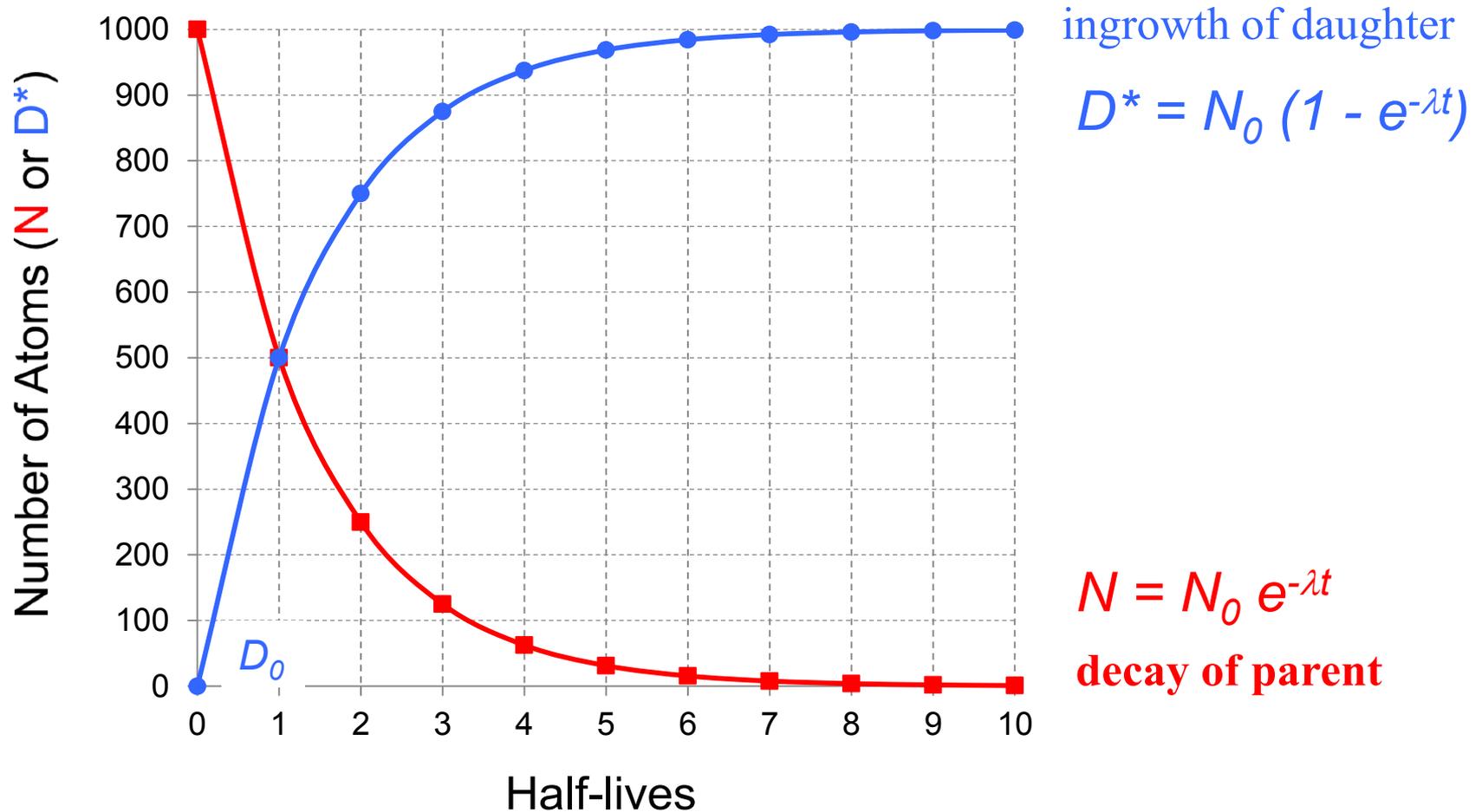
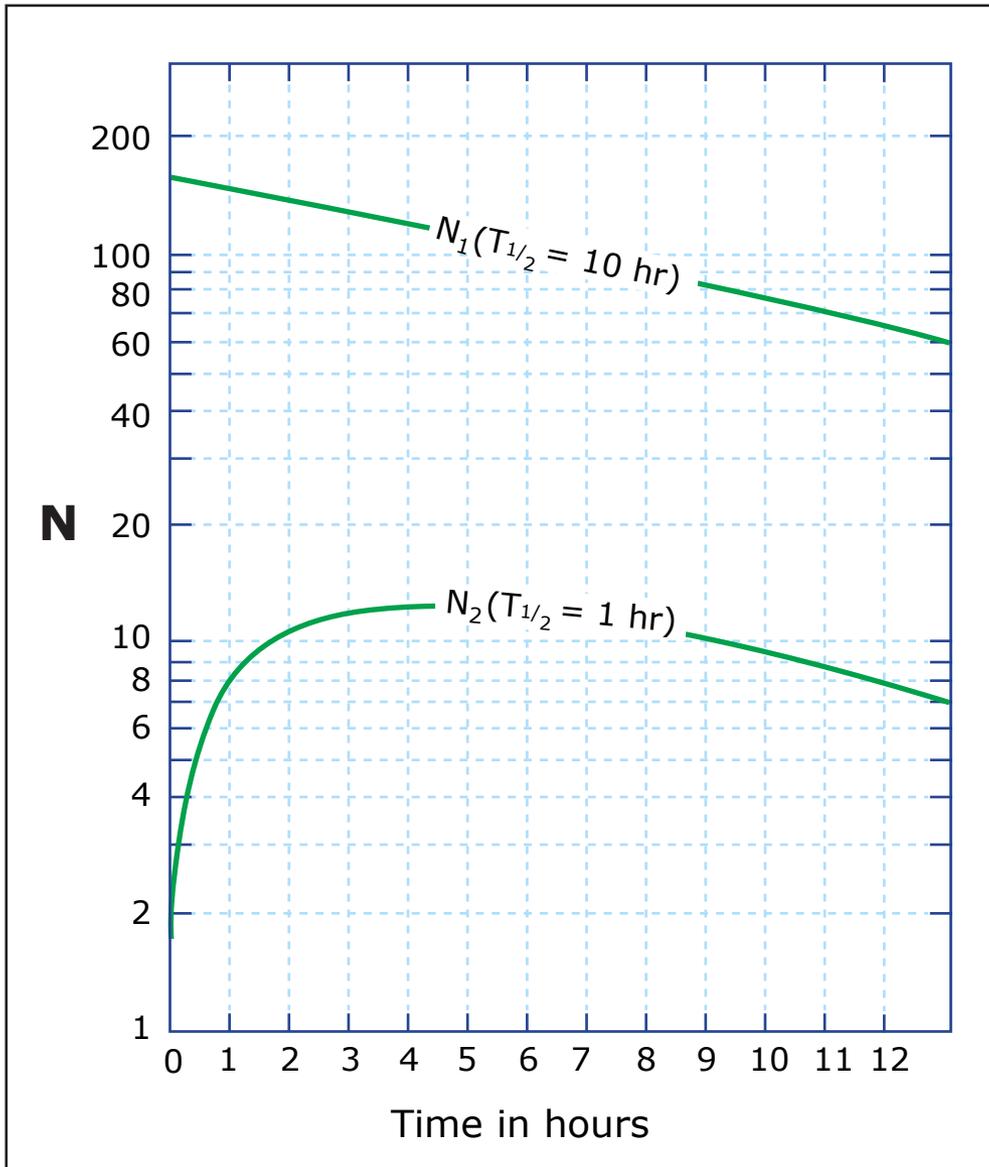


# *Simple Decay: Radioactive Parent $\Rightarrow$ Stable Daughter*



# *Decay Series: Radioactive Parent $\Rightarrow$ Radioactive Daughter*



Decay of parent

Ingrowth from parent  
and decay of daughter

## Consider the decay series $N_1 \rightarrow N_2 \rightarrow N_3$

Remember:

$$1) \quad -dN_1/dt = \lambda_1 N_1$$

Now we consider  $N_2$ , that is produced by decay of  $N_1$  and itself decays to  $N_3$ :

$$2) \quad dN_2/dt = \lambda_1 N_1 - \lambda_2 N_2$$

Remember:

$$3) \quad N_1 = N_{1,0} e^{-\lambda_1 t}$$

Substitute 3) into 2):

$$4) \quad dN_2/dt = \lambda_1 N_{1,0} e^{-\lambda_1 t} - \lambda_2 N_2$$

Rearrange:

$$5) \quad dN_2/dt + \lambda_2 N_2 - \lambda_1 N_{1,0} e^{-\lambda_1 t} = 0$$

Solving this first order differential equation for  $N_2$  yields:

$$6) \quad N_2 = \lambda_1 / (\lambda_2 - \lambda_1) N_{1,0} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_{2,0} e^{-\lambda_2 t}$$

The solution, as well as equivalent solutions for three nuclides and the general case, are known as Bateman (1910) equations/solutions.

