Introduction to Marine Radiochemistry

1. Isotopes and radioactive decay

2. Mathematical description of radioactive decay

3. Decay of a parent isotope to a stable daughter

    Example: radiocarbon dating

4. Decay series

    Math
    U, Th series in oceanography
    Examples : Th isotopes

Atoms and Chemical Elements

Atom: a nucleus surrounded by electrons:

Atomic radius ~ 10^{-8} cm

Nuclear radius ~ 10^{-12} cm

Nuclear density ~ 10^{14} g/cm^3 !

The nucleus consists primarily of

positively charged protons

electrically neutral neutrons

A chemical element is characterized by a specific number of protons in its nucleus; different isotopes of an element contain different numbers of neutrons

Notation

Z = atomic number (= number of protons in nucleus)

N = neutron number

A = Z + N = mass number

A

$$^{238}_{92}U$$

Z

(the "92" is redundant with "U" and is usually omitted)

Or, an element with several isotopes:

$$^{12}_{6}C, ^{13}_{6}C, ^{14}_{6}C$$

Holden, N. E., and F. W. Walker. *Chart of the Nuclides*. 11th ed. Schenectady, NY: General Electric Co., 1972.
Image removed due to copyright restrictions.

Chart of the nuclides: expanded view

Holden, N. E., and F. W. Walker. *Chart of the Nuclides*. 11th ed. Schenectady, NY: General Electric Co., 1972.
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The unstable nuclides -- "radionuclides"

If so many nuclides are unstable, why are they around?

1. Formed during initial nucleosynthesis, but decay very slowly: e.g., ^{238}U, ^{235}U, ^{232}Th

2. Formed by decay of slowly-decaying parent isotope

3. Formed by a naturally occurring process, e.g., comsogenic isotopes: ^{14}C

4. Anthropogenic: e.g. nuclear bomb testing and nuclear energy production, e.g., Pu isotopes, ^{3}H, ^{137}Cs,…

Example : β- Decay

$$Neutron \longrightarrow proton + electron$$

For example,

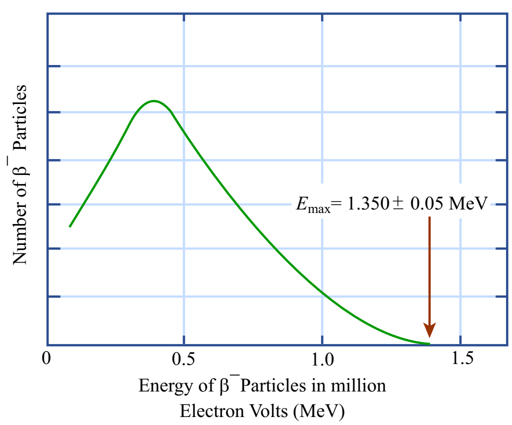
$${}^{40}_{19}K \longrightarrow {}^{40}_{20}Ca + \beta^{-} + \overline{\nu} + Energy$$

$$N_{daughter} = N_{parent} - 1$$
$$Z_{daughter} = Z_{parent} + 1$$
$$A_{daughter} = A_{parent}$$

- We can measure β- particles

The energy emitted is always the same for a given transition; the energy of the β particle varies up to a maximum. When $E_\beta < E_{max}$, a neutrino is emitted (υ)

Distribution of β energies:



Energy spectrum of beta particles emitted by $^{40}_{19}K$. Note that most of the beta particles are emitted with energies that are about one-third of the maximum or end point energy. During each beta decay, a neutrino is emitted with a kinetic energy equal to the difference between the maximum energy and the kinetic energy of the associated beta particle.

Figure by MIT OCW.

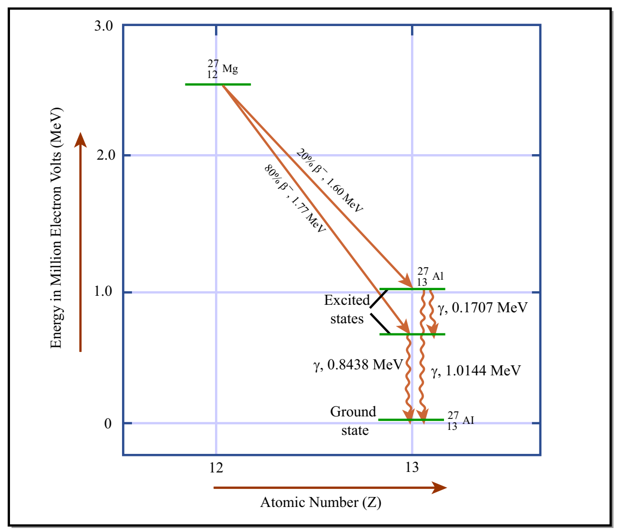


Figure by MIT OCW.

Example : α-decay

Decay by emission of a ^{4}He nucleus…

$$ {}^{228}_{90}Th \longrightarrow {}^{224}_{88}Ra + \alpha + Energy $$

$$ Energy \quad \frac{1}{2} M_{\alpha} v_{\alpha}^{2} \left(1 + \frac{M_{\alpha}}{M_{p}} \right) $$

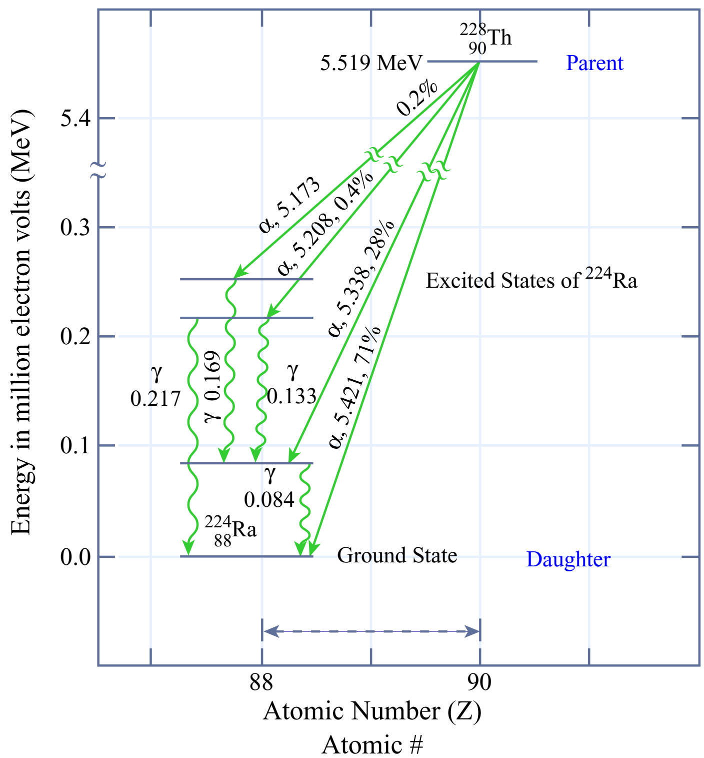
Kinetic energy of α-particle

“recoil” energy

$$ N_{daughter} \quad N_{parent} - 2 $$

$$ Z_{daughter} \quad Z_{parent} - 2 $$

$$ A_{daughter} \quad A_{parent} - 4 $$



Decay scheme diagram for the alpha decay diagram for the alpha decay of $^{228}_{90}Th$ to $^{224}_{88}Ra$. In this case, four different alpha particles are emitted with four complementary gamma rays.

