \qquad \text{dimensional analysis: } (g/g \ g \ n/mole) / (g/mol) = n$$

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

$$(5) \qquad I1_{EM} = (C_{EA} \, Ab_{I1EA} \, N \, f \, / \, AW_{EA}) + [C_{EB} \, Ab_{I1EB} \, N \, (1 - f) \, / \, AW_{EB}]$$

with

$I1_{EM}$ = 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

$Ab_{I1E\,A}$ = atomic abundance of isotope 1 of element E in component A

$Ab_{I1E\,B}$ = 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

$$(6) \qquad \left(\frac{I1_E}{I2_E}\right)_M = \frac{C_{EA} \, Ab_{I1EA} \, f \, AW_{EB} + C_{EB} \, Ab_{I1EB} \, (1 - f) \, AW_{EA}}{C_{EA} \, Ab_{I2EA} \, f \, AW_{EB} + C_{EB} \, Ab_{I2EB} \, (1 - f) \, AW_{EA}}$$

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

(7)
$$\frac{I1_E}{I2_E}\bigg)_M = \frac{C_{EA}\, Ab_{I1E\,A}\, f + C_{EB}\, Ab_{I1EB}\, (1 - f)}{Ab_{I2E\,A}\, [C_{EA}\, f + C_{EB}\, (1 - f)]}$$

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

$$(I1_E / I2_E)_M = R_M$$
$$(Ab_{I1EA} / Ab_{I2EA})_A = R_A$$
$$(Ab_{I1EB} / Ab_{I2EB})_B = R_B,$$

Then

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

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

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

and can be further simplified to

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

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 $^{87}Sr/^{86}Sr$ versus $^{87}Rb/^{86}Sr$, 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.

Linearized mixing hyperbola
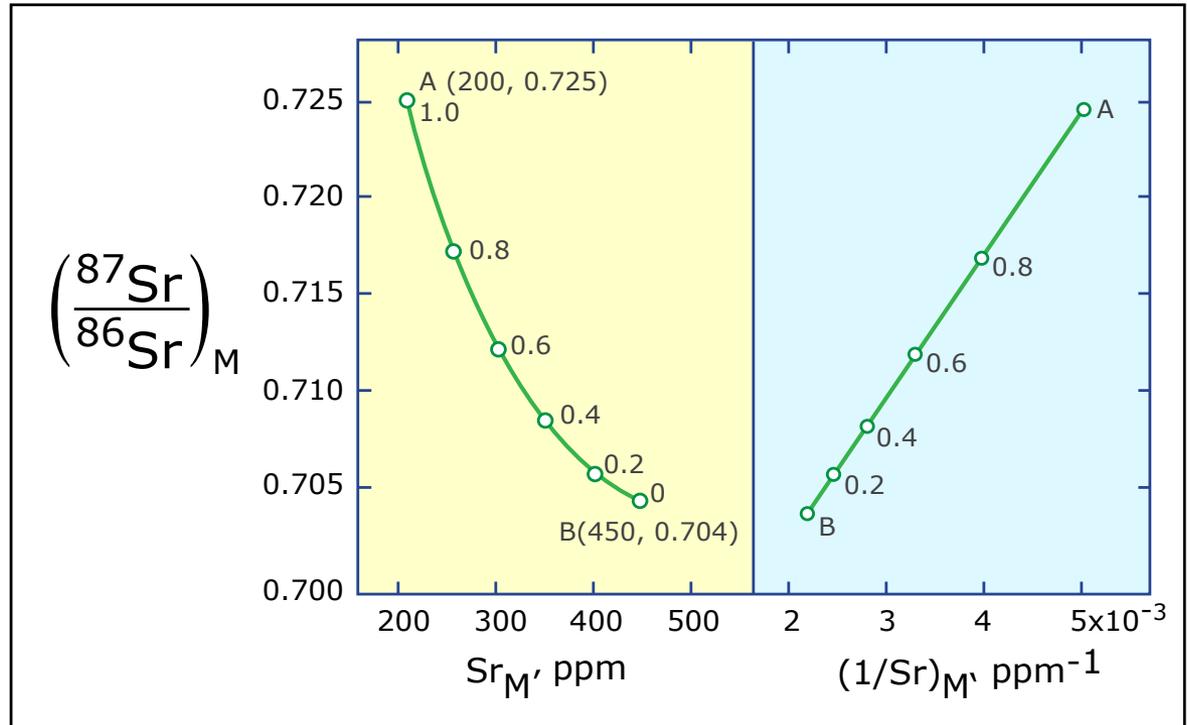
Image by MIT OpenCourseWare. After Figure 9.1 in Faure.