The first term in equation 6) is the number of  $N_2$  atoms decayed from  $N_1$  not yet decayed to  $N_3$

The second term in equation 6) is number of  $N_2$  atoms that remain from the initial  $N_{2,0}$

# The classic Bateman paper on the famous "Bateman equations"

Bateman, Harry. "The solution of a system of differential equations occurring in the theory of radioactive transformations." In *Proc. Cambridge Philos. Soc*, vol. 15, no. pt V, pp. 423-427. 1910.

*The solution of a system of differential equations occurring in the theory of radio-active transformations.* By H. BATEMAN, M.A., Trinity College.

[Read 21 February 1910.]

1. It has been shown by Prof. Rutherford\* that the amounts of the primary substance and the different products in a given quantity of radio-active matter vary according to the system of differential equations,

$$\left. \begin{aligned} \frac{dP}{dt} &= -\lambda_1 P \\ \frac{dQ}{dt} &= \lambda_1 P - \lambda_2 Q \\ \frac{dR}{dt} &= \lambda_2 Q - \lambda_3 R \\ \frac{dS}{dt} &= \lambda_3 R - \lambda_4 T \\ &\dots\dots\dots \end{aligned} \right\} \dots\dots\dots (1),$$

where  $P, Q, R, S, T, \dots$  denote the number of atoms of the primary substance and successive products which are present at time  $t$ .

Prof. Rutherford has worked out the various cases in which there are only two products in addition to the primary substance, and it looks at first sight as if the results may be extended to any number of products without much labour.

Unfortunately the straightforward method is unsymmetrical and laborious, and as the results of the calculations are needed in some of the researches which are being carried on in radio-activity the author has thought it worth while to publish a simple and symmetrical method of obtaining the required formulae.

2. Let us introduce a set of auxiliary quantities  $p(x), q(x), r(x), \dots$  depending on a variable  $x$  and connected with the quantities  $P(t), Q(t), R(t), \dots$  by the equations,

$$p(x) = \int_0^\infty e^{-xt} P(t) dt, \quad q(x) = \int_0^\infty e^{-xt} Q(t) dt \dots\dots (2).$$

It is easily seen that

$$\begin{aligned} \int_0^\infty e^{-xt} \frac{dP}{dt} dt &= -P(0) + x \int_0^\infty e^{-xt} P(t) dt \dots\dots\dots (3), \\ &= -P_0 + xp, \end{aligned}$$

\* *Radio-activity*, 2nd edition, p. 331.

*continue...*

If there are no atoms of the original daughter  $N_{2,0}$ , then 6) simplifies to:

$$7) \quad N_2 = \lambda_1 / (\lambda_2 - \lambda_1) N_{1,0} (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$



$$8) \quad ({}^{230}\text{Th}) = ({}^{230}\text{Th})_x + ({}^{230}\text{Th})_s \quad x = \text{excess, not supported}, \quad s = \text{supported from } ^{238}\text{U}$$

Let's first consider the excess activity only, at some time, t:

$$9) \quad ({}^{230}\text{Th})_x = ({}^{230}\text{Th})_{x,0} e^{-\lambda_{230} t}$$

Normalize by a "stable" isotope. Relative to the short-lived daughters,  $^{232}\text{Th}$  is "stable"

$$10) \quad ({}^{230}\text{Th}/{}^{232}\text{Th})_x = ({}^{230}\text{Th}/{}^{232}\text{Th})_{x,0} e^{-\lambda_{230} t}$$

**Application!**

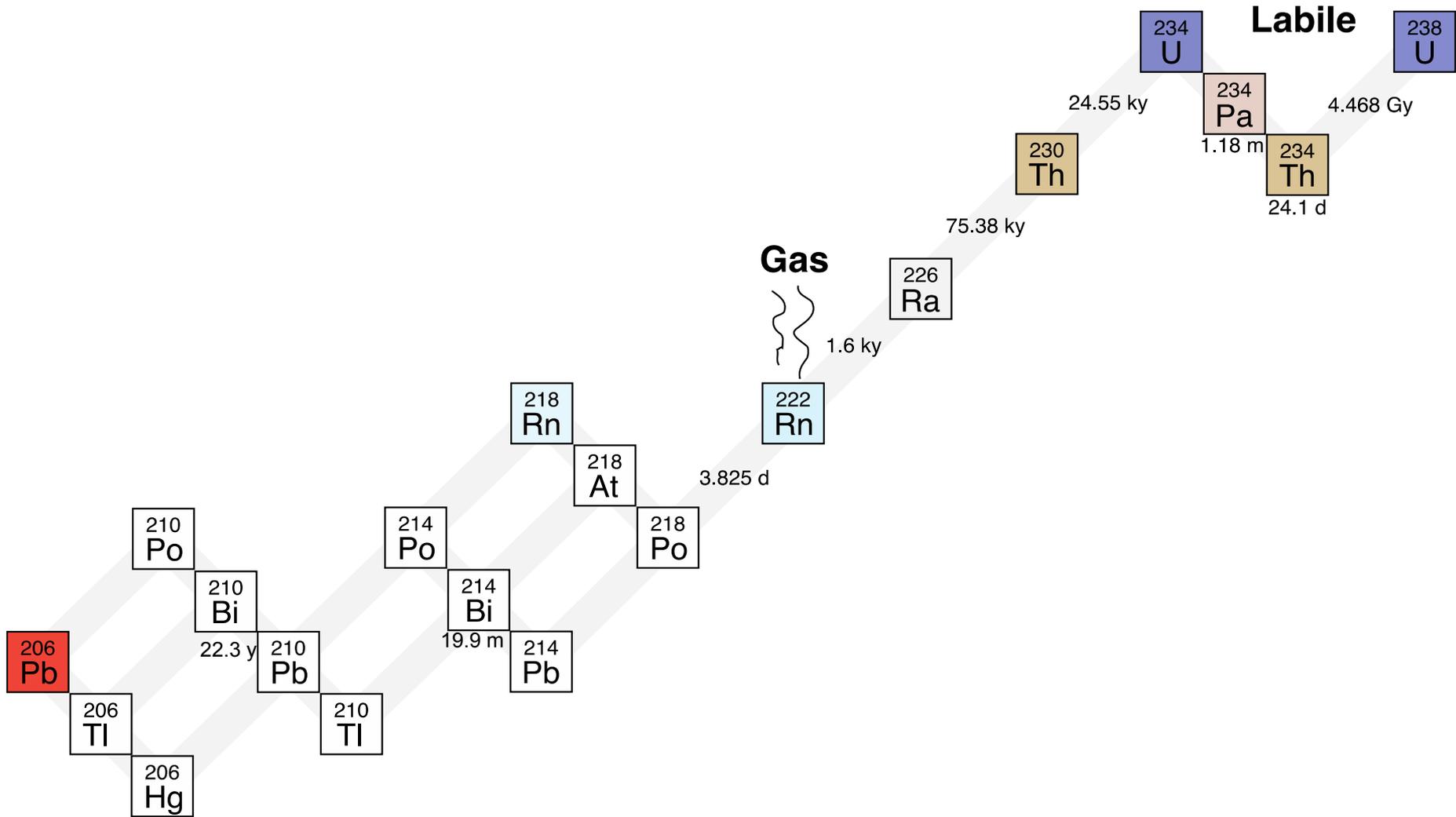
Now let's consider the  $^{238}\text{U}$ -supported ( $^{230}\text{Th}$ ) – see equation 7)

$$11) \quad ({}^{230}\text{Th})_s = \lambda_{234} / (\lambda_{230} - \lambda_{234}) {}^{234}\text{U}_0 (e^{-\lambda_{230} t} - e^{-\lambda_{234} t})$$