Figure by MIT OCW.

MATHEMATICAL DESCRIPTION OF RADIOACTIVE DECAY

- The decay rate of a radionuclide is proportional to the number of atoms of the radionuclide present
- The proportionality constant is the decay constant, a property of the particular radionuclide — for practical purposes, independent of T, P, ...

So:

The rate law is

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

decay constant

Often measured: decay rate

∴ Commonly used unit is the activity $= \lambda N$

e.g. in "dpm" = disintegrations per minute

ACTIVITY AND CONCENTRATION

Example 1:

Say: Conc. of $^{230}Th = 1 \times 10^{-12}$ moles/ℓ

Then:

$$\lambda_{^{230}Th} = 1.75 \times 10^{-11} \text{ min}^{-1}$$

$$A = 1 \times 10^{-12} \frac{\text{mol}}{\ell} \times 6.023 \times 10^{23} \frac{\text{atoms}}{\text{mol}} \times 1.75 \times 10^{-11} \text{ min}^{-1}$$

$$= \underline{10.56} \text{ dpm}$$

Example 2:

Suppose: A sediment has 2 $\frac{\text{dpm}}{\text{gram}}$ of both ^{238}U and ^{234}Th

$$\lambda_{^{238}U} = 2.92 \times 10^{-16} \text{ min}^{-1}$$

$$\lambda_{^{234}Th} = 2.0 \times 10^{-5} \text{ min}^{-1}$$

$\Rightarrow$ Concentrations :

$$^{238}U: \quad 2 \frac{\text{dpm}}{\text{gram}} \times \frac{1}{2.92 \times 10^{-16} \text{ min}^{-1}} = 6.8 \times 10^{15} \frac{\text{atoms}}{\text{gram}}$$

$$^{234}Th: \quad 2 \frac{\text{dpm}}{\text{gram}} \times \frac{1}{2.0 \times 10^{-5} \text{ min}^{-1}} = 1 \times 10^{5} \frac{\text{atoms}}{\text{gram}}$$

Commonly Used Definitions

Using the rate law,

$$\left.\begin{aligned} \frac{dN}{dt} &= -\lambda N \\ \text{with} \quad N(t=0) &= N_0 \end{aligned}\right\}$$

$$\Rightarrow \boxed{N = N_0 e^{-\lambda t}}$$ = Amount of radionuclide present vs. time

① **Half Life** ($t_{1/2}$)

- The time it takes for 50% of the atoms present to decay

$$0.5 N_0 = N_0 e^{-\lambda t_{1/2}}$$

$$\rightarrow \ln(0.5) = -\lambda t_{1/2}$$

OR

$$t_{1/2} = \frac{\ln 2}{\lambda} \approx \frac{0.693}{\lambda}$$

Example:

$$^{238}U: \; t_{1/2} = \frac{\ln 2}{2.92 \times 10^{-16}\ \text{min}^{-1}} = 4.51 \times 10^{9} \text{ years}$$

$$^{234}Th: \; t_{1/2} = \frac{\ln 2}{2 \times 10^{-5}\ \text{min}^{-1}} = 24.1 \text{ days}$$

② MEAN LIFE (τ)

- The average lifetime of an atom ...

$$\tau = -\frac{1}{N_0}\int_0^{N_0} t\, dN \qquad (1)$$

From the rate law,

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

and

$N = N_0$ at $t = 0$

$N = 0$ at $t = \infty$

$\Rightarrow$ (1) can be transformed to

$$\tau = -\frac{1}{N_0}\int_\infty^0 -t\lambda N\, dt$$

$$= -\frac{1}{N_0}\int_0^\infty \lambda t N_0 e^{-\lambda t}\, dt$$

$$= -\lambda\int_0^\infty t e^{-\lambda t} dt$$

Solution:

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

- The amount present decays to $\frac{1}{e}\cdot N_0$ during time τ
- $\tau = t_{1/2} \times \frac{1}{\ln 2} \approx 1.443 \times t_{1/2}$

~~TWO~~ ONE METHOD~~S~~ OF OBTAINING AGES FROM RADIONUCLIDE MEASUREMENTS

① Measure the quantity of the nuclide present in the sample ...

IF :
- Know the amount incorporated when the sample was formed
- know there have been no additions or removals (other than by decay) since formation

THEN:

USE : $N(t) = N_0 e^{-\lambda t}$

Log. of both sides ⟹

$$\boxed{\text{Age} = t = \frac{1}{\lambda} \ln \frac{N_0}{N}}$$

Example: <u>^{14}C DATING</u>

- Variations in atmosphere/ocean ^{14}C
- $t_{1/2}(^{14}C) \sim 5730$ yrs

  Age limit ~ 30,000 yrs.

Radiocarbon Dating Conventions

The age equation:

