Radioisotope Tracers

- Background info
  - Radioactive decay - concepts and equations
  - Radiometric dating
  - Secular equilibrium
- Case studies
  - ^{3}H and $^{3}H/^{3}He$
    - Transient Tracer
  - ^{14}C
    - Water Mass Tracer
  - $^{238}U \rightarrow {}^{234}Th$
    - Mixed-layer export via sinking particles

Radioisotopes and decay

Definitions

Parent – Original Radioactive Atom

Daughter – The Product of Decay

Decay Chain – A Series of Decays

Common modes of radioactive decay

Type	Emitted Particle	Δprotons	Δneutrons	Δatomic mass	Parent → daughter movement on periodic table	Example:
Alpha α	He^{2+}	-2	-2	-4	2 positions to the left	$^{238}U \rightarrow {}^{234}Th$
Beta β-	e^-	+1	-1	0	1 position to the right	$^{14}C \rightarrow {}^{14}N$
β+ & e^- capture (rare)	e^+	-1	+1	0	1 position to the left	$^{23}Mg \rightarrow {}^{23}Na$
K-capture (rare)	None	-1	+1	0	1 position to the left	$^{40}K \rightarrow {}^{40}Ar$

Decay is a property of the nucleus, and independent of chemistry, temperature, and pressure.

Radioactive Decay

Equation describing decay of a parent isotope to a daughter

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

where:

N = the number of atoms of the radioactive substance present

λ = the first order decay constant (t^{-1})

Integration from t=0 to later time t gives:

$$\ln\left(\frac{N}{N_0}\right) = -\lambda t \qquad \text{or} \qquad N = N_0 e^{-\lambda t}$$

where:

N_0 = number of atoms initially present

N = number of atoms present at time t

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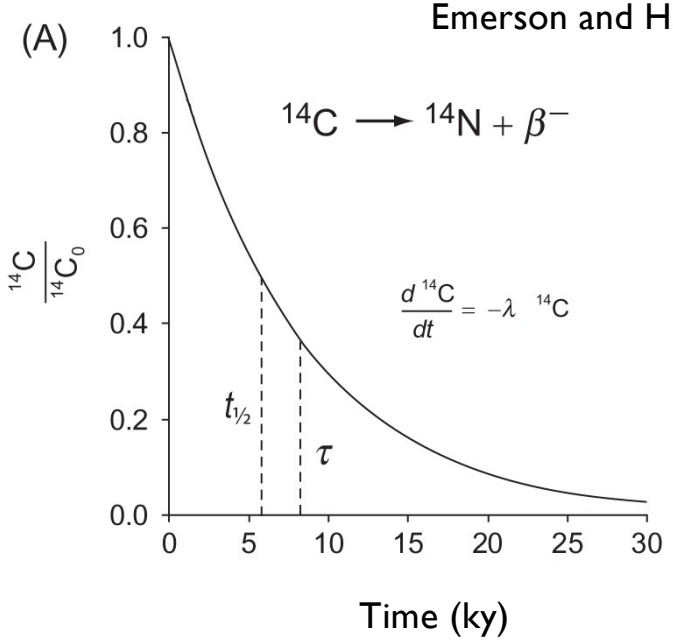
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where:

N_0 = number of atoms initially present

N = number of atoms present at time t

Emerson and Hamme, 7.1



Radioactive Decay

Activity (*A*) = decays per time (dpm or dps) –

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

λ = decay constant (t^{-1})
N = # of atoms (atoms) or concentration (atoms L^{-1})

Decay is proportional to the # of atoms present (first order)

Units:

Becquerel (Bq) = 1 dps (disintegrations per second)
Curie (Ci) = 3.7×10^{10} Bq = Activity of 1 gram of ^{226}Ra

- Activity is easier to measure than total number of atoms that have decayed

Radioactive Decay

Activity (*A*) = decays per time (dpm or dps) –

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

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N = # of atoms (atoms) or concentration (atoms L^{-1})

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

we can multiply both sides by the decay constant to get:

$$A = A_0 e^{-\lambda t}$$

- Activity is easier to measure than total number of atoms that have decayed

Half Life

The half life is defined as the time required for half of the atoms initially present to decay.

After one half life: $\frac{N}{N_0} = \frac{1}{2}$

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

$$-\ln\left(\frac{1}{2}\right) = \lambda t_{1/2} \qquad \text{or} \qquad 0.693 = \lambda t_{1/2}$$

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

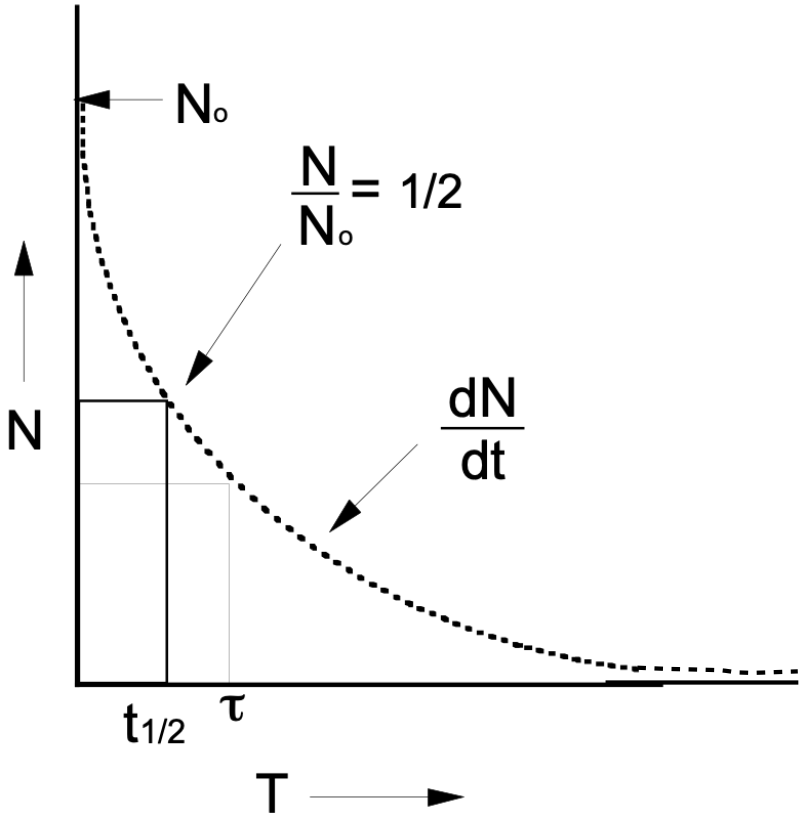
Mean Life, τ

i.e., Average Life of an Atom prior to decay

Mathematically, it is the integral of all lives of the atoms in a particular nuclide divided by the initial N (i.e., N_0):

$$\tau = \frac{1}{N_0}\int_0^\infty t\,dN = \frac{1}{N_0}\int_0^\infty t\lambda N dt = \lambda\int_0^\infty te^{-\lambda t}dt = \left[\frac{\lambda t+1}{\lambda}e^{-\lambda t}\right]_0^\infty = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693}$$

Decay curve



Mean Life (i.e., Average Life of an Atom):

$$\tau = \frac{1}{\lambda} = 1.44 \cdot t_{1/2}$$

Q. Why is the mean life longer than the half life?

Both N and A decrease exponentially

Radiometric Dating

If there are no other sources and sinks of N,

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

If the daughter product of the radioactive decay is stable, the amount of daughter product (N_D) produced by decay is:

$$N_D = N_{P0} - N_P$$

Since $N_P = N_{P0} e^{-\lambda t}$, $\quad N_D = N_{P0}(1-e^{-\lambda t})$

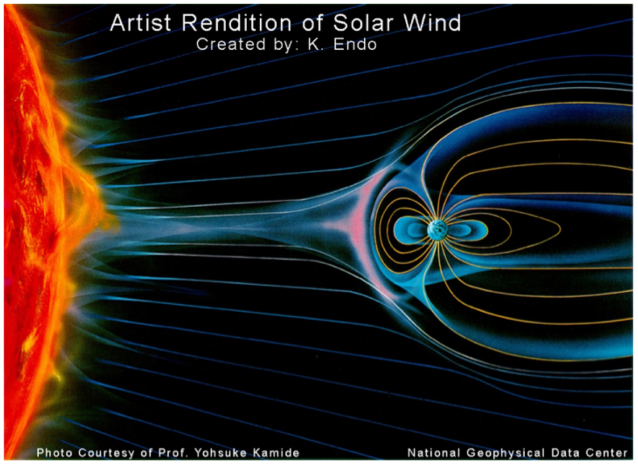
This all assumes that the daughter product is stable.