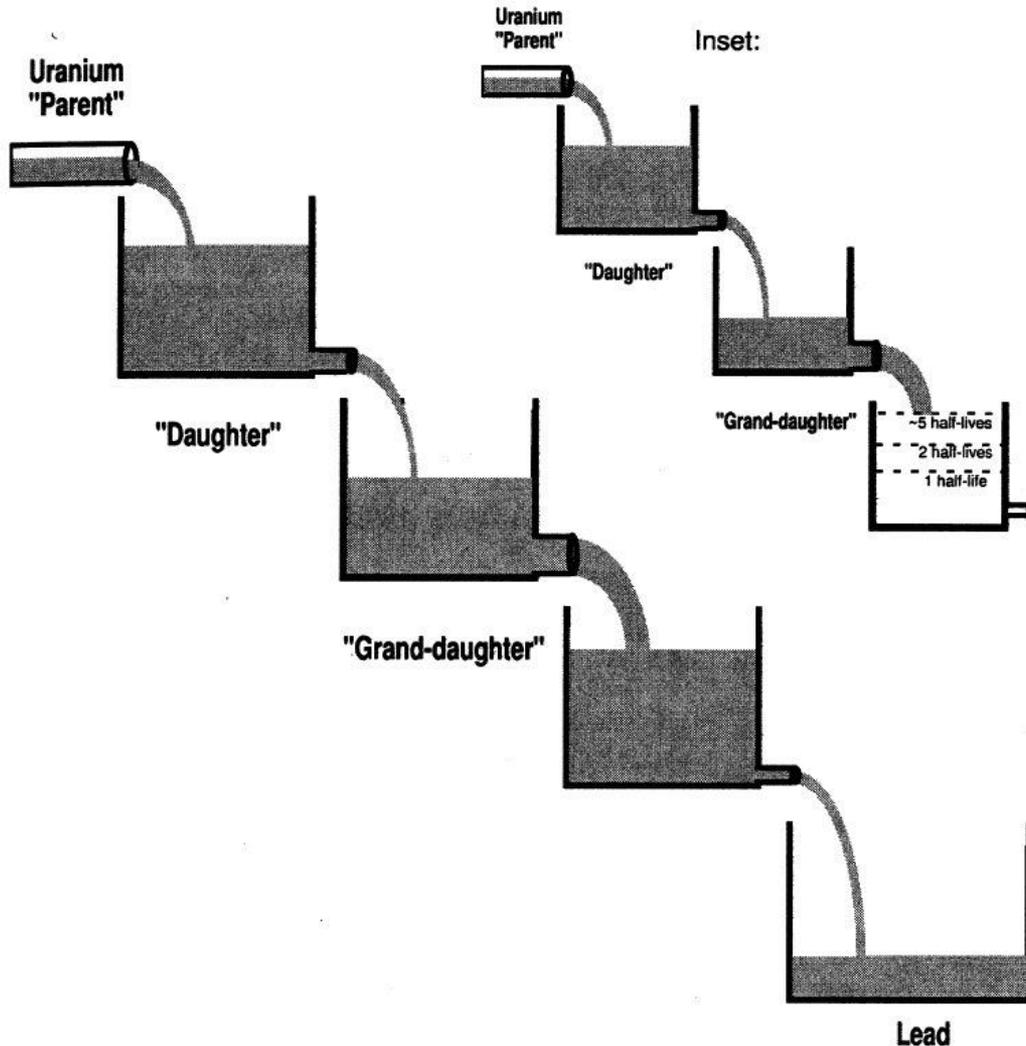
At secular equilibrium  $({}^{234}\text{U}) = ({}^{238}\text{U})$  then  ${}^{234}\text{U} \lambda_{234} = ({}^{238}\text{U})$

Also  $\lambda_{230} - \lambda_{234} \cong \lambda_{230}$  as  $\lambda_{234}$  is small:  $e^{-\lambda_{234} t} \cong 1$

# $^{238}\text{U}$ Decay Series



# $^{238}\text{U}$ Decay Series



$\pm$  constant supply  
from decay of  $^{238}\text{U}$

Size of spout  
equals  $\lambda$

Fill level in each  
tank equals  $N$

Flux equals  $(A)$

Courtesy of Mineralogical Society of America. Used with permission.

# *Application in determining chronologies of sediments*

Basic decay equation:  $N = N_0 e^{-\lambda t}$  assuming no U-supported activity

Replace time (t) with depth in sediment column (d) divided by sedimentation rate (sr)

$$t = d / sr$$

Decay equation:  $N = N_0 e^{-\lambda d/sr}$   $t = d / sr$

$$\ln N = \ln N_0 - \lambda d/sr$$

In a diagram of  $\ln N$  (y axis) and  $d$  (x axis) the slope (m) is

$$m = -\lambda / sr$$

and

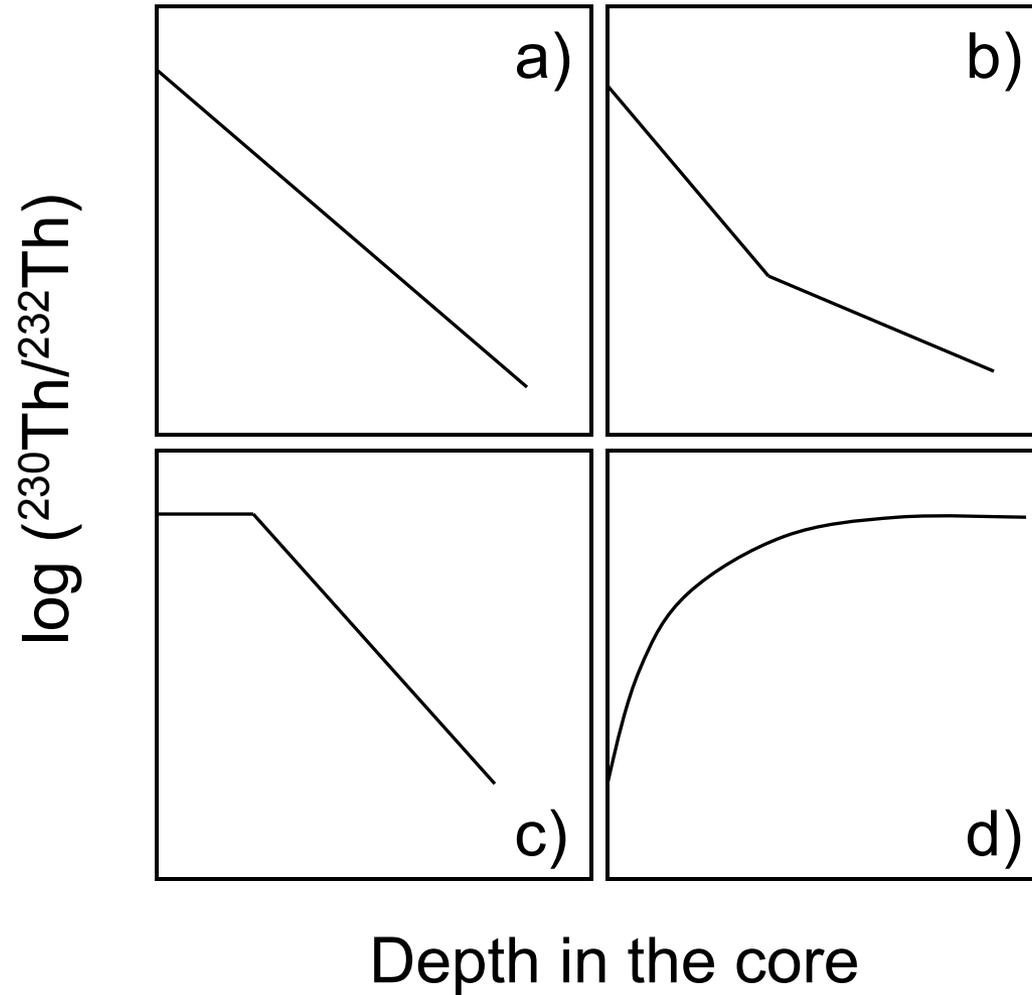
$$sr = -\lambda / m$$

Figure of  $\log(^{230}\text{Th}/^{232}\text{Th})_A$  versus Core Depth, cm, has been removed due to copyright restrictions.