$$Age = \frac{1}{\lambda_{14C}} \ln \left[\frac{A_o}{A}\right]$$

① Results reported as

"fraction modern" $= \dfrac{A}{A_o}$

"Modern" is <u>defined</u> to be

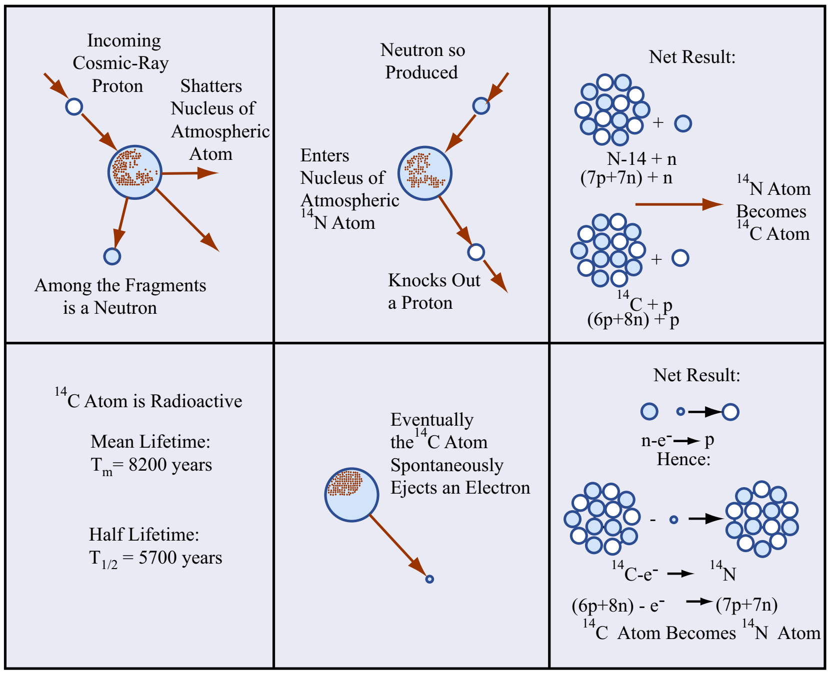
95% of the activity in 1950 of an oxalic acid standard, after making a specified correction for C isotope fractionation

② "Radiocarbon Age"

$$= 8033 * \ln \left[\frac{A_o}{A}\right]$$

for historic reasons, an <u>old</u> value of λ – incorrect! – is used.

(3) $$\Delta^{14}C \quad 1000 * \left(\overset{=}{e}^{(date-1950)} * f_m - 1 \right)$$



The "life cycle" of a carbon-14 atom. Created in the atmosphere by the collision of a neutron (produced by primary cosmic-ray protons) with a nitrogen atom, the average ^{14}C atom "lives" for 8200 years. Its life is terminated by the ejection of an electron with returns the atom to its original form, ^{14}N.

- ^{14}C is formed in the atmosphere.
- Rate of formation depends on cosmic ray flux
- 1/2 life = 5730 years

Figure by MIT OCW.

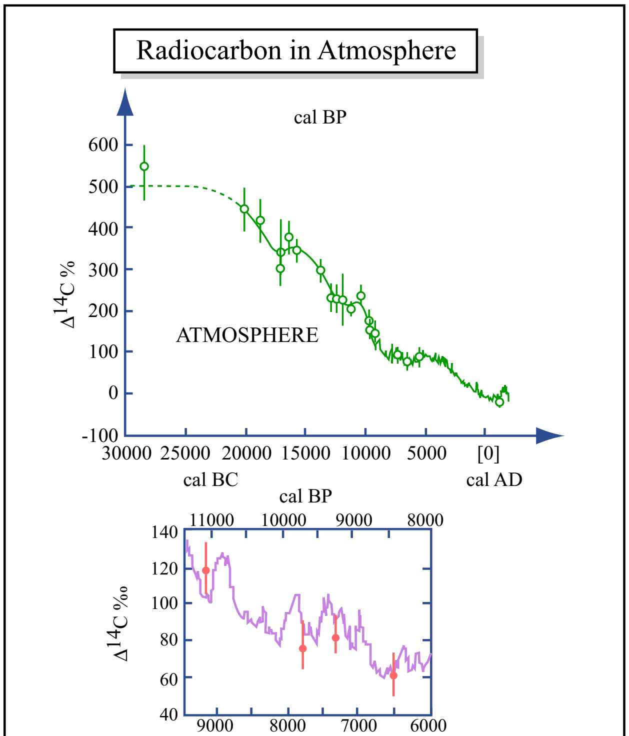
Since

(1) The true A_0 is unlikely to be the same as the defined A_0

(2) The slightly incorrect λ is used

(3) There may be "reservoir corrections"

Calibration curves must be used to convert conventional, "radiocarbon date" to a true, calendar date.



The atmosphere $\Delta^{14}C$ record as derived from: dendrochronologically calibrated bidecadal tree-ring ^{14}C measurements (▬ from 9440 BC to AD 1950), a cubic spline through the $^{234}U/^{230}Th$-calibrated coral ^{14}C averages corrected by 400 ^{14}C yr (— from 20,000 to 9440 BC), and a smooth transition from an assigned pre-25,000 BC steady-state value of 500‰ (- - -). The coral measurements (Bard et al. 1993) are shown as circles with 2 σ error bars. For the detailed coral/tree-ring comparison in the inset, the coral ages (1 σ error bars) were converted to cal ages using the marine calibration curve (Fig. 17) with ΔR = 0.

Figure by MIT OCW.

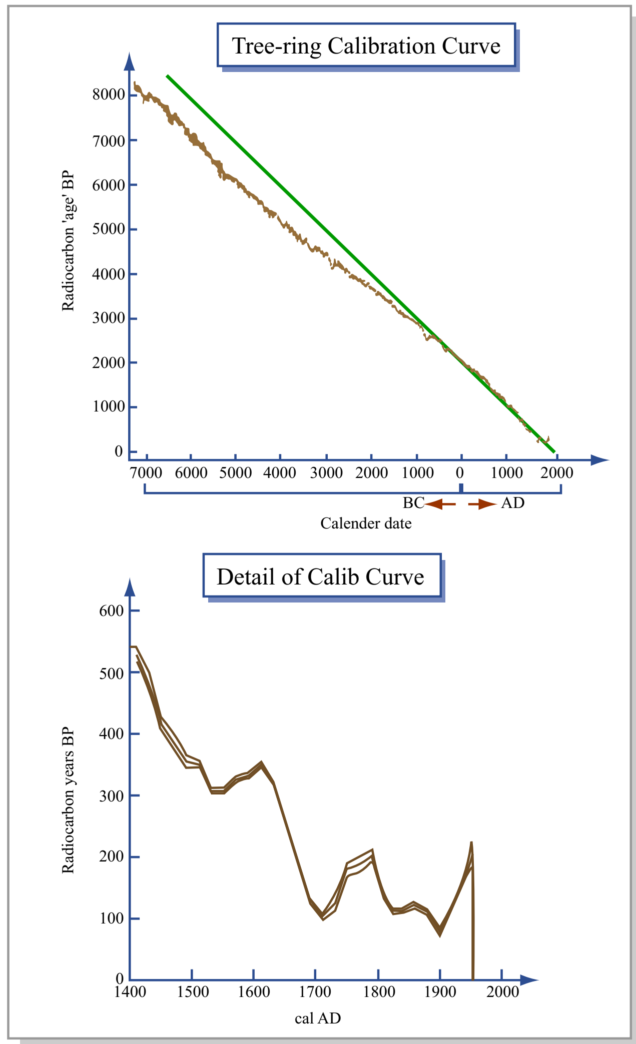
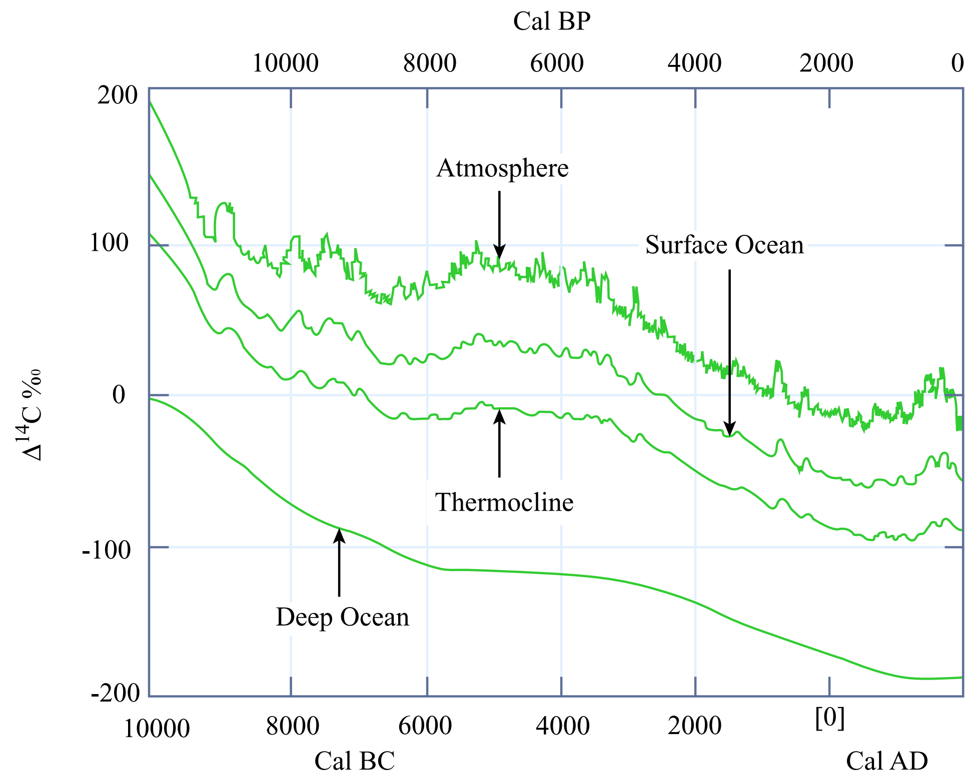