^{14}C - A quick primer

- ^{14}C formed primarily in the stratosphere via neutron capture by ^{14}N:

$$^{14}_{7}N + n \rightarrow ^{14}_{6}C + ^{1}H$$

- Production of ^{14}C is influenced by:
  - Flux of cosmic rays (decadal-centennial scale)
  - Geomagnetic shielding (centennial-millennial scale)
- Rapidly oxidized to $^{14}CO_2$



Useful Equations $\delta^{14}C$, $\Delta^{14}C$

Definitions:

$$\delta^{14}C = \left(\frac{{}^{14}C/C_{Sample}}{{}^{14}C/C_{Standard}} - 1 \right) \times 1000$$

$$\Delta^{14}C = \delta^{14}C - 2(\delta^{13}C + 25)\left(1 + \frac{\delta^{14}C}{1000}\right)$$

where:

$$\delta^{13}C = \left(\frac{{}^{13}C/{}^{12}C_{Sample}}{{}^{13}C/{}^{12}C_{Standard}} - 1 \right) \times 1000$$

Characteristics:

$^{14}C/C$ (for $\Delta^{14}C = 0$)

$= 1.18 \times 10^{-12}$

$t_{1/2} = 5730$ y

$\tau = 8270$ y

$\lambda = 1/8270$ y^{-1}

A "conventional ^{14}C age" is defined as:

$t = -8033 \ln(pMC)$, where $pMC = (A_{SN}(1950)/A_{ON}(1950))$

- pMC = Percent Modern Carbon
- 8033 years is the mean ^{14}C lifetime based on the half-life of 5568 years
- A_{SN} and A_{ON} are the fractionation-corrected specific ^{14}C activities of the sample and standard, respectively, measured in AD 1950

pMC of 1.0 is equivalent to:

- 1.176×10^{-12} $^{14}C/C$-atoms (at -25‰ $\delta^{13}C$)
- 13.56 dpm/g-C
- 226.0 µBq/mg-C

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Notes:

- pMC mixes linearly, while ^{14}C age will not!
- t =0 in 1950
- pMC uses the "Libby" decay constant of 1/8033 yr^{-1}, which is different than "Cambridge" decay constant given earlier (1/8270 yr^{-1})

Conventional ^{14}C age vs. Calendar Age

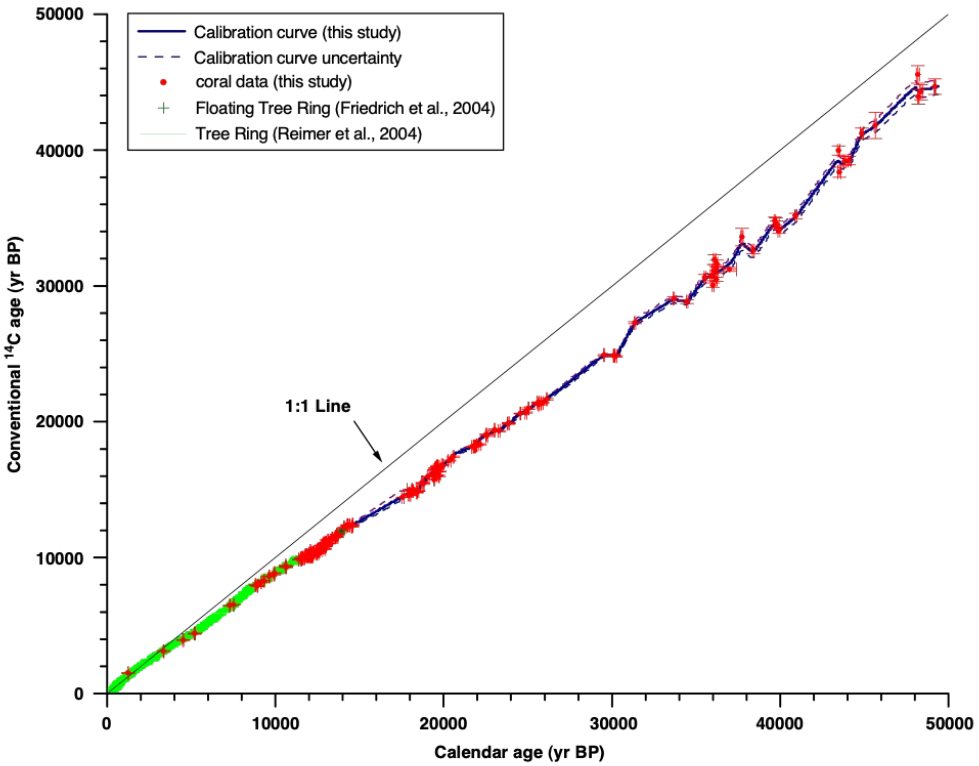


Fig. 3. Our coral calibration curve plotted with 1% confidence limits (corresponds to 3σ uncertainties for normal distributions) and coral data plotted with 1σ error bars. Calibration curve is compared to the tree ring chronologies (Reimer et al., 2004; Friedrich et al., 2004).

Fairbanks et al., 2005

Conventional ^{14}C age vs. Calendar Age

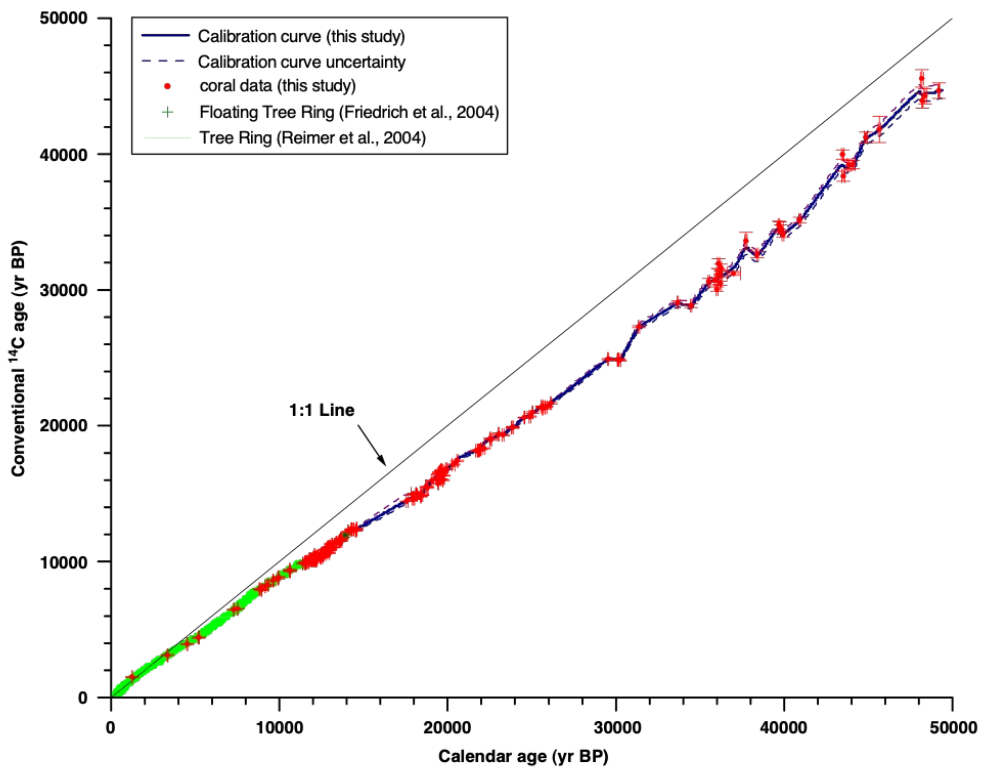


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Reservoir effect

Radiocarbon samples obtain their carbon from a different source (or reservoir) than atmospheric carbon.

The average difference between a radiocarbon date of a terrestrial sample (e.g., wood), and marine $CaCO_3$ is about 400 radiocarbon years. This apparent age of oceanic water is caused both by:

- The delay in exchange rates between atmospheric CO_2 and ocean bicarbonate.
- Dilution effect caused by the mixing of surface waters with upwelled deep waters which are very old.

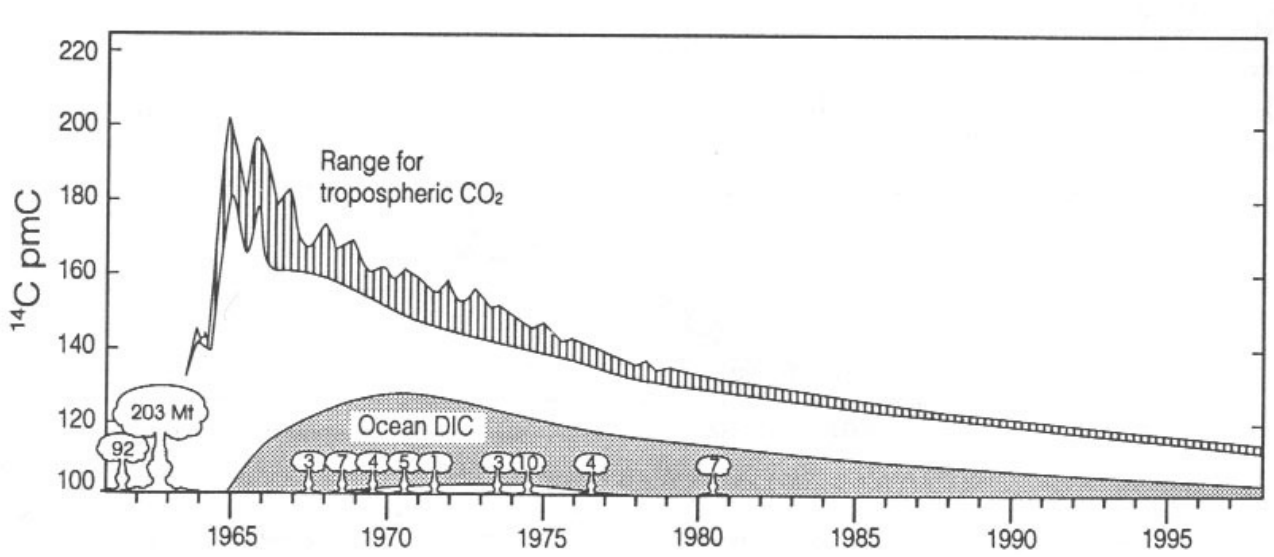
Suess effect

Since about 1890, emissions of radiocarbon-free fossil fuel CO_2 into the atmosphere has diluted the the atmospheric radiocarbon signal by about 2%.