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

$$K = \frac{(Sr/Nd)_M}{(Sr/Nd)_C}$$

$\dfrac{^{143}Nd}{^{144}Nd}$

M

C

K = 0.1
K = 0.5
K = 1
K = 2
K = 10

0.01
0.05
0.1
0.5

X_C

$^{87}Sr/^{86}Sr$
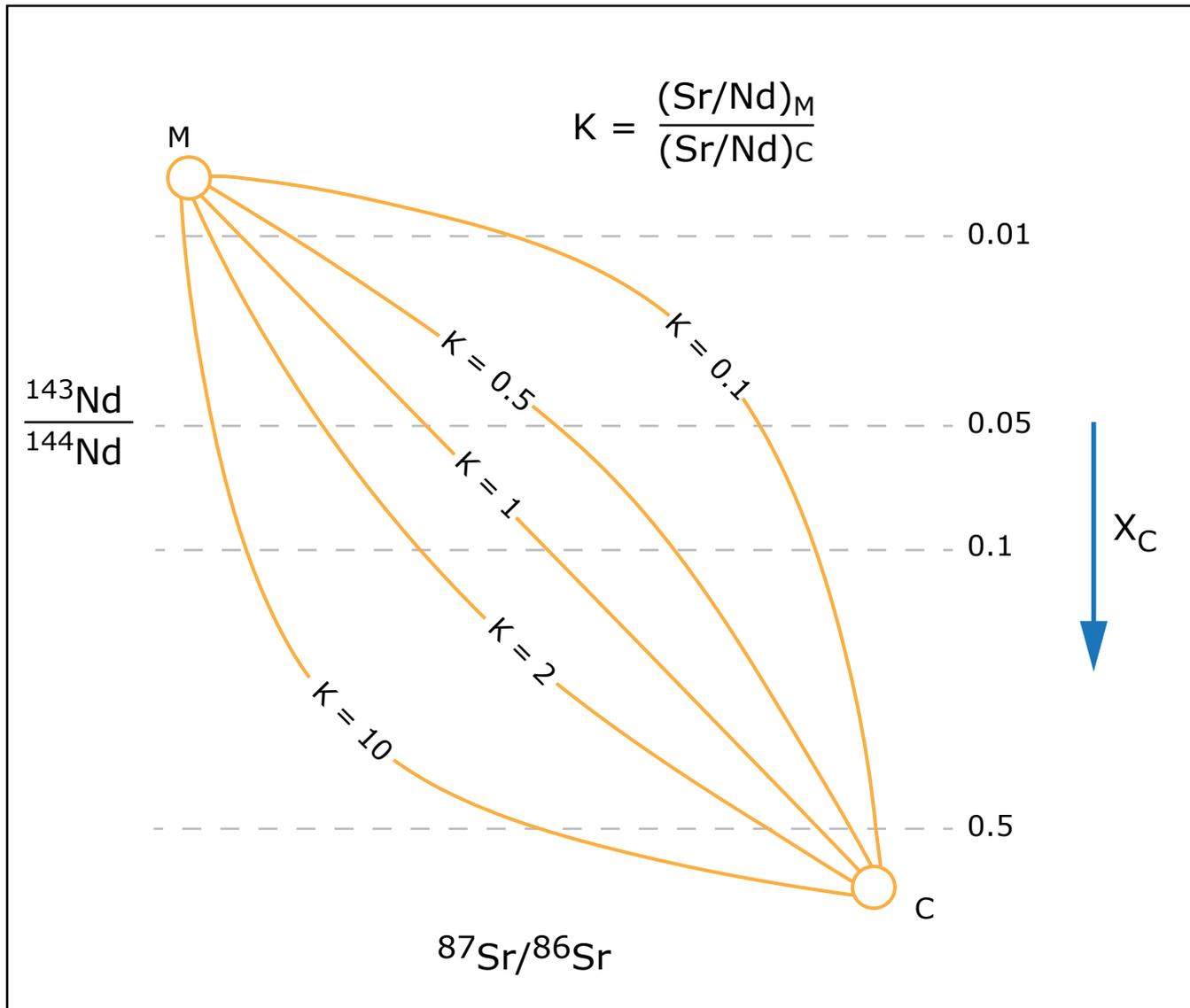
Image by MIT OpenCourseWare.