Figure by MIT OCW.

Reservoir Effects

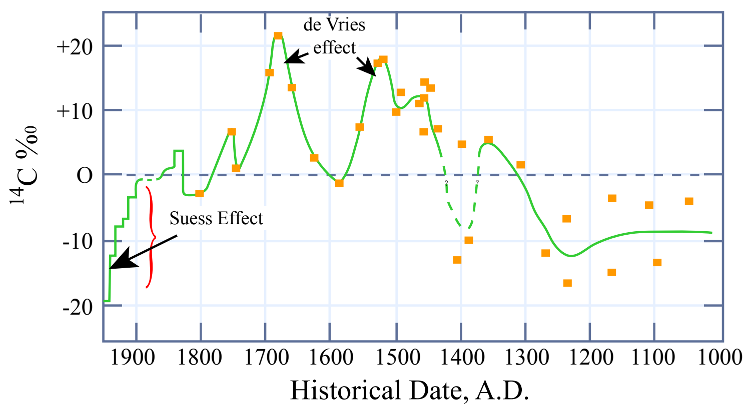


Atmospheric $\Delta^{14}C$ (bidecadal values) as used for the model calculations and calculated surface ocean (0-75 m), thermocline (75-1000 m), and deep ocean (1000-3800 m) $\Delta^{14}C$ values. These estimates are from a model of the ocean / atmosphere carbon cycle.

Figure by MIT OCW.

Anthropogenic Perturbations of Atmospheric ^{14}C content

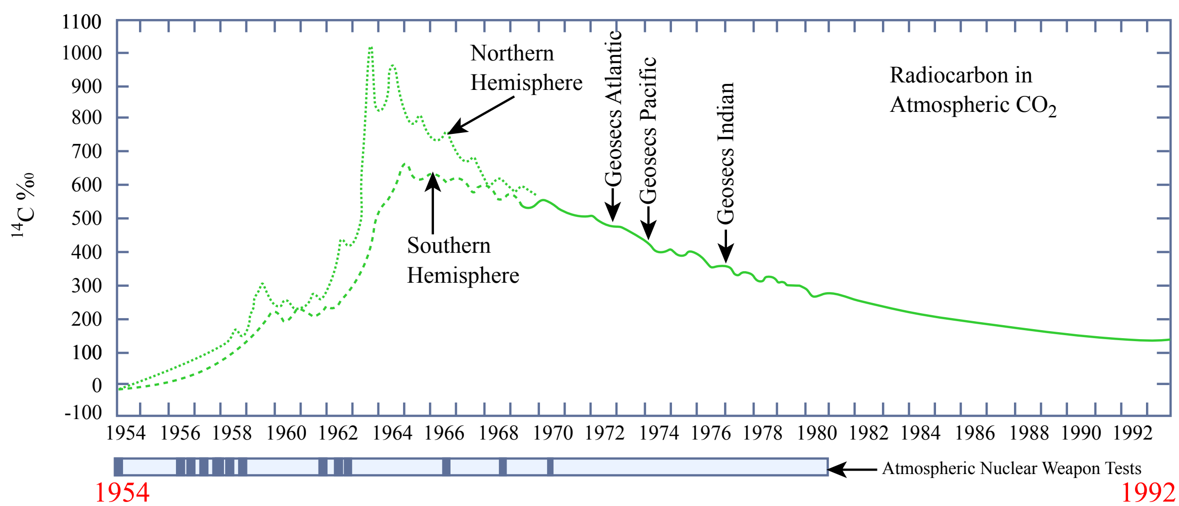
1. The Suess Effect



Deviation of the initial radiocarbon activity in per mil of wood samples of known age relative to 95 percent of the activity of the oxalic acid standard of the National Bureau of Standards. The observed activities were corrected for carbon isotope fractionation and recalculated using a value of 5730 years for the half-life of ^{14}C. The decline in the radiocarbon content starting at about 1900 results from the introduction of fossil CO_2 into the atmosphere by the combustion of fossil fuels (Suess effect). The anomalously high radiocarbon activity around 1710 and 1500 A.D. is known as the "de Vries effect." Its causes are not understood.

Figure by MIT OCW.