Atom bomb effect

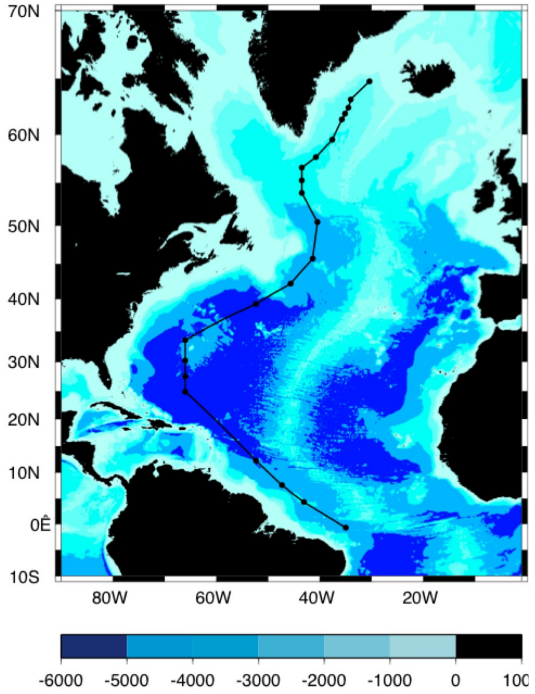
Thermonuclear tests produced 'bomb' ^{14}C, which almost double the amount of ^{14}C activity in terrestrial carbon bearing materials. In the northern hemisphere the amount of artificial carbon in the atmosphere reached a peak in 1963 (in the southern hemisphere around 1965) at about 100% above normal levels.

^{14}C in tropospheric CO_2 and in DIC of the surface ocean

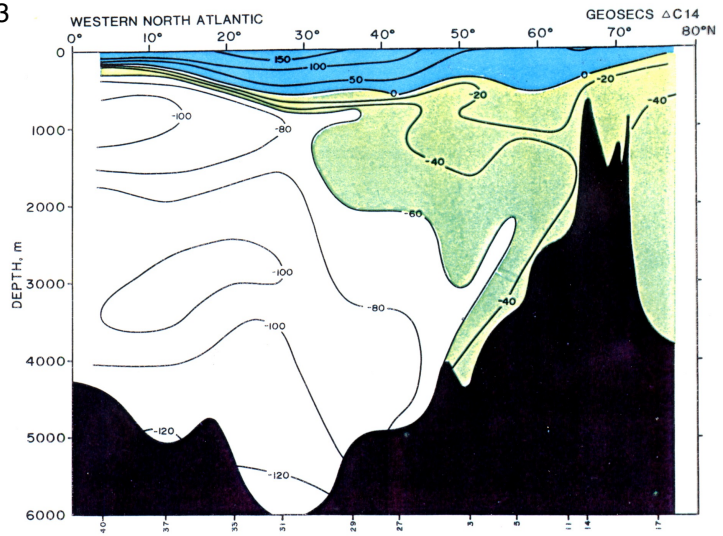


- ^{14}C content of the northern hemisphere increased almost twofold during the mid-1960s as a consequence of the atmospheric testing of thermonuclear bombs (annual total testing given in megatons).
- Increase in southern hemisphere was lower
- Since about 1970 the concentrations have been very similar around the globe.
- Oceanic ^{14}C increased through the uptake of atmospheric ^{14}C.

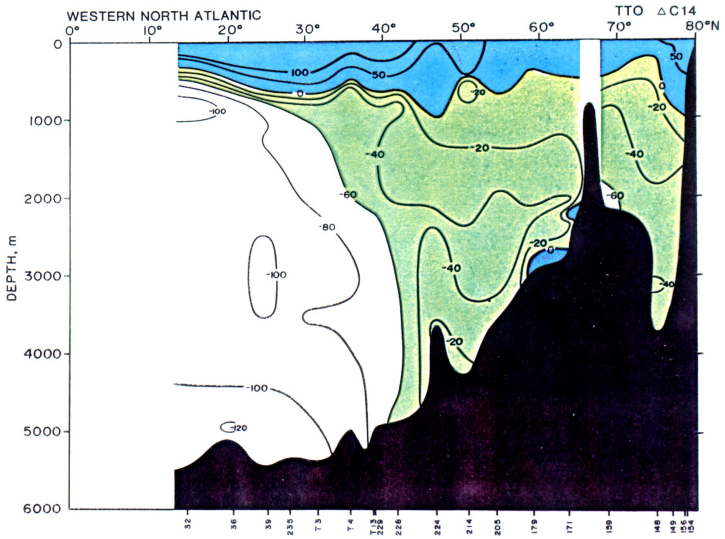
Clark and Fritz, 1997



1972-1973



1981

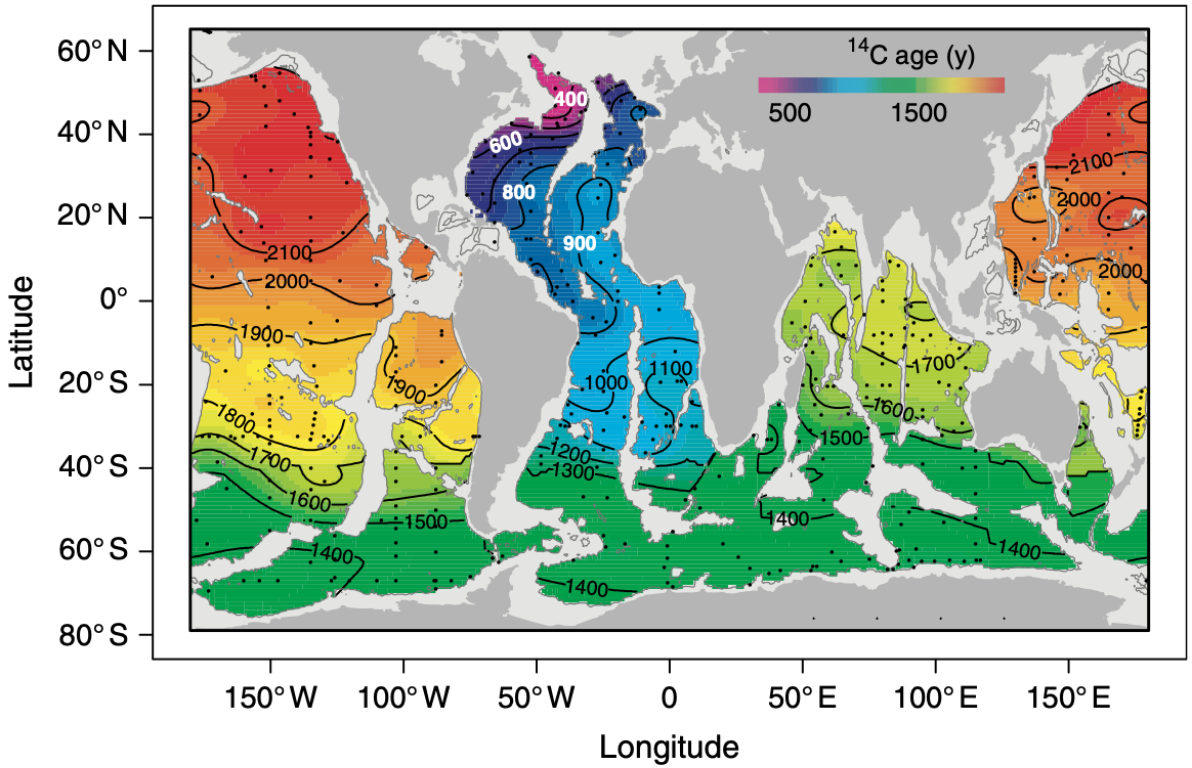


Bomb $^{14}C = \Delta^{14}C > -50‰$

Rule of thumb for comparing $\Delta^{14}C$ and age:

- 10% decrease in $\Delta^{14}C$ is roughly 80 year in increase in age

^{14}C age of DIC at 3000 m depth, determined during WOCE



Note:

- ^{14}C age of surface ocean is 400 years, because of incomplete air-sea exchange with atmosphere, and due to supply of old, deep carbon from below.

Emerson & Hedges, 2008

Secular Equilibrium

- The activity of a radioactive parent and daughter will eventually become equal
  - Assumes closed system
  - Assumes parent and daughter stay in contact
- Departures from this equilibrium can be used to calculate fluxes or rates

Secular Equilibrium

N_1: Parent
N_2: First daughter
N_3: Second daughter

Consider a system of three isotopes: $N_1 \xrightarrow{\lambda_1} N_2 \xrightarrow{\lambda_2} N_3$

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 \left(e^{-\lambda_1 t} - e^{-\lambda_2 t} \right) + N_2^0 e^{-\lambda_2 t}$$

$\lambda_2 - \lambda_1 \to 0$; $e^{-\lambda_2 t} \to 0$; $N_2^0 e^{-\lambda_2 t} \to 0$

For $\lambda_2 >> \lambda_1$, ($t_{1/2,2} << t_{1/2,1}$) the $e^{-\lambda_2 t}$ terms decay very fast.