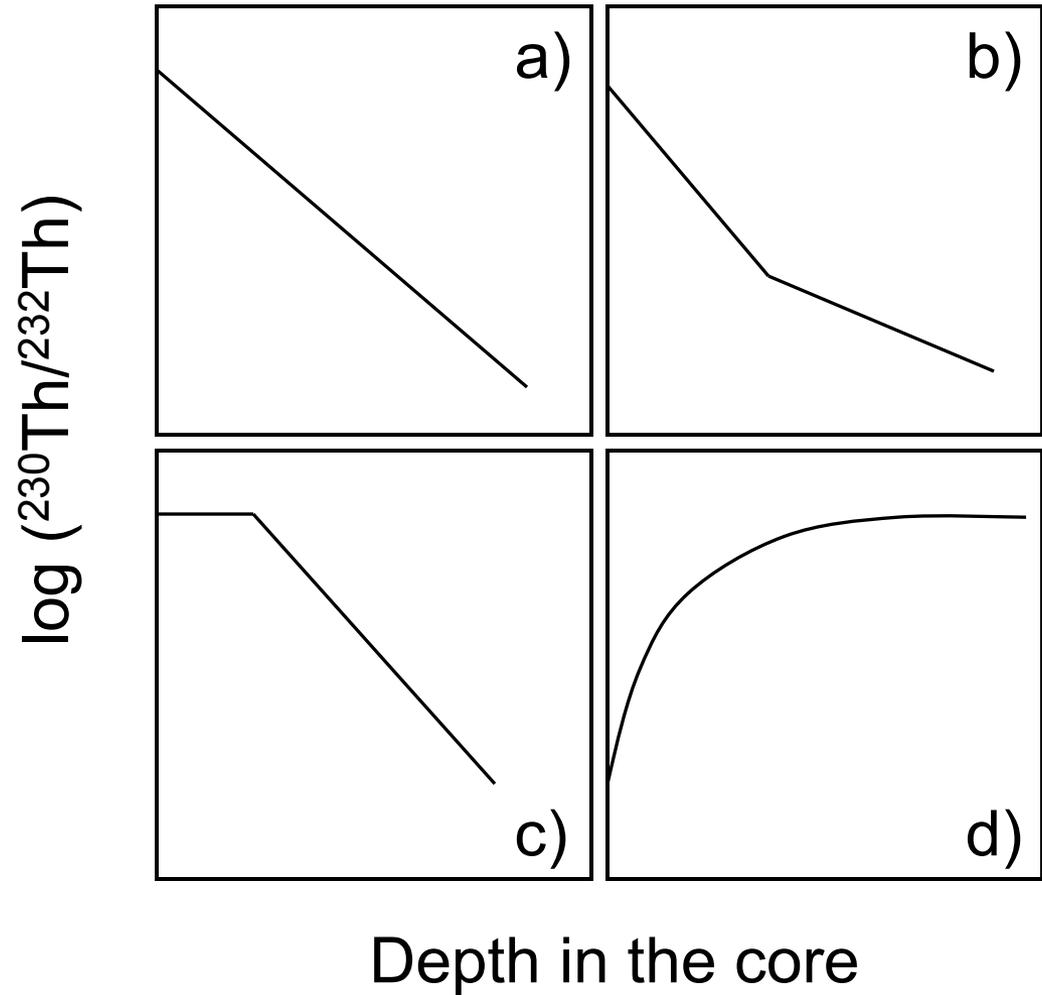
Faure, Gunter. "Principles of Isotope Geology." (John Wiley & Sons, 1986): 367.

This method is also known as the ionium ( $^{230}\text{Th}$ ) method of dating.

# *Complications...*



# *Complications...*



- a) Constant sedimentation rate
- b) Change in sedimentation rate
- c) Mixing at the top
- d)  $^{238}\text{U}$ -supported  $^{230}\text{Th}$  dominates

*continue...*

If there are no atoms of the original daughter  $N_{2,0}$ , then 6) simplifies to:

$$7) \quad N_2 = \lambda_1 / (\lambda_1 - \lambda_2) N_{1,0} (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$



$$8) \quad (^{230}\text{Th}) = (^{230}\text{Th})_x + (^{230}\text{Th})_s \quad \text{x = excess, not supported, } s = \text{supported from } ^{238}\text{U}$$

Let's first consider the excess activity only, at some time, t:

$$9) \quad (^{230}\text{Th})_x = (^{230}\text{Th})_{x,0} e^{-\lambda_{230} t}$$

Normalize by a "stable" isotope. Relative to the short-lived daughters,  $^{232}\text{Th}$  is "stable"

$$10) \quad (^{230}\text{Th}/^{232}\text{Th})_x = (^{230}\text{Th}/^{232}\text{Th})_{x,0} e^{-\lambda_{230} t}$$

**Application!**

Now let's consider the  $^{238}\text{U}$ -supported ( $^{230}\text{Th}$ ) – see equation 7)

$$11) \quad (^{230}\text{Th})_s = \lambda_{234} / (\lambda_{230} - \lambda_{234}) ^{234}\text{U}_0 (e^{-\lambda_{234} t} - e^{-\lambda_{230} t})$$

At secular equilibrium,  $(^{234}\text{U}) = (^{238}\text{U})$  then  $^{234}\text{U} \lambda_{234} = (^{238}\text{U})$

Also  $\lambda_{230} - \lambda_{234} \cong \lambda_{230}$  as  $\lambda_{234}$  is small:  $e^{-\lambda_{234} t} \cong 1$

*continue...*

$$11) \quad {}^{230}\text{Th}_s = \lambda_{234}/(\lambda_{230} - \lambda_{234}) {}^{234}\text{U}_0 (e^{-\lambda_{234}t} - e^{-\lambda_{230}t})$$

$$\lambda_{230} {}^{230}\text{Th}_s = \lambda_{234} {}^{234}\text{U}_0 (1 - e^{-\lambda_{230}t})$$

$$12) \quad ({}^{230}\text{Th})_s = {}^{238}\text{U}_0 (1 - e^{-\lambda_{230}t})$$

From equation 9)  $({}^{230}\text{Th})_x = ({}^{230}\text{Th})_{x,0} e^{-\lambda_{230}t}$

$$({}^{230}\text{Th}) = ({}^{230}\text{Th})_{x,0} + ({}^{230}\text{Th})_s$$

Total  ${}^{230}\text{Th}$  activity = initial excess  ${}^{230}\text{Th}$  activity +  ${}^{238}\text{U}$ -supported activity

$$13) \quad ({}^{230}\text{Th}) = ({}^{230}\text{Th})_{x,0} e^{-\lambda_{230}t} + {}^{238}\text{U} (1 - e^{-\lambda_{230}t})$$

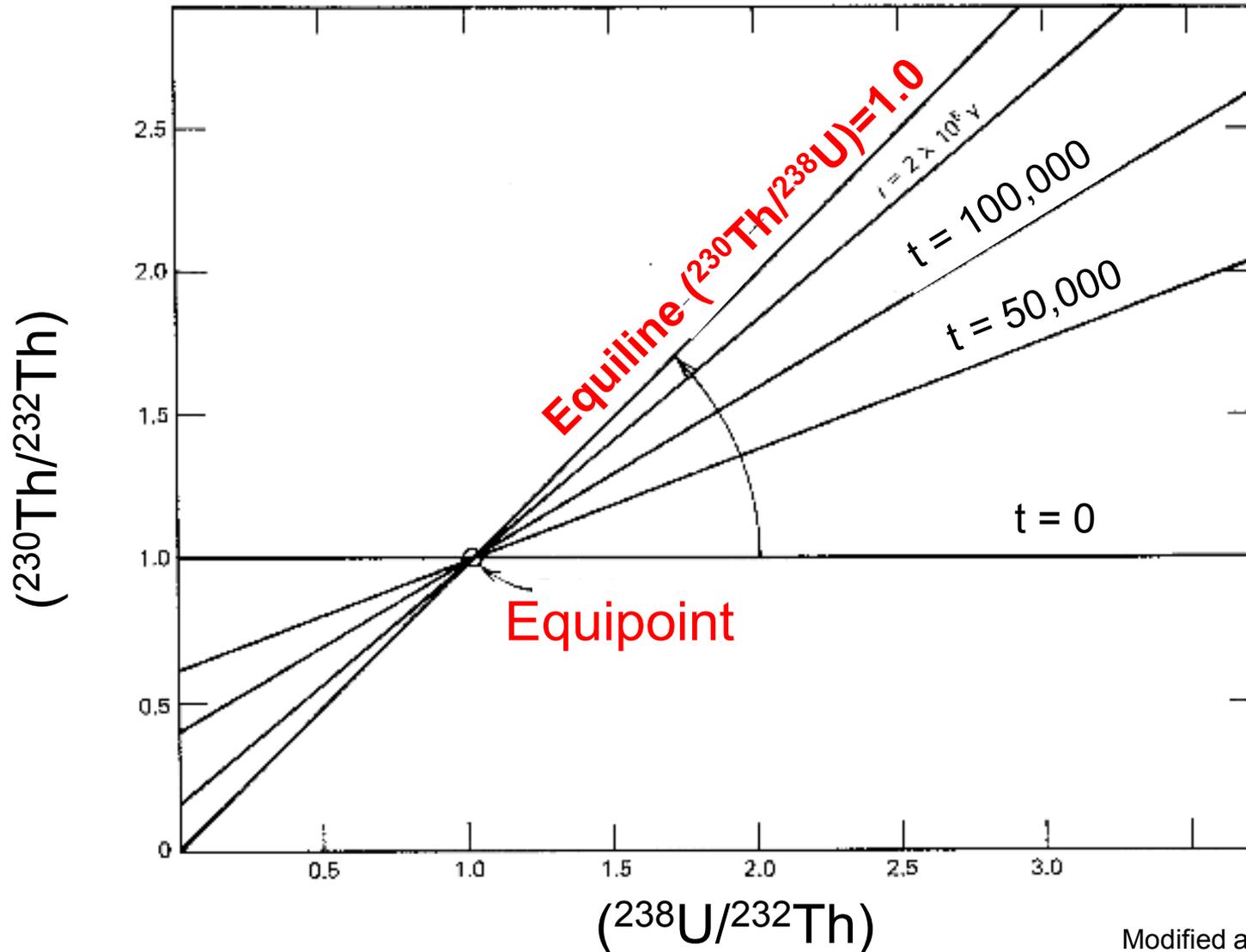
Normalize to  ${}^{232}\text{Th}$

$$14) \quad ({}^{230}\text{Th}/{}^{232}\text{Th}) = ({}^{230}\text{Th}/{}^{232}\text{Th})_{x,0} e^{-\lambda_{230}t} + ({}^{238}\text{U}/{}^{232}\text{Th}) (1 - e^{-\lambda_{230}t})$$