2. Bomb Testing

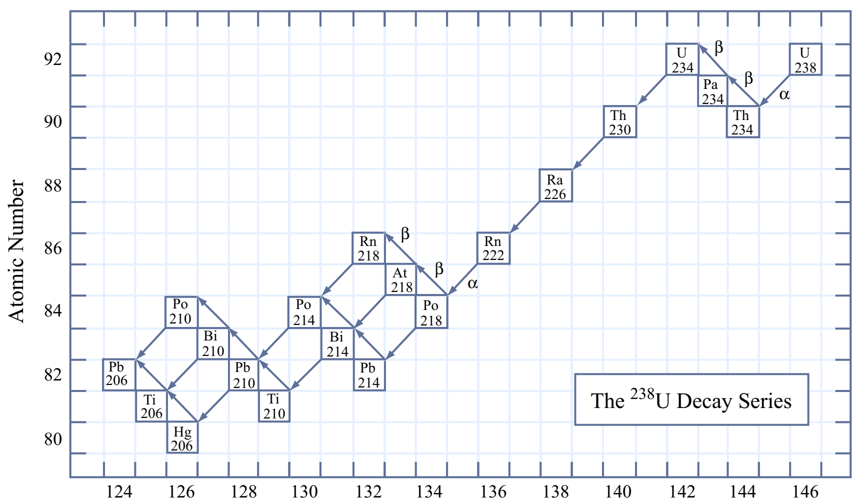


Observed time history for the $^{14}C/C$ ratio in ground level air. Before 1970, a clear difference can be seen between the northern and southern hemispheres, and also a clear seasonality appears in both records. These features are related to injections of bomb ^{14}C from stratosphere to troposhpere (mainly in the northern hemisphere). Times and magnitudes of the atmospheric weapons tests are shown. Although the test ban treaty was implemented at the begining of 1963, several small Chinese and French atmospheric tests were conducted after this time.

Figure by MIT OCW.

Abundances, Half-Lives, and Decay Constants of the Principle Naturally Occurring Isotopes of Uranium and Thorium				
Isotope	Abundance %	Half-Life y	Decay Constant y^{-1}	Reference
^{238}U	99.2739	4.510×10^{9} 4.468×10^{9}	1.537×10^{-10} 1.55125×10^{-10}	1 2
^{235}U	0.7204	0.7129×10^{9} 0.7038×10^{9}	9.722×10^{-10} 9.8485×10^{-10}	3 2
^{234}U	0.0057	2.48×10^{9}	2.806×10^{-6}	4
^{232}Th	100	13.890×10^{9} 14.008×10^{9}	4.990×10^{-11} 4.948×10^{-11}	5 6

1. Kovarik and Adams (1955)
2. Jaffey et al. (1971)
3. Fleming et al. (1952)
4. Strominger et al. (1958)
5. Picciotto and Wilgain (1956)
6. LeRoux and Glendenin (1963)



The Decay of ^{238}U to Stable ^{238}Pb

Figure by MIT OCW.

DESCRIBING DECAY IN A DECAY SERIES

$$N_1 \xrightarrow{\lambda_1} N_2 \xrightarrow{\lambda_2} N_3 \longrightarrow \dots \text{ stable end product}$$

Parent, N_1

1) $\left.\begin{array}{l} \dfrac{dN_1}{dt} = -\lambda_1 N_1 \\ N_1(t=0) = N_1^\circ \end{array}\right\} \quad N_1 = N_1^\circ e^{-\lambda_1 t}$

Daughter, N_2

2) $\left.\begin{array}{l} \dfrac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \\ \qquad = \lambda_1 N_1^\circ e^{-\lambda_1 t} - \lambda_2 N_2 \\ N_2(t=0) = N_2^\circ \end{array}\right\}$

$$\Rightarrow \boxed{N_2 = N_2^\circ e^{-\lambda_2 t} + \frac{\lambda_1 N_1^\circ}{\lambda_2 - \lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)}$$

What if: Longer-lived parent decays to shorter-lived daughter, i.e., $\lambda_2 \gg \lambda_1$?

THEN: a) $e^{-\lambda_2 t} \ll e^{-\lambda_1 t}$

b) $\lambda_1 \ll \lambda_2$

$$\Rightarrow \boxed{N_2 = N_2^\circ e^{-\lambda_2 t} + \frac{\lambda_1 N_1^\circ}{\lambda_2} e^{-\lambda_1 t}}$$

DECAY IN A DECAY SERIES : $\lambda_2 \gg \lambda_1$

$$\boxed{N_2 = N_2^0 e^{-\lambda_2 t} + \frac{\lambda_1 N_1^0}{\lambda_2} e^{-\lambda_1 t}}$$

$N_2^0 = 0$

After several N_2 half-lives, i.e., $t \gg \frac{1}{\lambda_2}$ ...

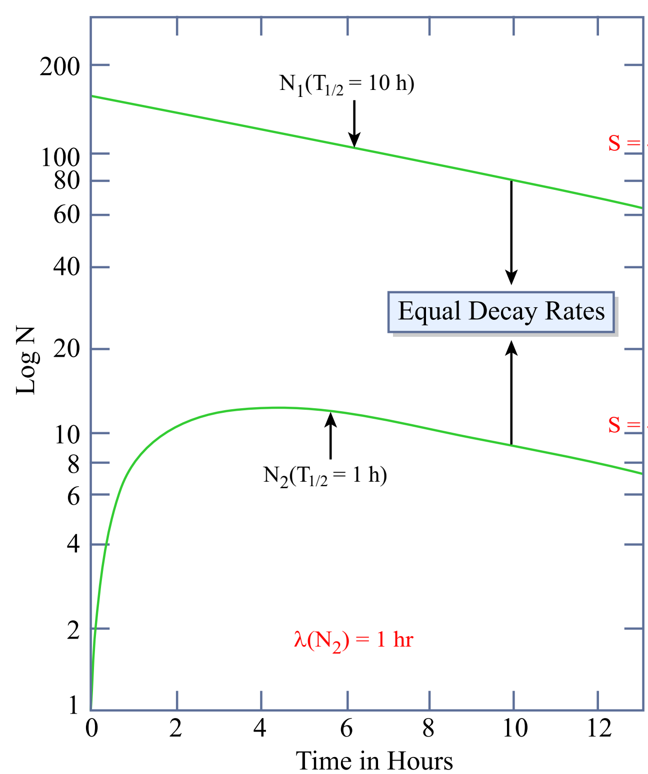
- 1^{st} term $\rightarrow 0$
- $\lambda_1 N_1^0 e^{-\lambda_1 t} = A_1 = \lambda_1 N_1$

$\Rightarrow$

$$\boxed{\lambda_2 N_2 = \lambda_1 N_1}$$

EQUAL DECAY RATES
"
EQUAL ACTIVITIES
"
"SECULAR EQUILIBRIUM"

- Reached after a few ½-lives of the shorter-lived daughter. IN A CLOSED SYSTEM



Decay of a long-lived parent (N_1) to a short-lived daughter (N_2). The half-life of the parent is 10 hours, while that of the daughter is 1 hour. The number of daughter atoms increases as a function of time from an initial value of zero. Eventually in this system the ratio of parent to daughter assumes a constant value equal to $\lambda_2 - \lambda_1/\lambda_1$, and a radiochemical equilibrium is thereby established. Note that the ordinate is in units of log N which is related to 1n N by 1n N = 2.303 log N.