After about 5 mean-lives of N_2, we have:

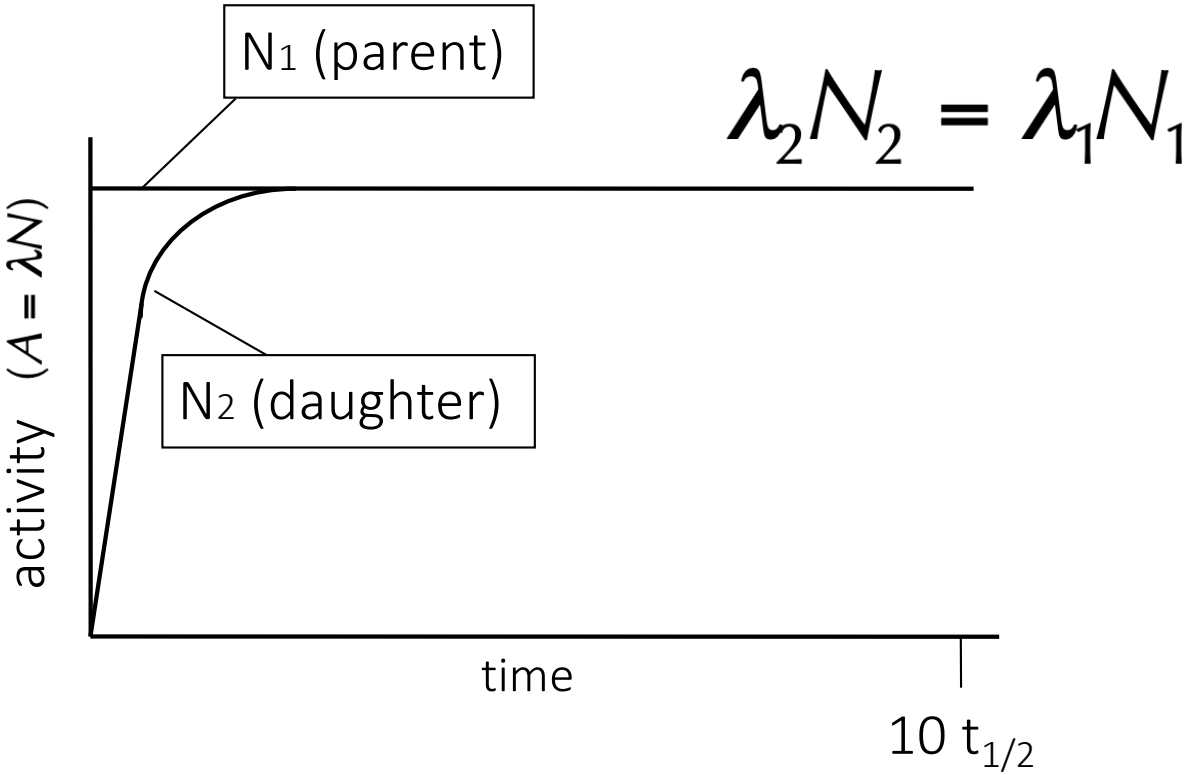
$$N_2 \xrightarrow{t > 5/\lambda_2} \frac{\lambda_1}{\lambda_2} N_1^0 e^{-\lambda_1 t} = \frac{\lambda_1}{\lambda_2} N_1$$

$$\lambda_2 N_2 = \lambda_1 N_1 \qquad A_2 = A_1$$

It takes about 5 mean-lives of N_2 to reach secular equilibrium, in which the ratio of parent to intermediate daughter is fixed. After this point the initial amount of N_2 in the system no longer matters.

Note the N_3 does not participate in secular equilibrium, it just accumulates.

Secular Equilibrium



$$\lambda_2 N_2 = \lambda_1 N_1$$

Secular Equilibrium

$$\lambda_2 N_2 = \lambda_1 N_1$$

- Note that the above equation for secular equilibrium assume no other source and no other removal mechanism. Nevertheless, we know that this is generally not the case in the ocean.
- However, this is what makes radionuclides so useful!
- For example, what if the daughter nuclide is removed by processes other than decay (e.g., scavenging)?

Secular Equilibrium – use of decay series

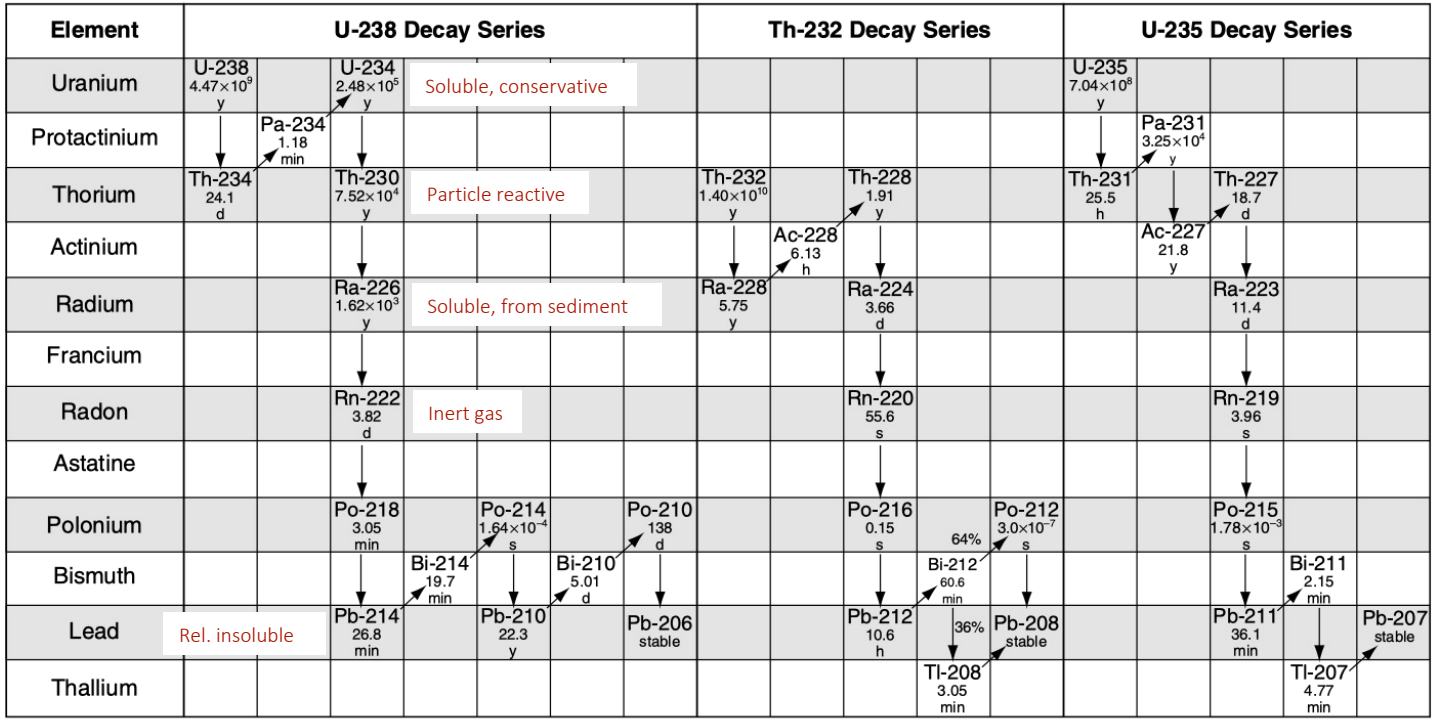


Figure 5.18. A chart of the nuclides showing the decay pathways and half lives of isotopes in the three naturally occurring decay chains. Arrows that point downward indicate α decay, in which a nucleus loses two neutrons and two protons, thus decreasing in atomic number by 2 and atomic mass by 4. The arrows that slant upward to the right indicate β decay, inwhich a neutron in the nucleus becomes a proton (one negative charge is lost from the nucleus), causing an increase in atomic number but little change in atomic mass.