If  $({}^{230}\text{Th}/{}^{232}\text{Th})$  is plotted against  $({}^{238}\text{U}/{}^{232}\text{Th})$ , equation 14) is a linear equation, the so-called

***${}^{230}\text{Th}$ - ${}^{238}\text{U}$  isochron diagram***

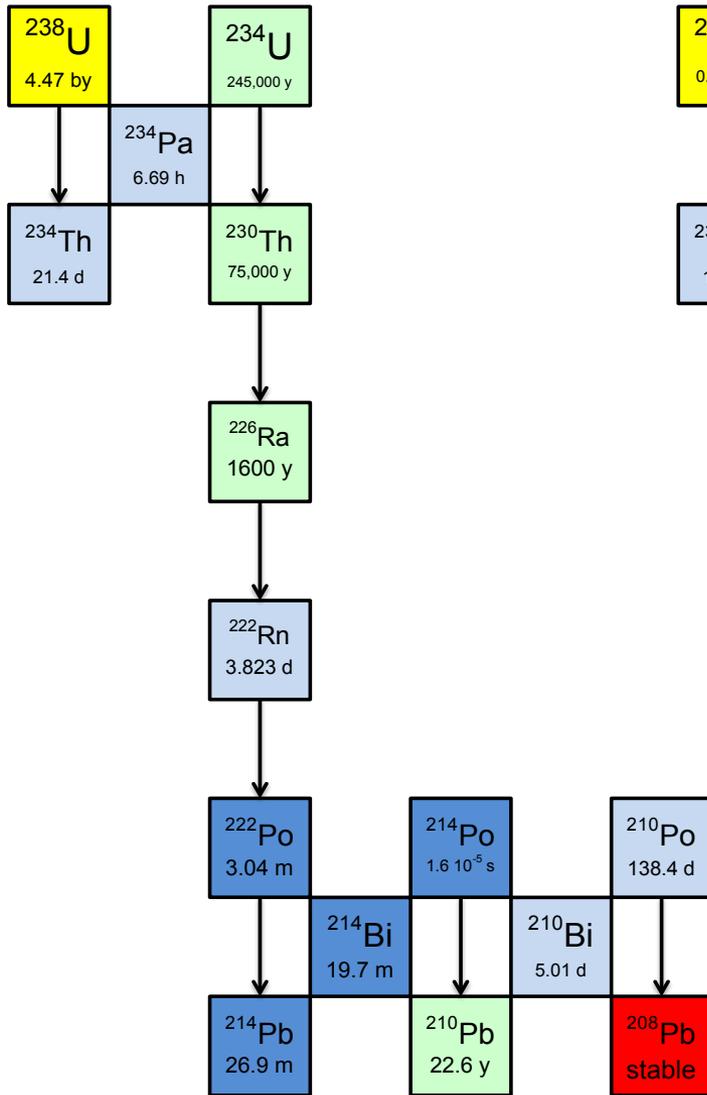
# $^{230}\text{Th}$ - $^{238}\text{U}$ isochron diagram



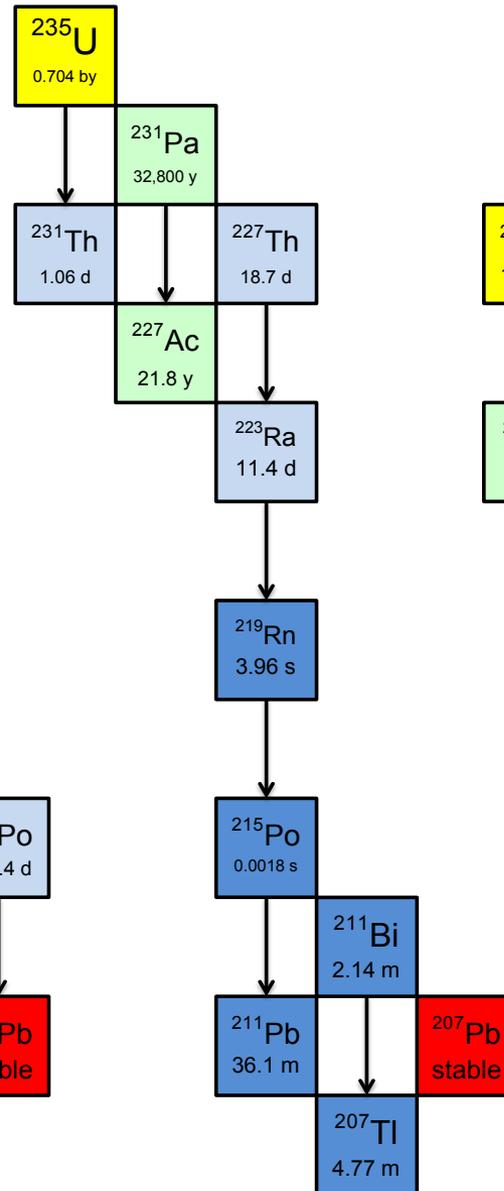
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Modified after figure 21.7 of Faure, Gunter. "Principles of Isotope Geology." (John Wiley & Sons, 1986): 379.