Figure by MIT OCW.

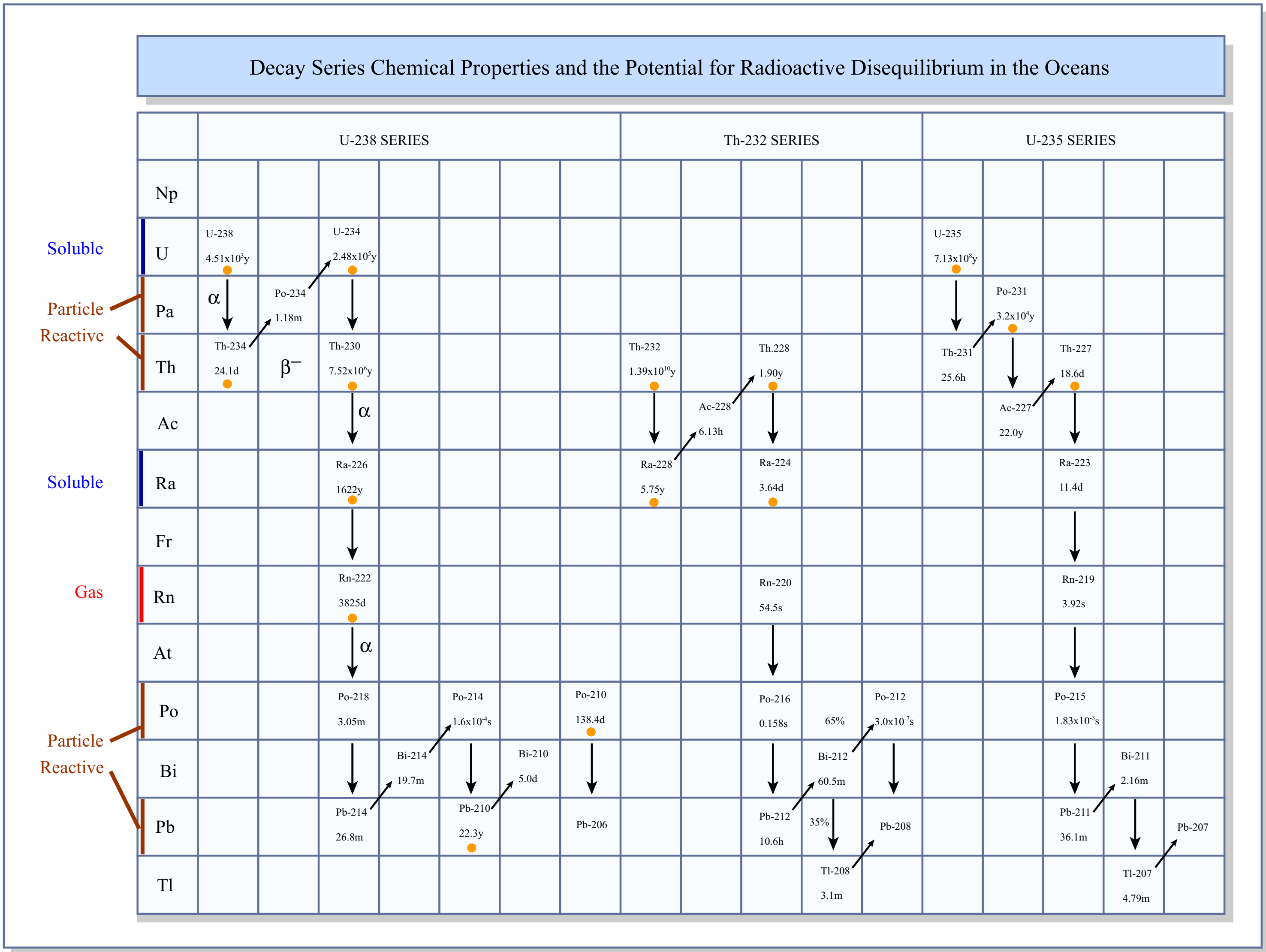
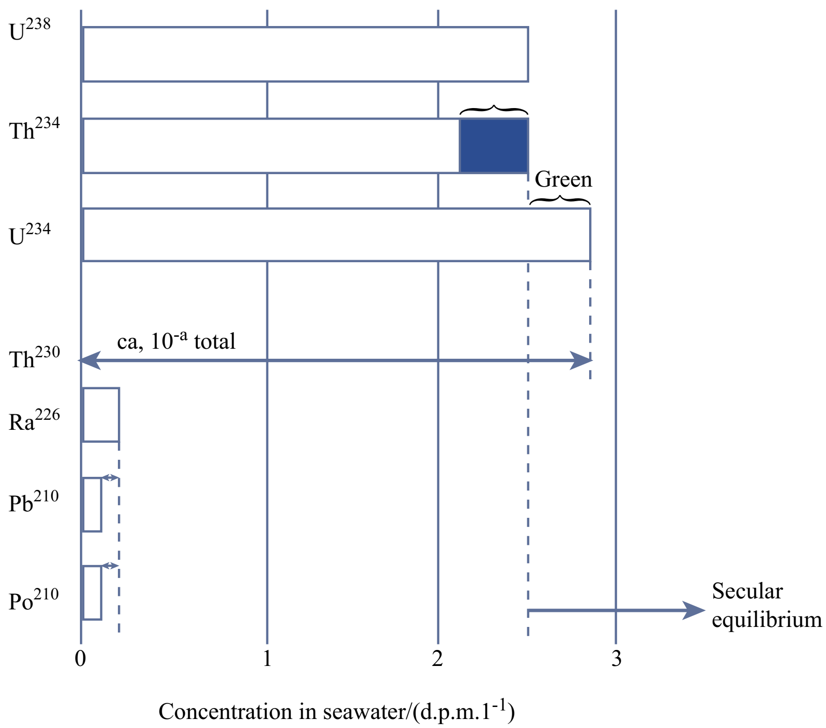


Figure by MIT OCW.