238-U Decay Series

Labile

238 U	4.468 Gy
234 U	24.55 ky
234 Pa	1.18 m
234 Th	24.1 d
230 Th	75.38 ky
226 Ra	1.6 ky

Gas

| 222 Rn | 3.825 d |
| 218 Rn |
| 218 At |
| 218 Po |
| 214 Po |
| 214 Bi | 19.9 m |
| 214 Pb |
| 210 Po |
| 210 Bi | 22.3 y |
| 210 Pb |
| 210 Tl |
| 206 Pb |
| 206 Tl |
| 206 Hg |

Peucker-Ehrenbrink, 2012

The Pb-Pb method of dating

$^{207}Pb/^{204}Pb$ (y-axis)

$^{206}Pb/^{204}Pb$ (x-axis)

Primordial Pb

The Pb-Pb method of dating

Growth curve

t=today

t=3.0 bya

t=3.5 bya

t=4.0 bya

t=4.5 bya

Primordial Pb

$^{207}Pb/^{204}Pb$

$^{206}Pb/^{204}Pb$
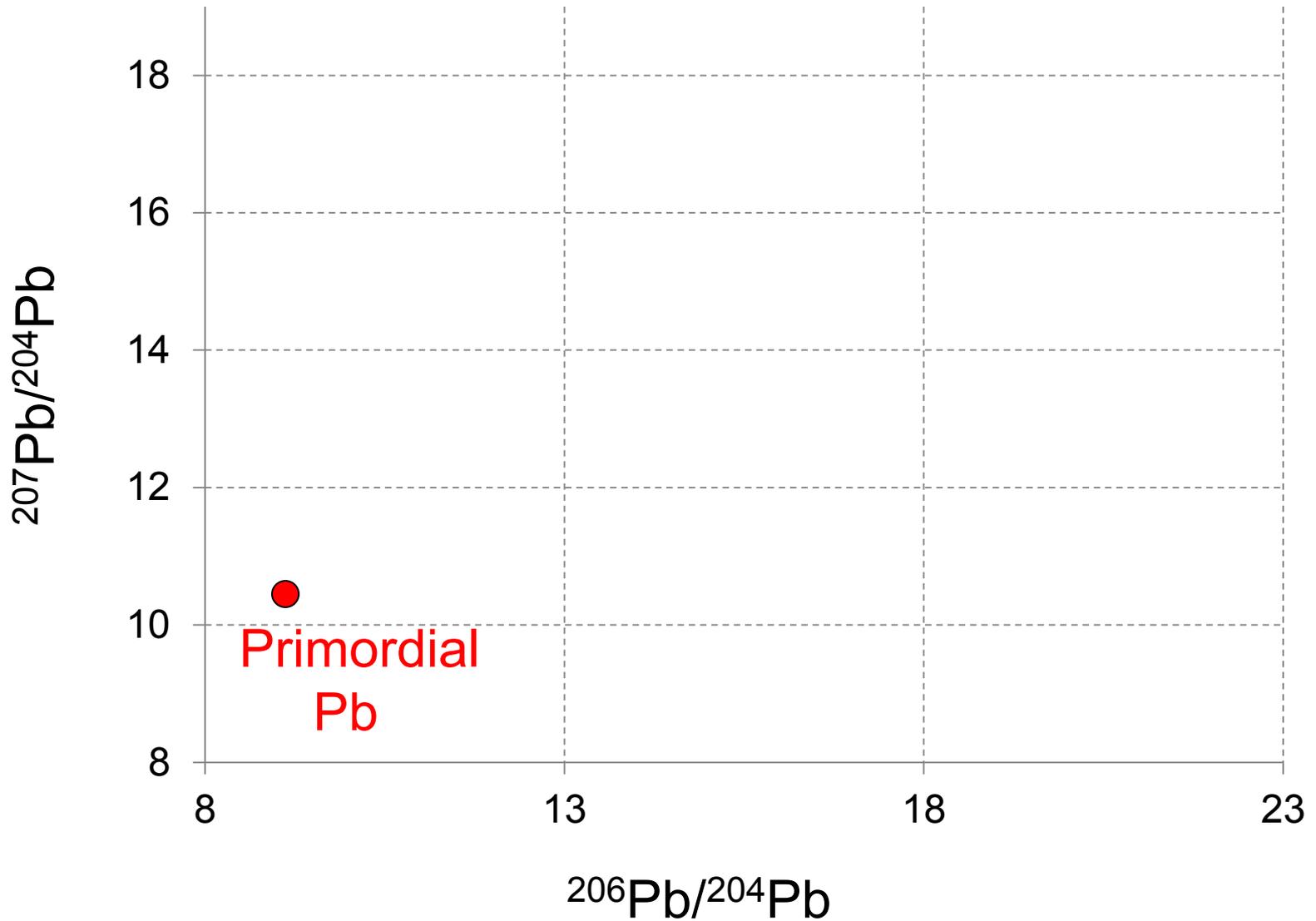
bya = billion years ago