Emerson and Hedges, 2008

Secular Equilibrium – use of decay series

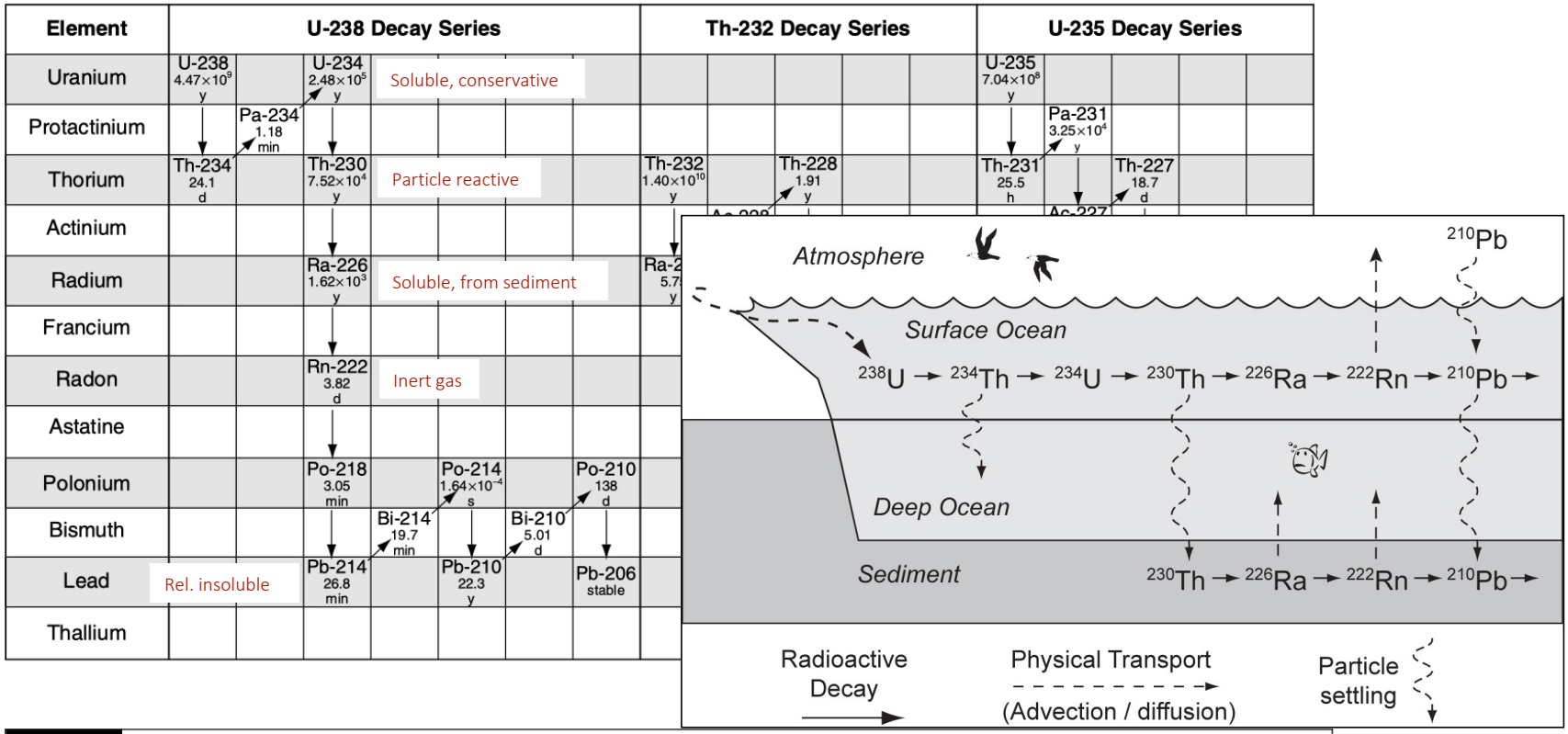
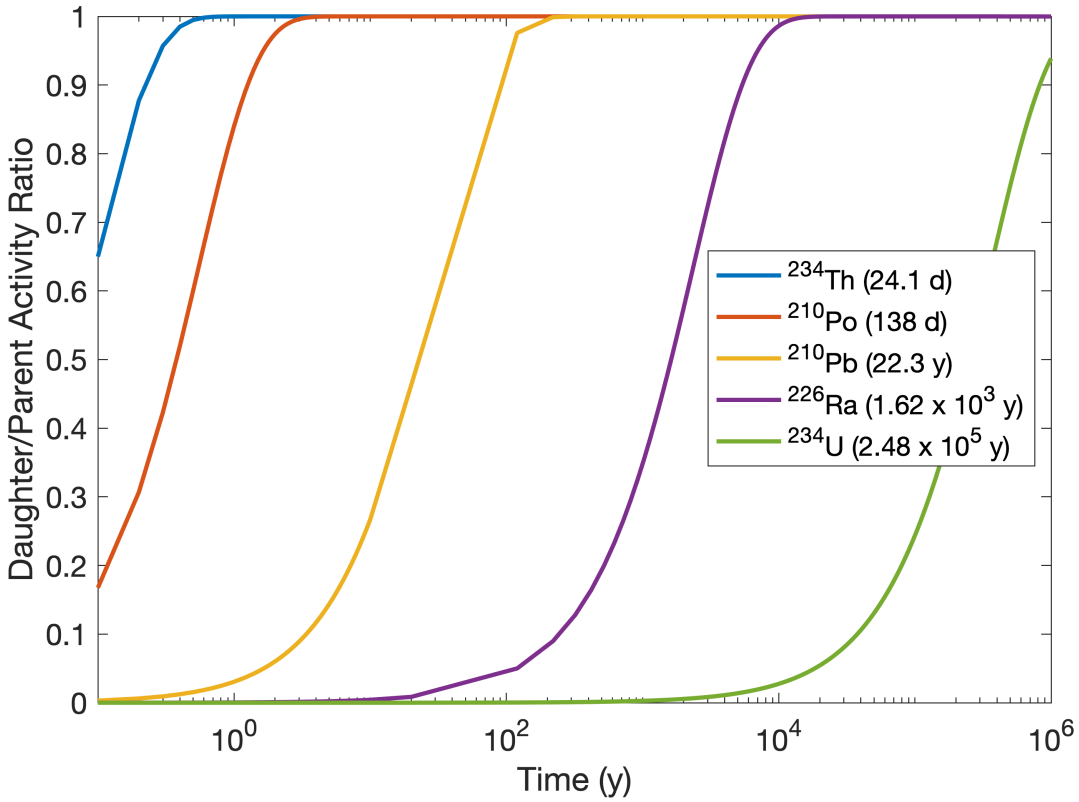
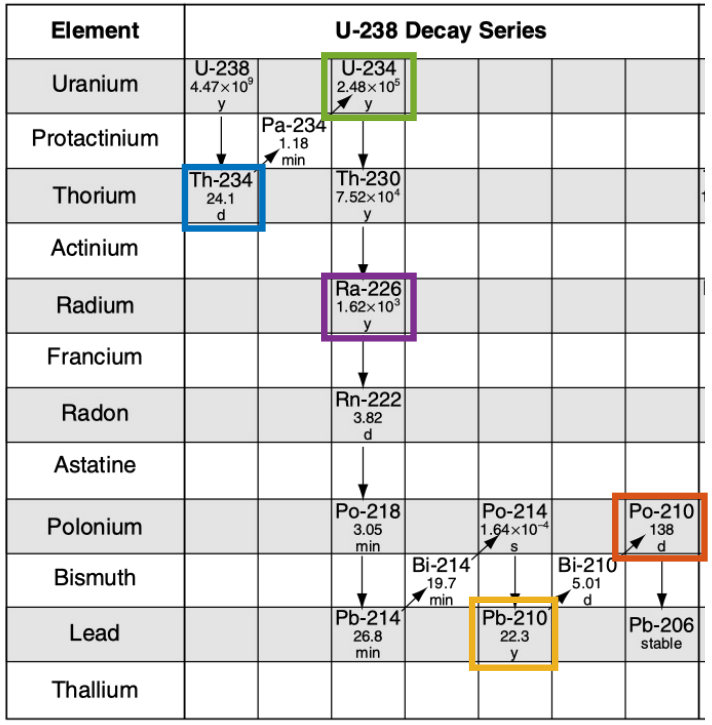


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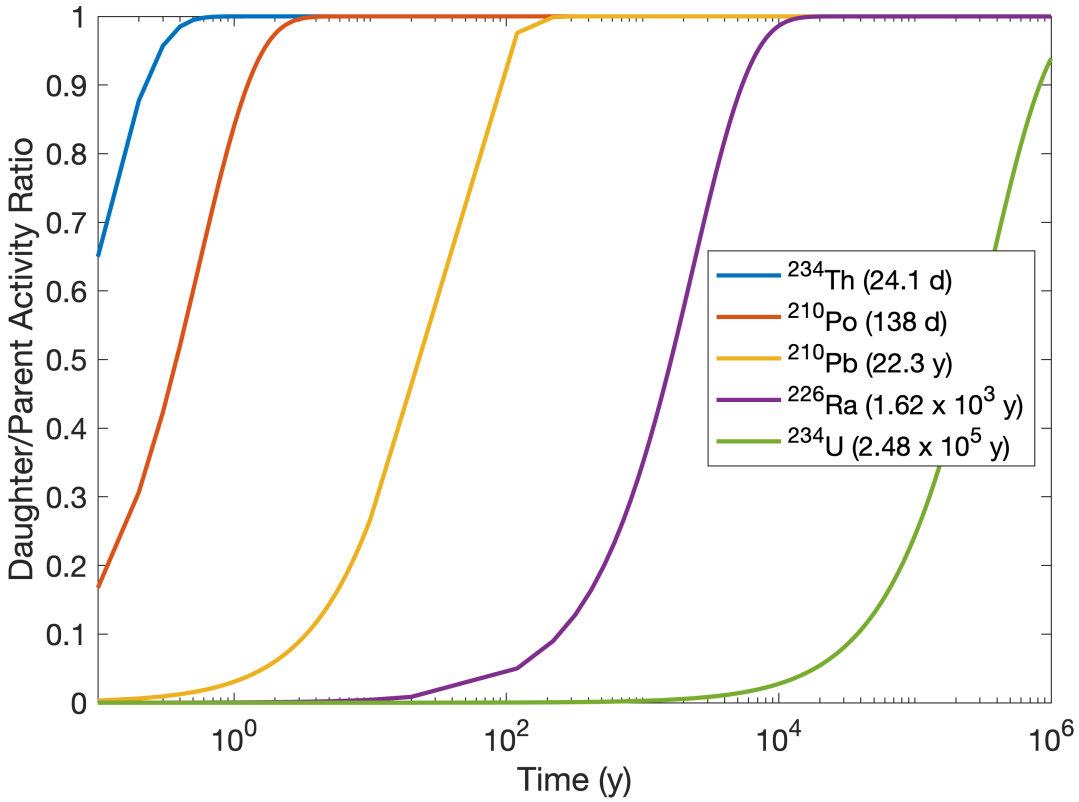
Emerson and Hedges, 2008