The U^{238} Series in Seawater



Concentrations of the longer-lived members of the U^{238} decay series in seawater arranged in descending order within the series. The values chosen are representative of deep ocean water. Somewhat different relationships are found in the surface waters. Shaded areas represent the suspended particulate fraction. Deficiencies of Th^{230} and Pb^{210} relative to their parent nuclides result from scavenging. A Th^{234} deficiency is not found because of the short half-life, but a significant uptake by the suspended particles is evident.

Figure by MIT OCW.

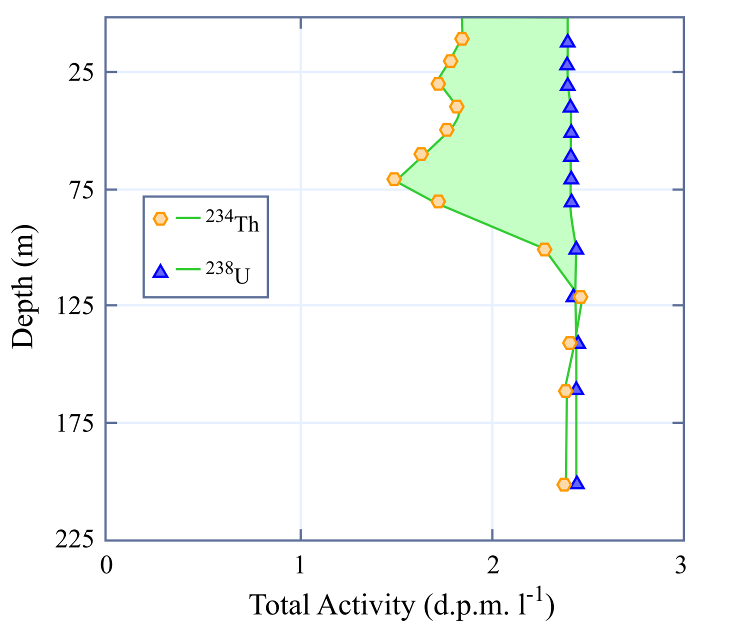
USES OF ^{238}U SERIES DISEQUILIBRIUM IN THE OCEANS (a few examples)

Disequilibrium between	in →	use
$^{234}Th/^{238}U$	water column	scavenging rates
$^{230}Th/^{234}U$		
$^{210}Pb/^{226}Ra$		
$^{222}Rn/^{226}Ra$	surface ocean	gas exchange
	sediments	solute transport
$^{230}Th/^{234}U$	sediments	sed accumulation + mixing rates
$^{234}Th/^{238}U$		
$^{210}Pb/^{226}Ra$		

(... and more ...)

$\underline{\text{EXAMPLE}}$: $\boxed{\text{Removal of particle-reactive elements from the surface ocean.}}$

$$\underset{\text{"conservative"}}{{}^{238}U} \xrightarrow{\lambda_{238}} {}^{234}Th \underset{t_{1/2} = 24.1 \text{ days}}{\xrightarrow{\lambda_{234}}} {}^{234}U$$



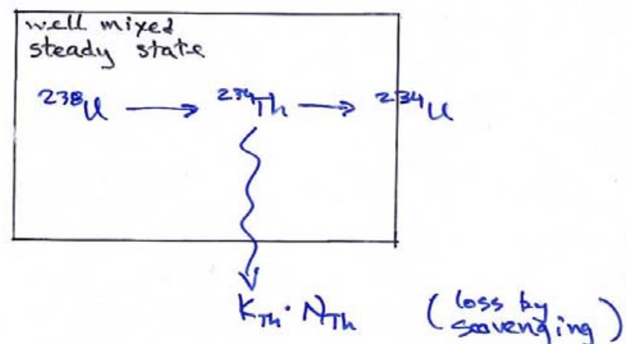
Typical profile of ^{234}Th in the upper open ocean. Shaded area represents disequilibrium between total ^{234}Th and ^{238}U. Data taken from VERTEX 3 (ref. 11.)

Figure by MIT OCW.

$A_{234} < A_{238}$: removal on time scale of ~ a few ½ lives of ^{234}Th

$A_{234} \cong A_{238}$ slower removal (or no removal)

Box model for surface ocean ^{234}Th



Mass balance for ^{234}Th

[Production by decay of ^{238}U] = [Loss by decay of ^{234}Th] + [Loss by scavenging]

(1) $\lambda_{238} N_{238} = \lambda_{234} N_{234} + k_{234} N_{234}$

Define: $\frac{1}{k_{TH}} = \tau_{scav} =$ "residence time of ^{234}Th with respect to scavenging"

(1) → (2) $A_{238} = A_{234} + \frac{1}{\tau_{scav}} N_{234}$

→ (3) $\lambda_{234} A_{238} = \lambda_{234} A_{234} + \frac{1}{\tau_{scav}} A_{234}$

⋮ (rearrange)

$$\Longrightarrow \tau_{scav} = \left[\frac{1}{\lambda_{234}}\right] \left(\frac{A_{234}/A_{238}}{1 - A_{234}/A_{238}} \right)$$

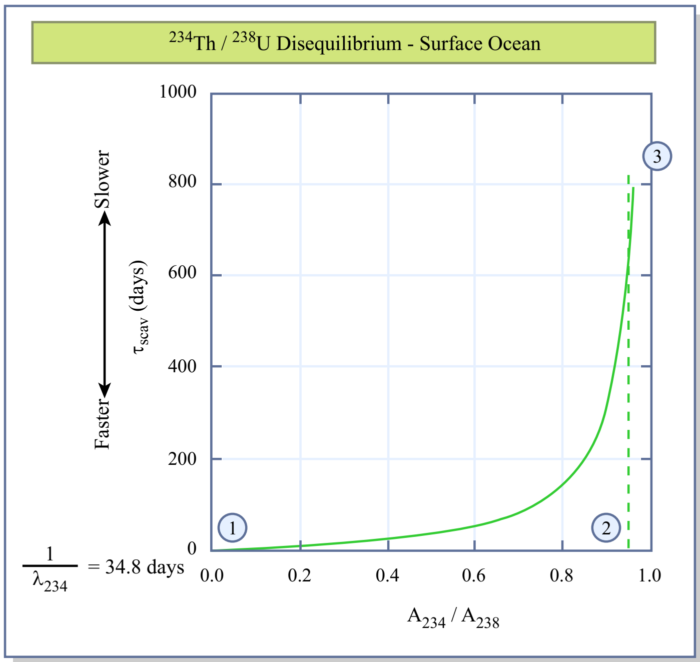


Figure by MIT OCW.