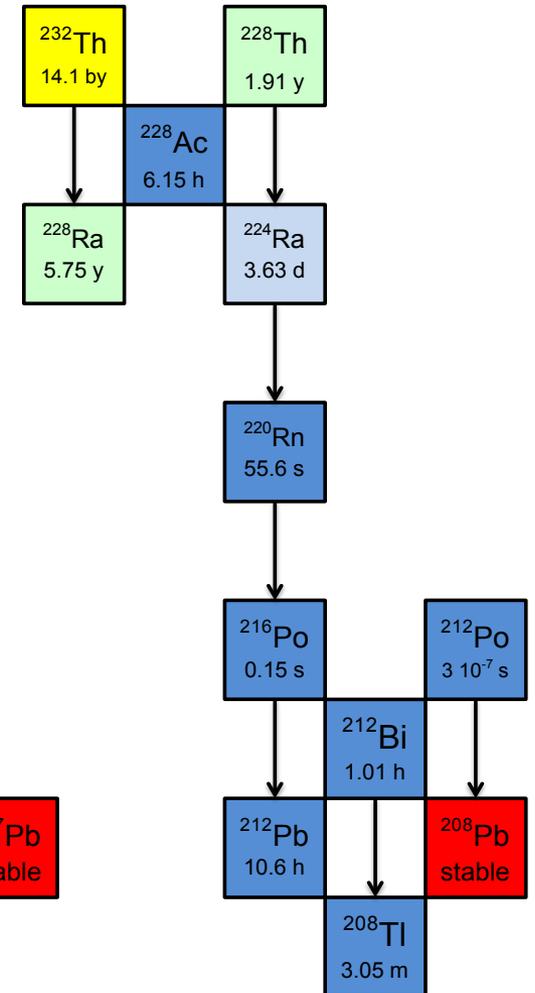
## $^{238}\text{U}$ -series



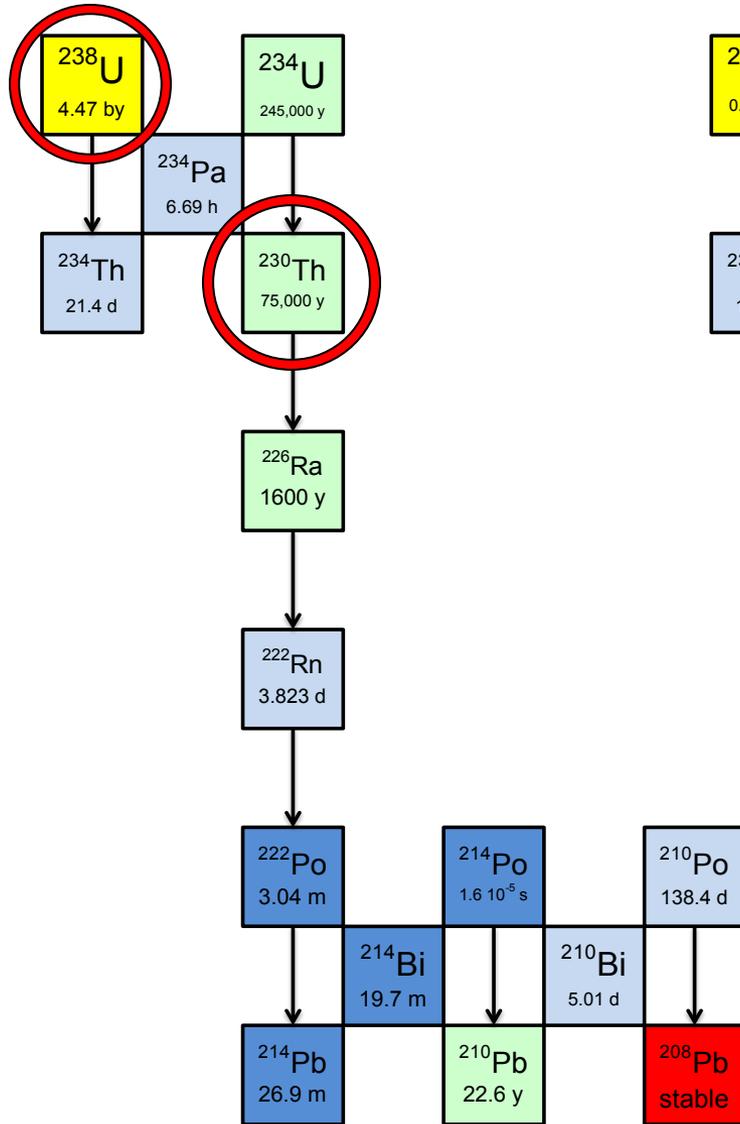
## $^{235}\text{U}$ -series



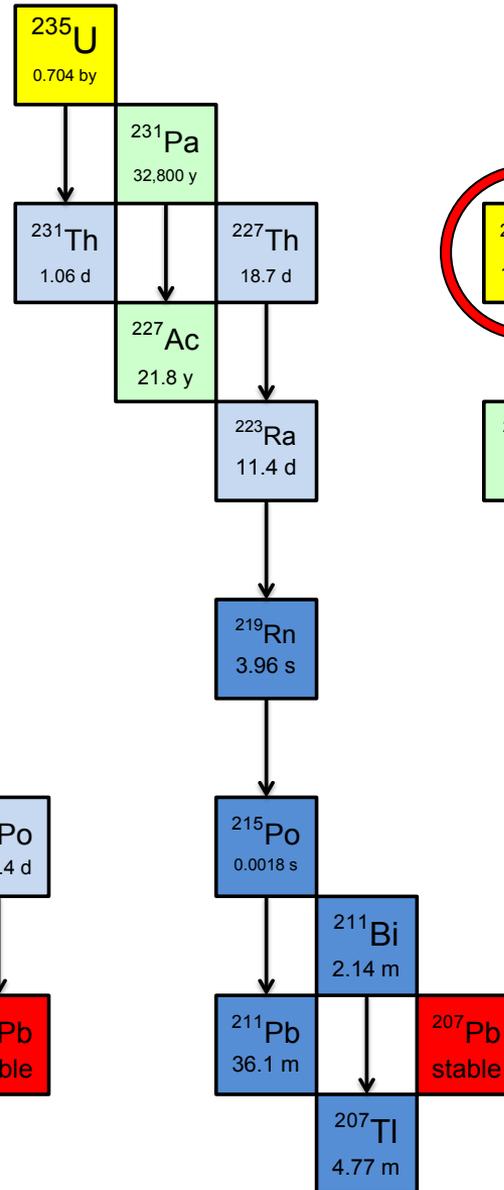
## $^{232}\text{Th}$ -series



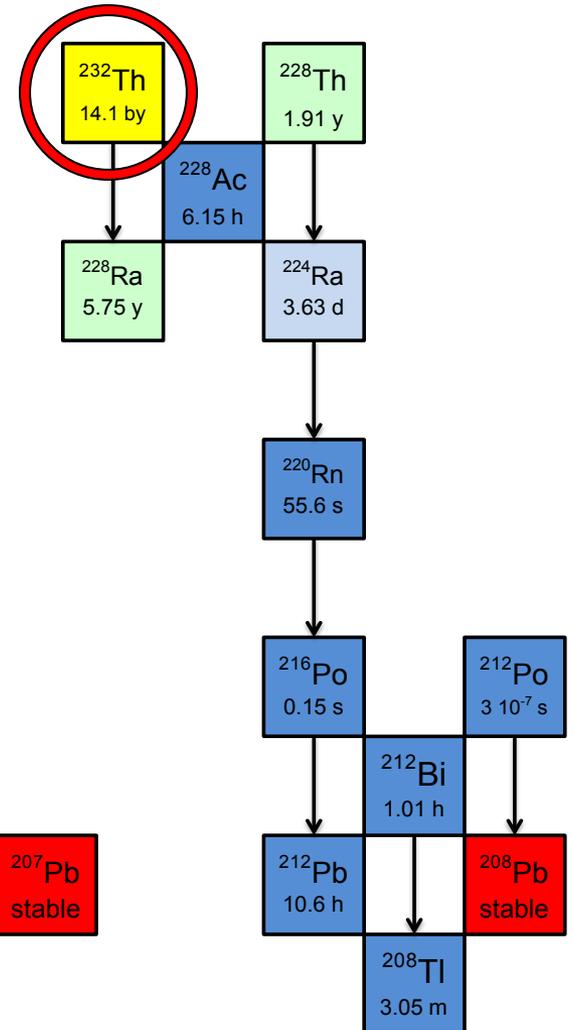
## $^{238}\text{U}$ -series



## $^{235}\text{U}$ -series



## $^{232}\text{Th}$ -series

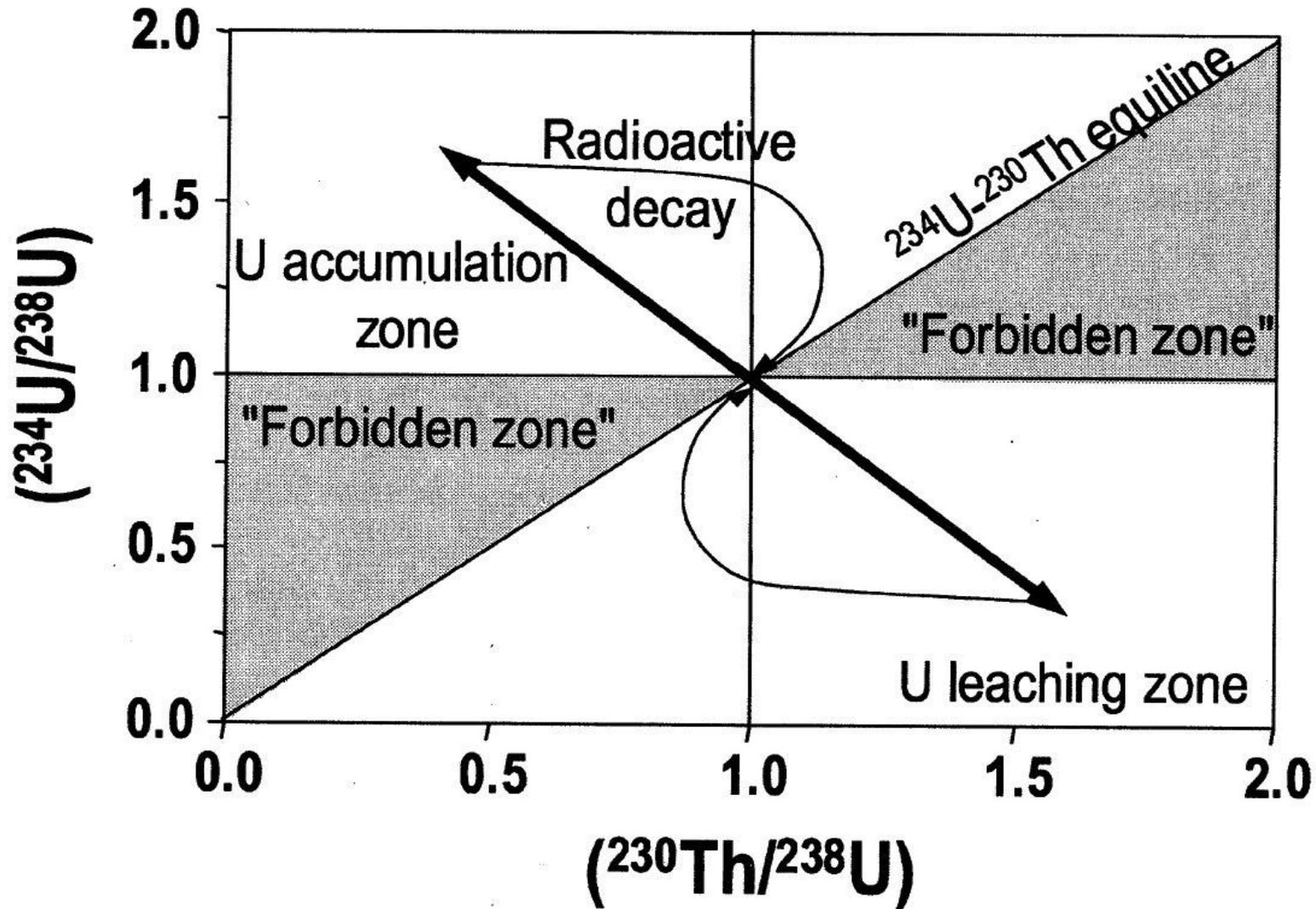


## *$^{226}\text{Ra} - ^{230}\text{Th}$ disequilibrium diagram*

Figure of radioactive disequilibria between  $^{226}\text{Ra}$ - $^{230}\text{Th}$  and  $^{238}\text{U}$ - $^{230}\text{Th}$  in lavas from austral and southern volcanic zones removed due to copyright restriction.