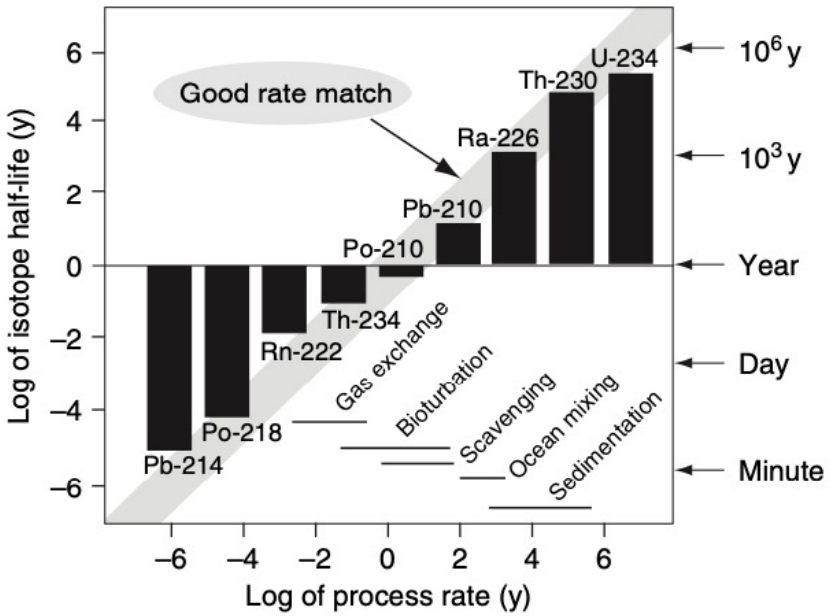
The longer the half-life of the daughter, the longer it takes to achieve a daughter/parent ratio of 1





Process of interest needs to be matched to half-life





Isotopes that have been used in Oceanography

These tracers have a range of origins, chemistries and half lives.

steady state | transient

Isotope	$t_{1/2}$ (y)	Origin			
		Cosmic Rays	U+Th Series	Weapons Testing	Other Anthro.
		Water Tracers			
^{14}C	5,730	✓		✓	
^{226}Ra	1,600		✓		
^{32}Si	250	✓			
^{39}Ar	270	✓			
^{137}Cs	30.2			✓	
^{90}Sr	28.6			✓	
^{3}H	12.33	✓		✓	
^{85}Kr	10.7			✓	✓
^{228}Ra	5.8		✓		
^{7}Be	0.15	✓			
^{222}Rn	0.01		✓		
		Particulate Tracers			
^{239}Pu	24,400			✓	✓
^{230}Th	75,440		✓		
^{240}Pu	6,540			✓	✓
^{210}Pb	22.3		✓		
^{228}Th	1.9		✓		
^{210}Po	0.38		✓		
^{234}Th	0.07		✓		

Tritium

- Production
  - Produced in the upper atmosphere by interaction of nitrogen, and to a lesser extent, oxygen with fast neutrons from cosmic rays.

$$^{14}_{7}N + n \rightarrow ^{12}_{6}C + ^{3}_{1}H$$

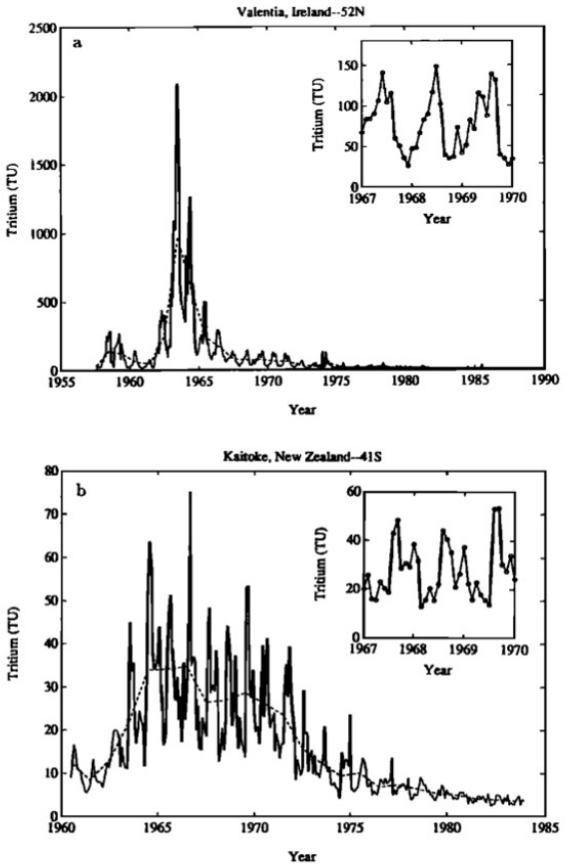
- Inventory
  - 1 TU = [T]/[H] = 1×10^{-18} TU=Tritium Unit
  - 1 TU = 3.2 pCi/kg H_2O = 0.12 Bq/kg H_2O
  - Natural level in precipitation ~ 5 TU
  - 'Bomb tritium' max. levels ~1000 to 2000 TU
- In 1973
  - natural T: ~2.5%
  - nuclear power plant T: 0.02%
  - bombs: 97.5%

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 97, NO. C4, PAGES 5481–5492, APRIL 15, 1992

A Model Function of the Global Bomb Tritium Distribution in Precipitation, 1960–1986

SCOTT C. DONEY,[1] DAVID M. GLOVER, AND WILLIAM J. JENKINS
Chemistry Deptartment, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

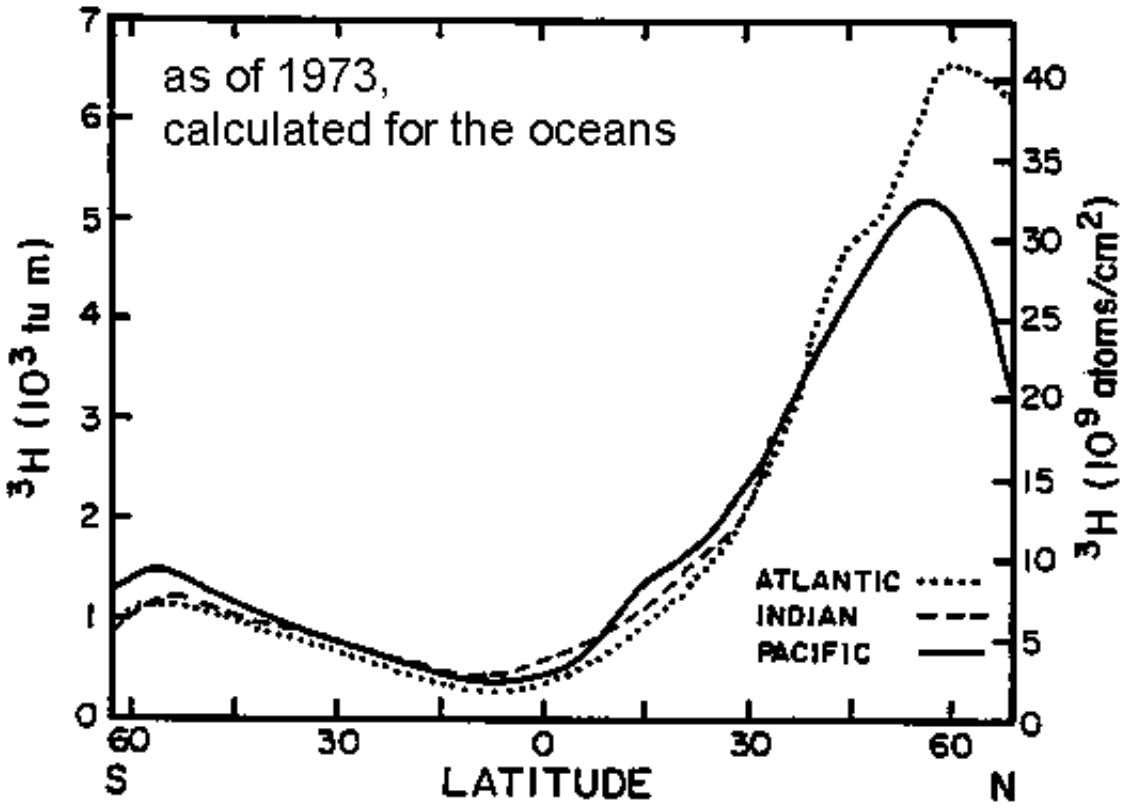
Note change in scale between N.H. and S.H.



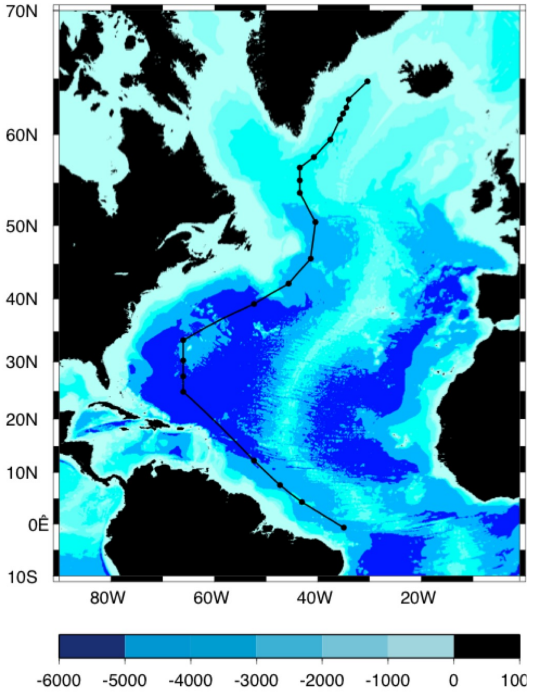
N.H.