The Pb-Pb method of dating

The Pb-Pb method of dating

Geochron,
the present-day
isochron

$^{207}Pb/^{204}Pb$

$^{206}Pb/^{204}Pb$
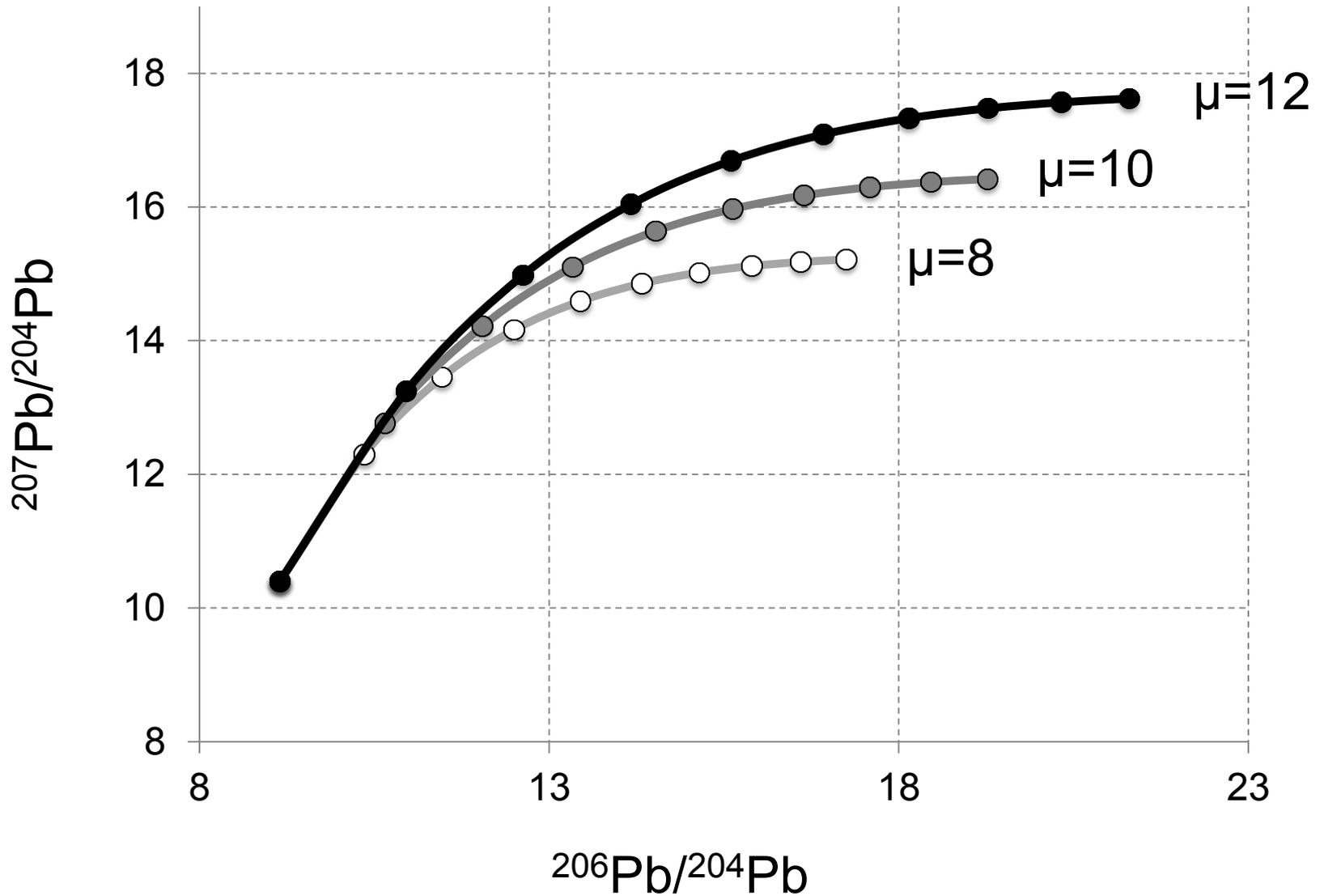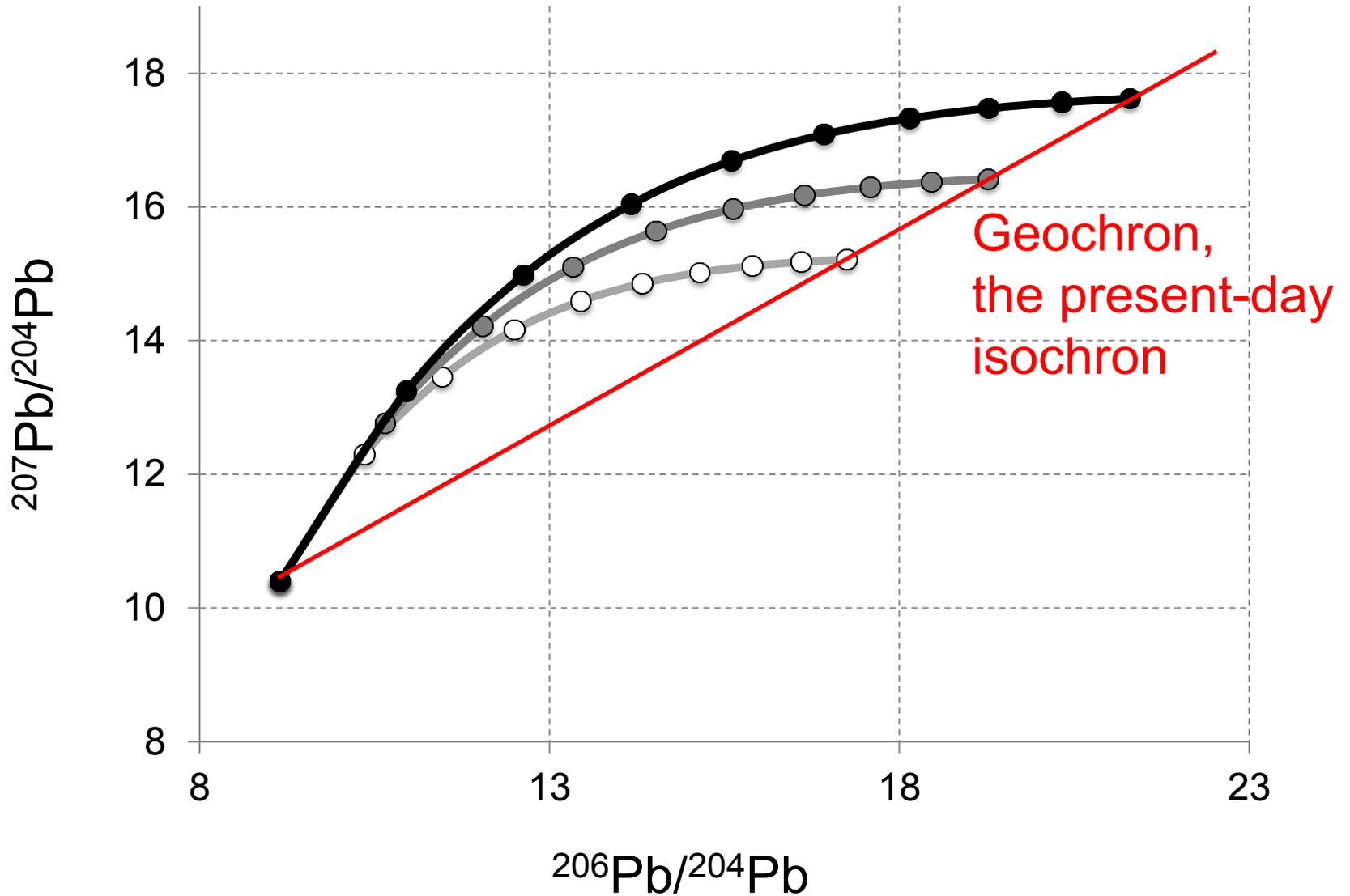
12.744 Marine Isotope Chemistry
Fall 2012