After Figure 1 in Sigmarsson, O., J. Chmeleff, J. Morris, and L. Lopez-Escobar. "Origin of  $^{226}\text{Ra}$ - $^{230}\text{Th}$  disequilibria in arc lavas from southern Chile and implications for magma transfer time." *Earth and Planetary Science Letters* 196, no. 3 (2002): 189-196.

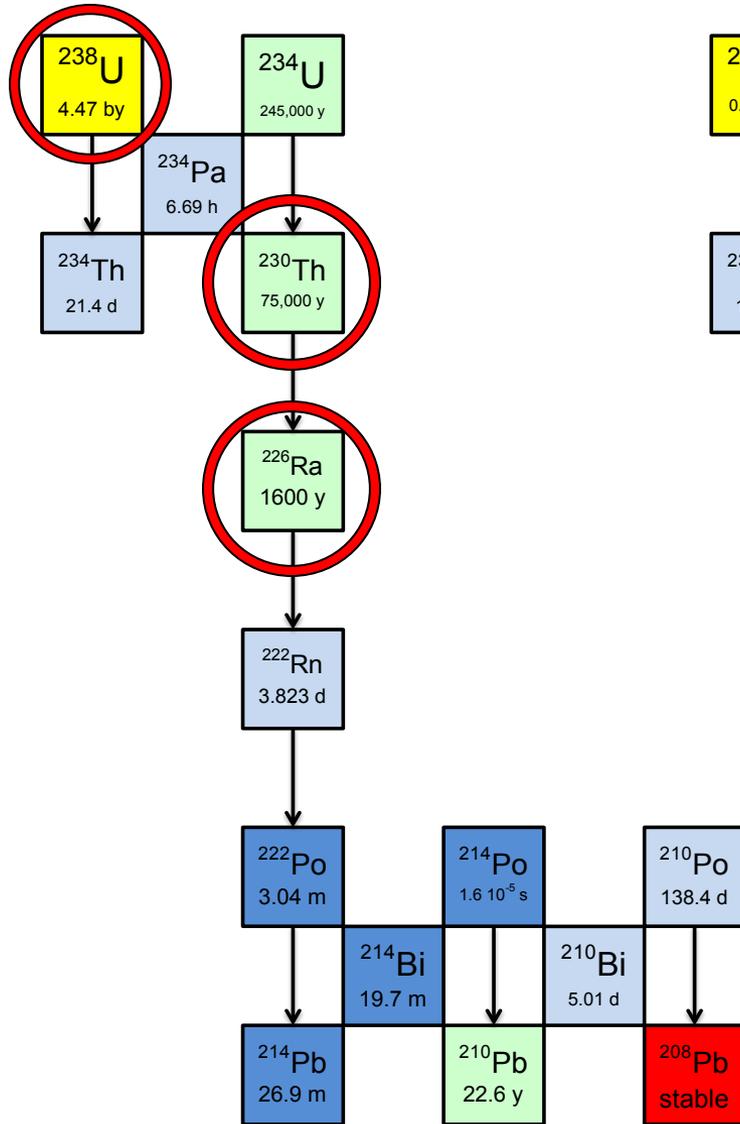
*$^{230}\text{Th}$ - $^{234}\text{U}$ - $^{238}\text{U}$  activity ratio diagram*



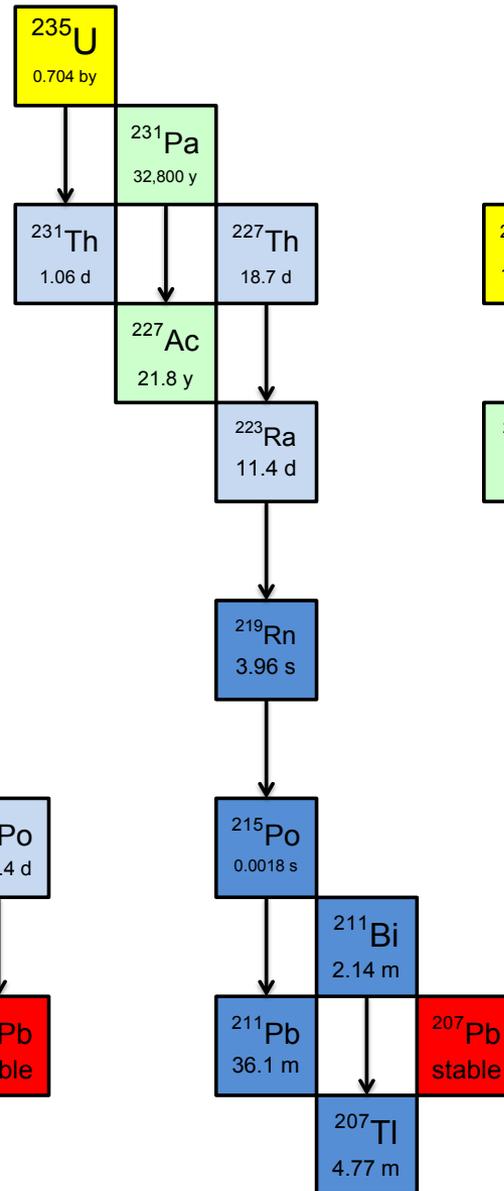
Courtesy of Mineralogical Society of America. Used with permission.

From: Chabaux, Riotte and Dequincey, *U-Th-Ra Fractionation during weathering and river transport*. In: Bourdon et al. (Eds), *Uranium-series geochemistry, Rev. Mineral. Geochem.*, vol. 52, chapter 13, 533-576.