S.H.

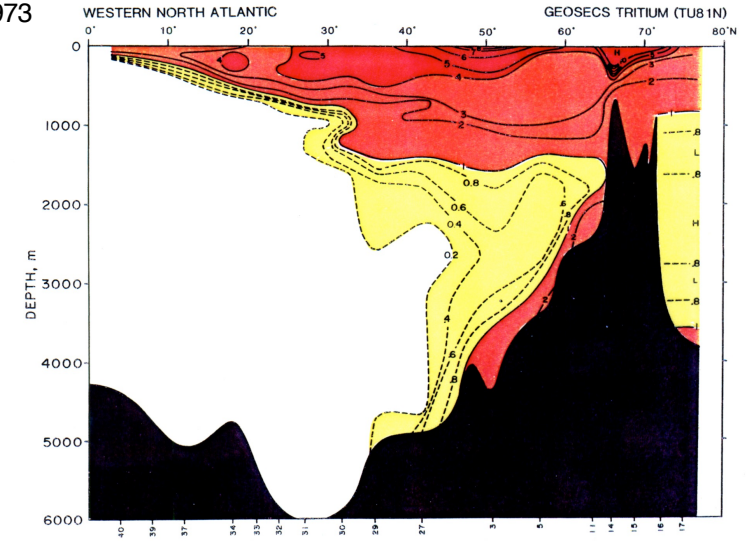
Fig. 1. Monthly tritium concentrations in precipitation plotted versus time from (*a*) Valentia, Ireland (51.9°N), and (*b*) Kaitoke, New Zealand (41.1°S). The dashed lines connect the annual average tritium concentrations at each station. Note the change of scale between the northern and southern hemisphere stations. The insets highlight the seasonal tritium cycle for the years 1967–1970.



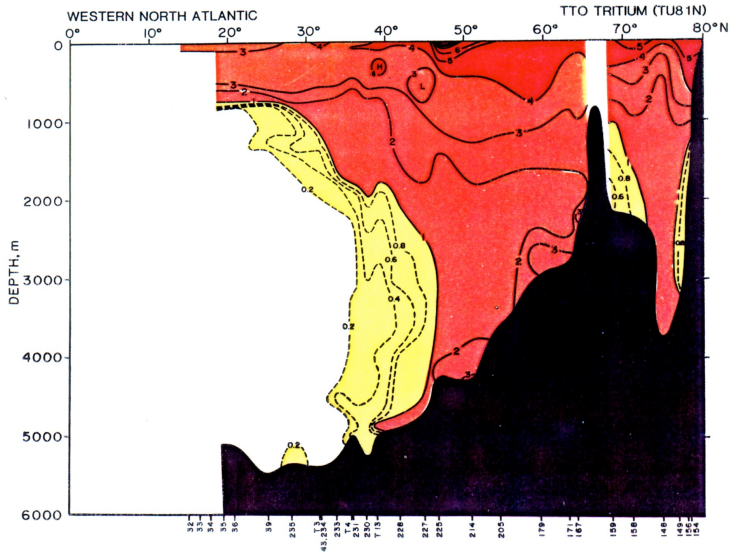
- ^{3}H produced by atmospheric nuclear weapons tests (late 1950s and early 1960s).
- Oxidized to water and rained out over the oceans and continents over the years after the tests.
- Since the tests were largely in the Northern Hemisphere, most of the ^{3}H (about 80%) has been deposited north of the equator, predominantly at higher latitudes.



1972-1973



1981



$^3H/^3He$ dating

Tritium was produced during atmospheric bomb testing and entered the ocean as precipitation.

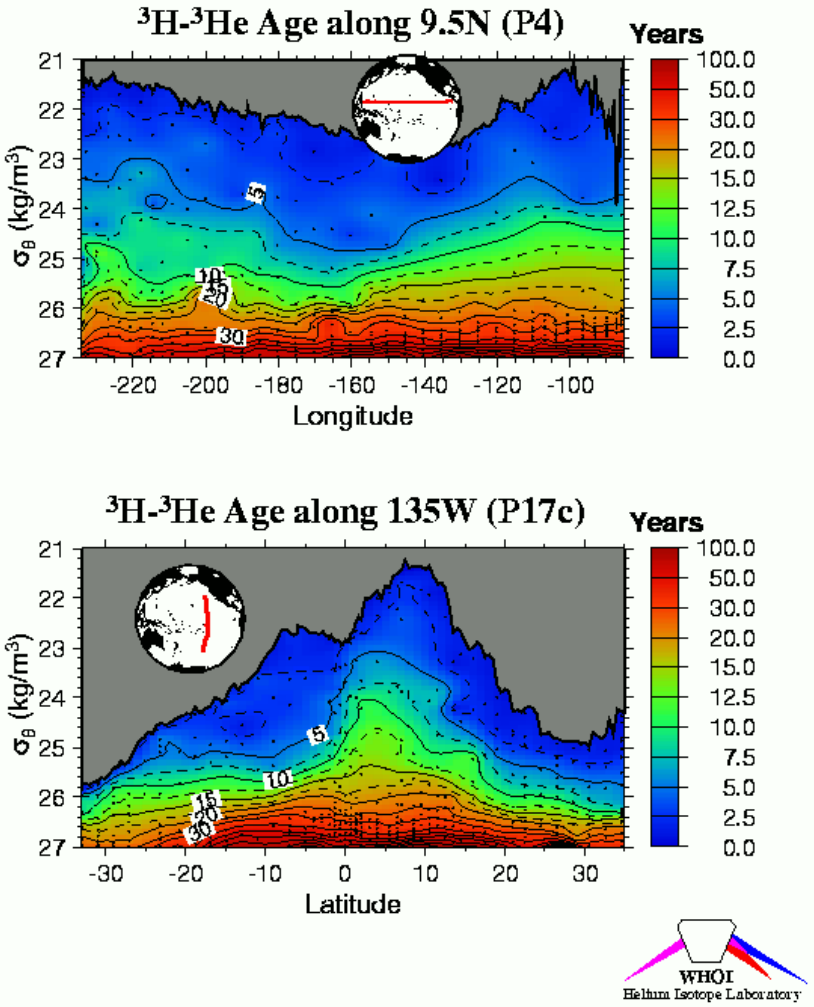
Tritium is radioactive with $t_{1/2}$ = 12.33 y ($\lambda = 1.78 \times 10^{-9}$ s^{-1})

The daughter product ^3He is stable.

In contact with the atmosphere [^3He] is assumed to be in equilibrium with the atmosphere.

The age can be calculated as follows:

$$\text{Age} = \frac{t_{1/2}}{\ln 2} \ln\left(1 + \frac{^3\text{He}}{^3\text{H}}\right)$$


^{3}H-^{3}He Age along 9.5N (P4)
Years
100.0
50.0
30.0
20.0
15.0
12.5
10.0
7.5
5.0
2.5
0.0
21
22
23
24
25
26
27
σ_θ (kg/m^3)
5
10
15
20
30
-220
-200
-180
-160
-140
-120
-100
Longitude
^{3}H-^{3}He Age along 135W (P17c)
Years
100.0
50.0
30.0
20.0
15.0
12.5
10.0
7.5
5.0
2.5
0.0
21
22
23
24
25
26
27
σ_θ (kg/m^3)
5
10
15
20
30
-30
-20
-10
0
10
20
30
Latitude
WHOI
Helium Isotope Laboratory

Rates and Mechanisms of Water Mass Transformation in the Labrador Sea as Inferred from Tracer Observations*

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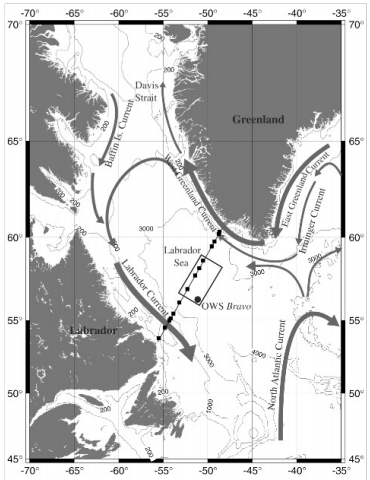


FIG. 1. Schematic of the circulation in the Labrador Sea. Major currents are indicated. Also shown is a typical WOCE AR7W cruise track and the nominal position of OWS Bravo. Solid squares show locations of stations occupied in Jun 1993 and at which samples for ^{3}H and ^{3}He were collected. Region used to define ''central Labrador Sea'' is marked by a rectangle.