Plot for the scavenging model:

$$\boxed{\tau_{scav} = \frac{1}{\lambda_{234}} \left[\frac{A_{234}/A_{238}}{1 - A_{234}/A_{238}} \right]}$$

1. $A_{234}/A_{238} \longrightarrow 0$: the greater the ^{234}Th deficit, the faster the scavenging
2. if can measure ratio to ~ 5%, slowest scavenging you can measure is τ scav ~ 600 days
3. $A_{234}/A_{238} \longrightarrow 1$: the smaller the deficit, the slower the scavenging

How to quantify scavenging in the deep ocean, where $A_{234Th} = A_{238U}$?

Use:

$$^{234}U \longrightarrow {}^{230}Th \longrightarrow {}^{226}Ra$$

^{234}U : conservative, $t_{1/2}$ = 245,000 yr

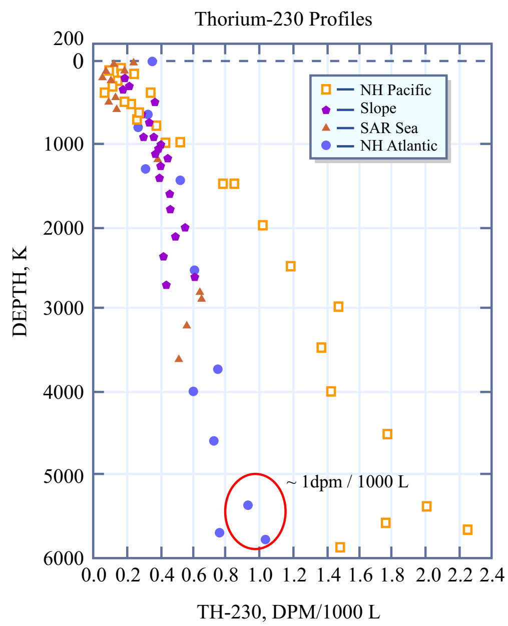
^{230}Th : particle reactive, $t_{1/2}$ = 75,200 yr

Apply the same model :

$$\tau_{scav} = \frac{1}{\lambda_{230}} \left[\frac{A_{230}/A_{234}}{1 - A_{230}/A_{234}} \right]$$

$$\frac{1}{\lambda_{230}} = 108 \text{ ky}$$

^{230}Th in the Deep Ocean



Thorium-230 distributions measured in ocean-water profiles by alpha-counting.

Figure by MIT OCW.

Note: $A_{234_U} \sim 1.14 \times A_{238_U} \doteq 2.7$ dpm/l

$$\tau_{scav} = 108{,}000 \left[\frac{.001/2.7}{1 - .001/2.7} \right]$$

$$= 40 \text{ years}$$

The ^{230}Th is nearly all removed from the water column ...
it must fall with particles to the sediments.

A particle reaching the sediment surface contains:

^{234}U in mineral lattice
$\downarrow$
^{230}Th in equilibrium with this ^{234}U

+

^{230}Th adsorbed to particle in water column

<u>supported</u> ^{230}Th, constant over time

<u>Excess</u> ^{230}Th, which decays over time

SUPPOSE:

① Sediment accumulates at a constant rate, S

Then: depth in sediments is related to time:

$$Z = t \cdot S \Rightarrow t = Z/S$$

② Sedimenting particles carry a constant flux of ^{230}Th

- We know:

  Excess ^{230}Th decays by

  $$A(t) = A(t=0)\, e^{-\lambda t}$$

- Convert from <u>time</u> to <u>depth</u> in <u>seds.</u>

  $A(t) \longrightarrow A(z)$

  $A(t=0) \longrightarrow A(z=0)$ [constant flux $\Rightarrow$ constant A_0]

  $\lambda t \longrightarrow \lambda z/s$

- So:

  In a steadily accumulating sediment with constant s (and no mixing of sediments)

  $$A(z) = A(z=0)\, e^{-\lambda z/s}$$

  $A(z) \rightarrow$ <u>Excess</u> ^{230}Th

IDEALIZED ^{230}Th PROFILE IN SEDIMENT

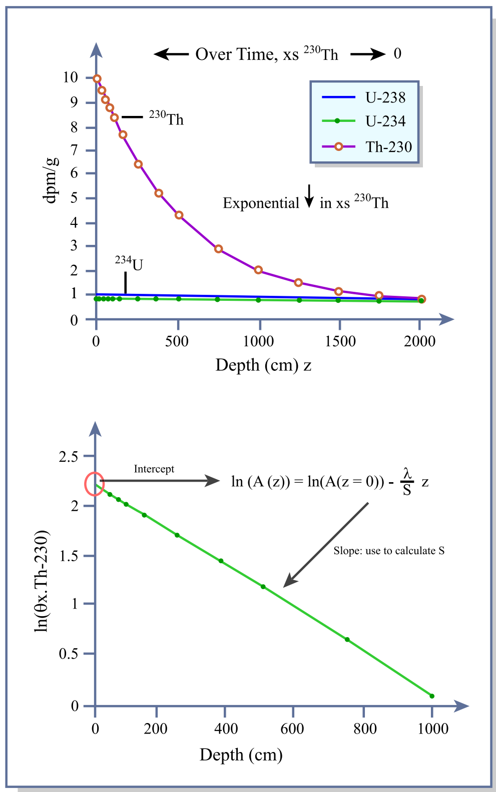
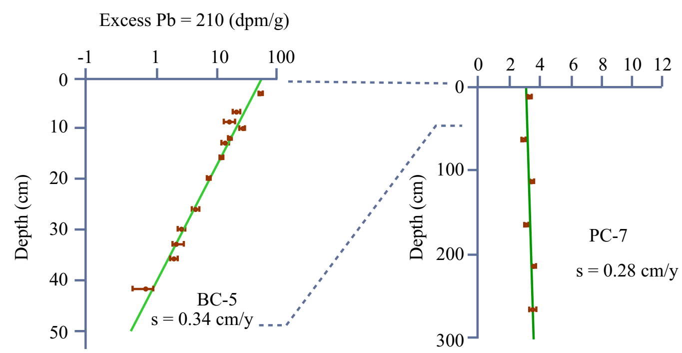


Figure by MIT OCW.

A real example: rapidly accumulating sediments near Antarctica

(DeMaster et al. 1991, Mar. Chem. 35, 489-502)



Depth profiles of excess ^{210}Pb and ^{14}C age (organic carbon fraction) for a box core and a piston core collected from the eastern Bransfield strait. The agreement in accumulation rates indicates that bioturbation has a negligible effect on the distribution of these naturally occurring radionuclides in the seabed.

Figure by MIT OCW.

Note:

Different time scales of measurement:

- Excess ^{210}Pb $(= A_{^{210}Pb} - A_{^{226}Ra})$

  $t_{1/2} \cong 22$ yrs

- ^{14}C $t_{1/2} \approx 5730$ yrs