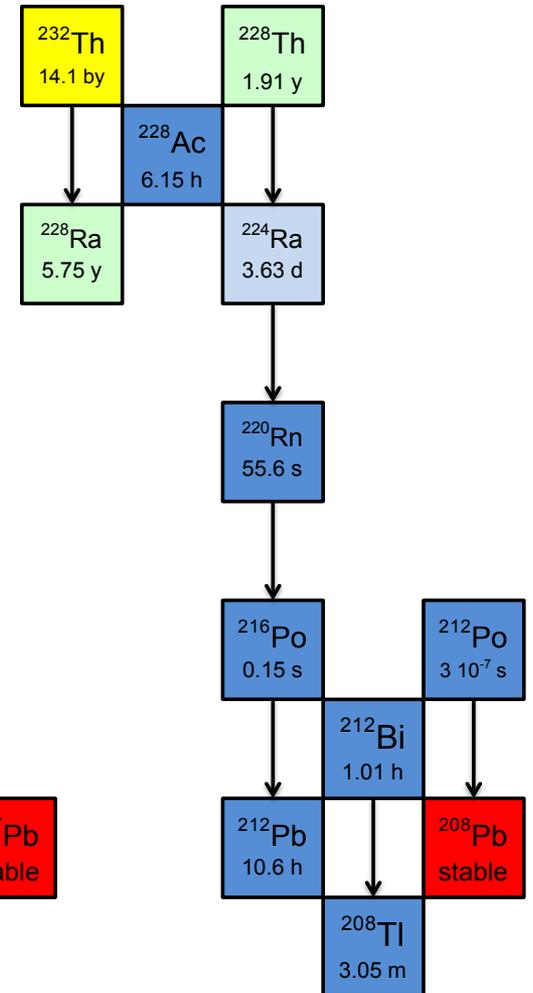
## $^{238}\text{U}$ -series



## $^{235}\text{U}$ -series



## $^{232}\text{Th}$ -series

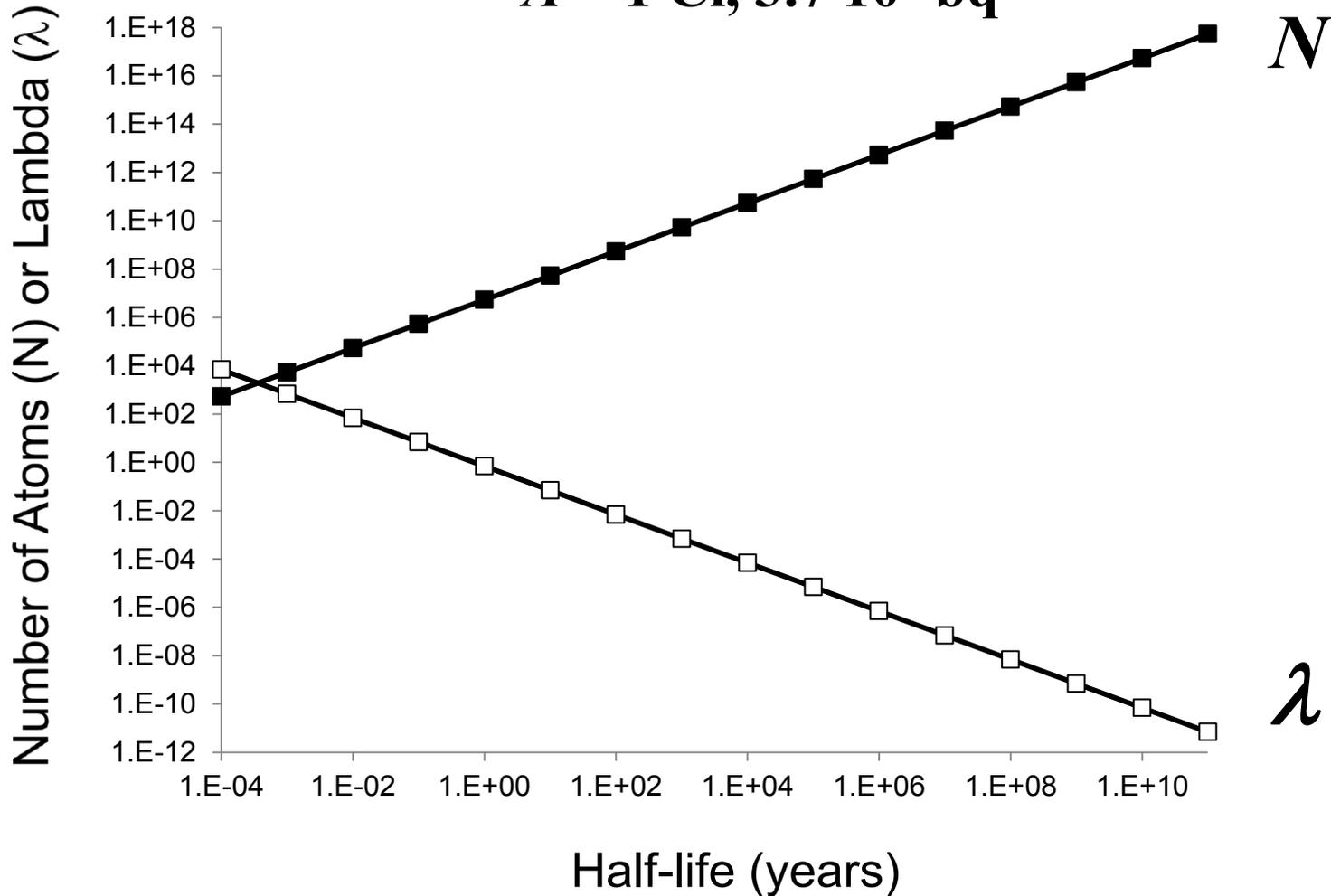


# Further Reading...

- Bourdon, B. et al. (Ed.) Uranium-Series Geochemistry, Rev. Mineral. & Geochem., vol. 52, p. 20-21 (general solution to U-series equations).
- Bourdon, B. et al. (Ed.) Uranium-Series Geochemistry, Rev. Mineral. & Geochem., vol. 52, p. 2-7 (U-series introduction).
- DecaySeries toy (simple Excel file).

$$Activity = (\lambda N)$$

$$A = 1 \text{ Ci}, 3.7 \cdot 10^6 \text{ bq}$$



## *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

$$N^* = 2N$$

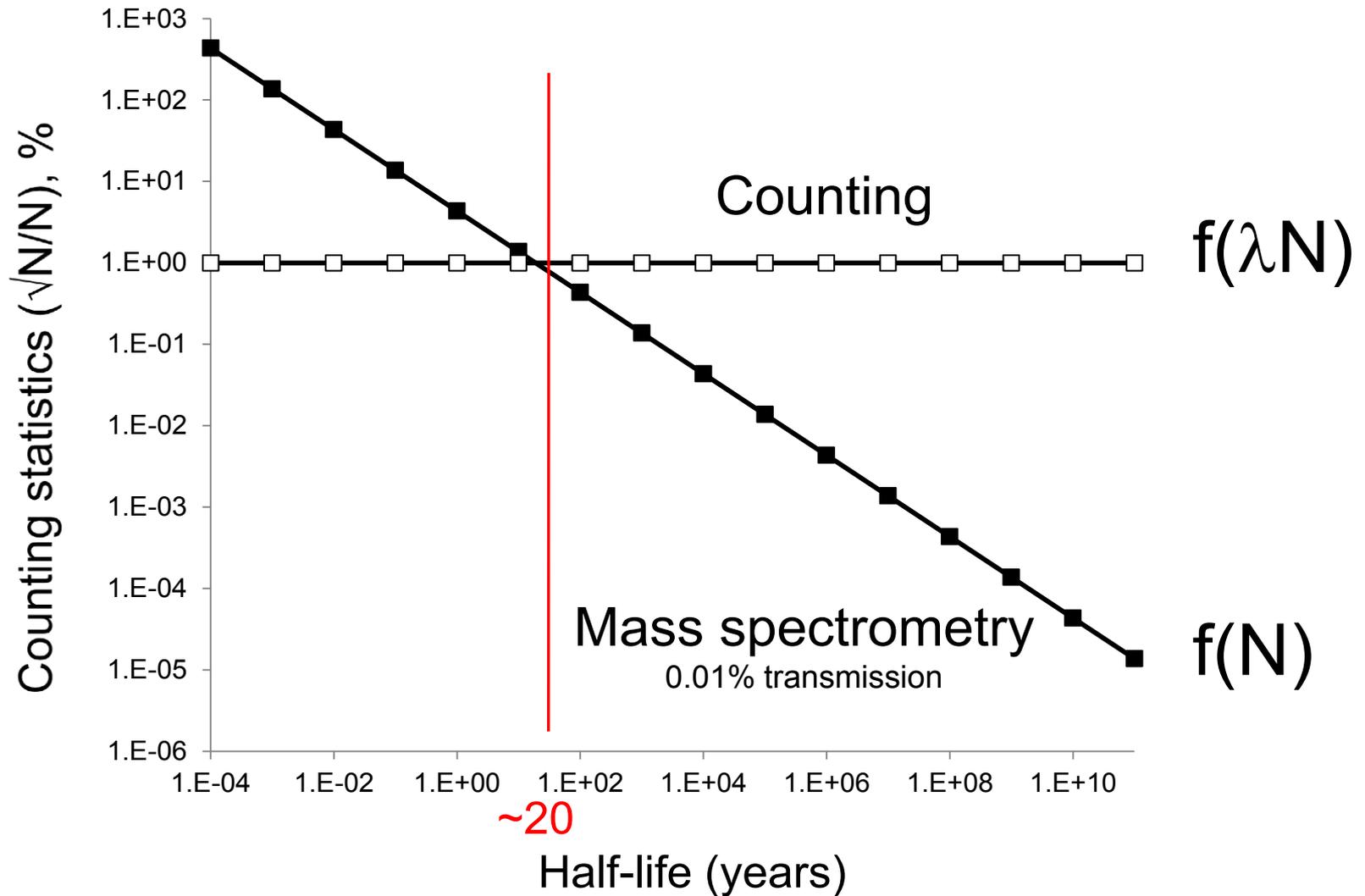
the fractional uncertainty is  $\sqrt{(2N)}/2N = 1/\sqrt{(2N)}$

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, or count rate). 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.  $m_2 = m_4$ , if  $m_1$  and  $m_3$  are isotopes in the numerator). This trend is often distinct from a instrumental fractionation trend and helps to assess what process dominates the uncertainty of your analysis.

# Measurement Uncertainty



# The Reporting of Data & Uncertainties

$$\text{mean concentration} = \bar{C} = \sum_{i=1}^N \frac{C_i}{N}$$

$$\text{r.m.s. deviation from average} = \sigma = \left\{ \sum_{i=1}^N \frac{(C_i - \bar{C})^2}{N} \right\}^{1/2}$$

Text removed due to copyright restrictions.

See page 70 of Warren, Warren S. *The physical basis of chemistry*. Academic Press, 2000.

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12.744 Marine Isotope Chemistry  
Fall 2012

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