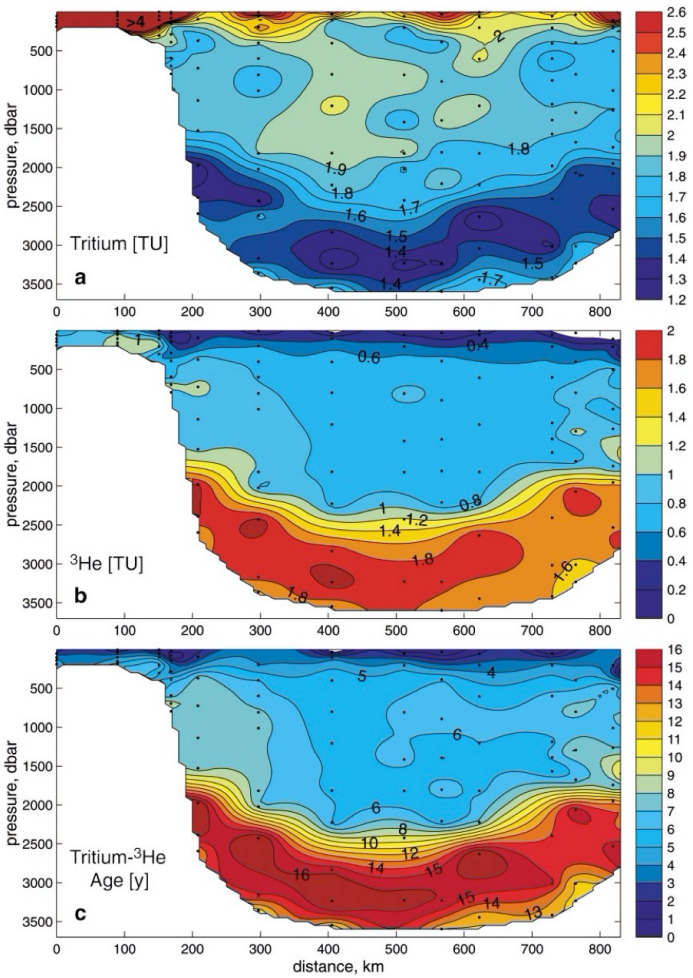


FIG. 4. Sections of (a) ^{3}H, (b) ^{3}He, and (c) ^{3}H–^{3}He age across the Labrador Sea along the WOCE AR7W section occupied in Jun 1993.

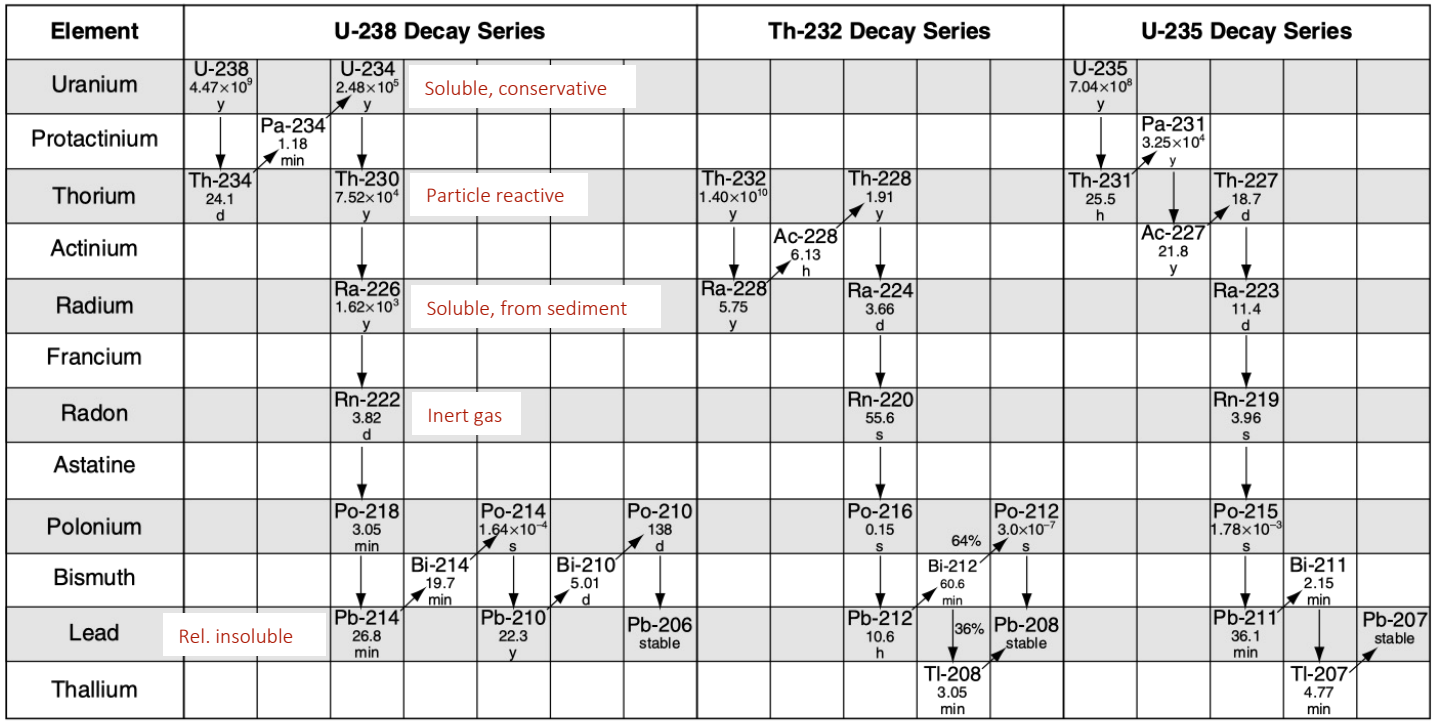


Figure 5.18. A chart of the nuclides showing the decay pathways and half lives of isotopes in the three naturally occurring decay chains. Arrows that point downward indicate α decay, in which a nucleus loses two neutrons and two protons, thus decreasing in atomic number by 2 and atomic mass by 4. The arrows that slant upward to the right indicate β decay, inwhich a neutron in the nucleus becomes a proton (one negative charge is lost from the nucleus), causing an increase in atomic number but little change in atomic mass.

Emerson and Hedges, 2008

^{234}Th and ^{238}U in the Upper Ocean

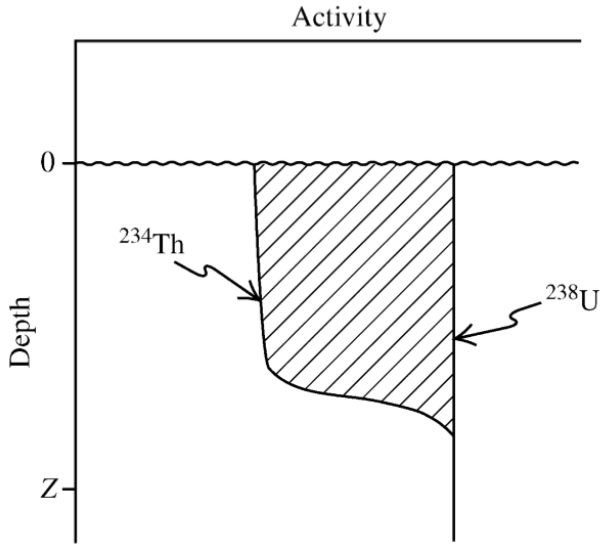


Figure 4 Schematic illustration of concentration profiles of ^{234}Th and ^{238}U in the upper water column. The integrated deficit of ^{234}Th (hatched area) is used to compute the flux of particulate ^{234}Th exported from surface waters.

- ^{238}U and ^{234}Th in secular equilibrium
- Deficit of ^{234}Th ($t_{1/2}$= 24.1 days) relative to its source (i.e., ^{238}U) is due to scavenging
- Th removed from solution, sorbed onto particles

Anderson, 2003

^{234}Th Removal Rate

$$\frac{dN_{^{234}Th}}{dt} = N_{^{238}U}\lambda_{^{238}U} - N_{^{234}Th}\lambda_{^{234}Th} - N_{^{234}Th}\kappa \pm \nu$$

Production — Decay — Removal — Physical processes

$$\frac{dN_{Th}}{dt} = A_U - A_{Th} - N_{Th}\kappa \pm \nu$$

- Assume negligible advection and diffusion
- Multiply by λ_{Th} to convert to activity
- Assume steady state: $dA_{Th}/dt = 0$

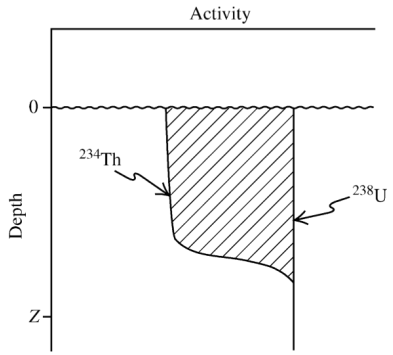
$$\frac{dA_{Th}}{dt} = 0 = \lambda_{Th}\left(A_U - A_{Th}\right) - A_{Th}\kappa$$

$$A_{Th}\kappa = \lambda_{Th}\left(A_U - A_{Th}\right)$$ ← Removal rate (dpm L^{-1} d^{-1})

^{234}Th Flux Calculation

$$\text{Flux} = \kappa A_{Th} z = (A_U - A_{Th}) \lambda_{Th} \; z \; 10^3$$

dpm m^{-2} d^{-1} — water depth of mixed layer — dpm L^{-1} — d^{-1} — m — L m^{-3}



- Deficit of thorium integrated over the water column, gives the flux of thorium.
- To calculate flux of any element or compound in the particles, multiply ^{234}Th flux by the ratio (in the particles) of ^{234}Th to the species of interest.
  - *e.g.*, C flux = ^{234}Th flux * $(C / {}^{234}Th)_{\text{sinking particles}}$
- Flux of thorium related to flux of particles, and therefore related to flux of C.