



Connecting the U-Th and U-Pb Chronometers: New Algorithms and Applications

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ABSTRACT

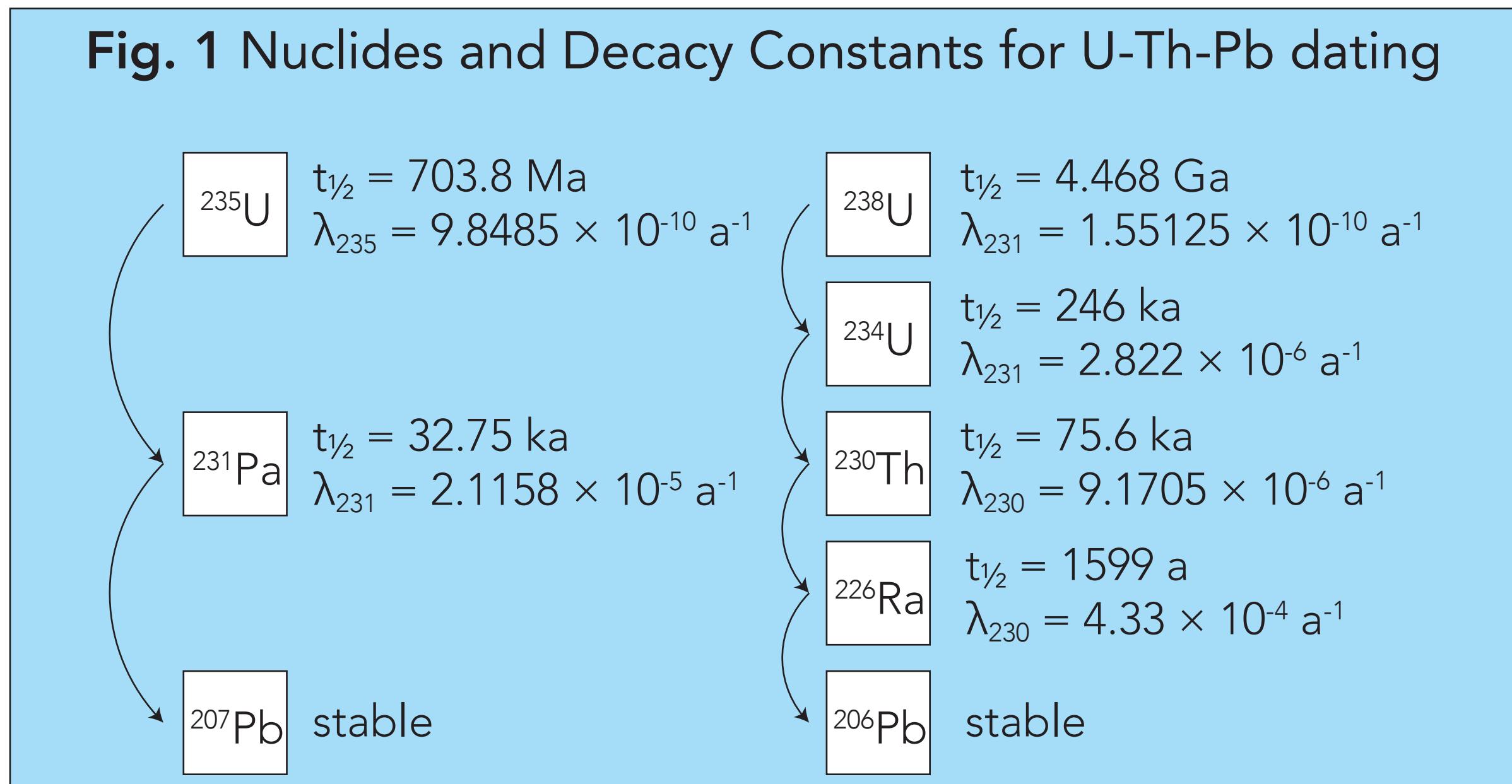
The U-Th and U-Pb geochronometers are important clocks for separate intervals of the geologic timescale. U-Th dates exploit disequilibrium in the ^{238}U intermediate daughter isotopes ^{234}U and ^{230}Th , and are often used to date corals and speleothems that are zero age through ~800 ka. The U-Pb system relies on secular equilibrium decay of ^{238}U to ^{206}Pb and ^{235}U to ^{207}Pb over longer timescales, and can be used to date samples from <1 Ma to 4.5 Ga. Disequilibrium plays a role in young U-Pb dates, but only as a nuisance correction.

Both chronometers can produce dates with uncertainties <0.1% near the center of their applicable age ranges, but become less precise at their intersection, when the ^{238}U decay chain approaches secular equilibrium and there has been little time for ingrowth of radiogenic Pb. However, if measurements or assumptions about both chronometers can be made, then they can be combined into a single, more informed date. Coupling the datasets can improve their precision and accuracy and help interrogate the assumptions that underpin each.

Working with this data is difficult for two reasons. The Bateman equations are long and cumbersome for U decay chains that include ^{238}U , ^{234}U , ^{230}Th , ^{226}Ra , ^{206}Pb and ^{235}U , ^{231}Pa , and ^{207}Pb . Also, Pb measurements often comprise varying amounts of radiogenic Pb from locally heterogeneous U concentrations mixed with varying amounts of common Pb. At present there is no established, flexible computational framework to combine information from measurements and/or assumptions of these parameters, and no way to visualize and interpret the results.

1. URANIUM SERIES DECAY CHAINS

Uranium isotopes slowly decay to lead over geologic timescales. After the initial U decay there are a number of intermediate daughter isotopes with different half lives.



2. THE DATA

A revolution in solution and laser-ablation inductively coupled plasma mass spectrometry (ICP-MS) has led to an explosion in U-series and U-Pb data. For carbonates in particular, this means high-precision $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ measurements, even close to secular equilibrium for multicollector solution analyses. For U-Pb, laser ablation provides the ability to characterize U concentrations at high spatial resolution, to locate and analyze small, isochronous sample volumes with measurable radiogenic Pb ingrowth. The set of measured data for a small region of speleothem or coral, or even zircon, might therefore look like the table at left.

WHC1 (Winnat's Head Cave)			
Measured, isochronous U-Pb data (LIC-ICPMS)			
$^{238}\text{U}/^{206}\text{Pb}$	+1σ (%)	$^{207}\text{Th}/^{206}\text{Pb}$	+1σ (%)
11908	4.52	0.6201	1.36
6021	3.27	0.7211	0.79
17158	3.76	0.5303	0.66
17403	3.15	0.5206	1.13
18284	4.33	0.5085	2.18
18324	3.70	0.4953	1.49
19407	3.37	0.4950	1.30
20253	3.35	0.4950	3.71
21634	2.88	0.4713	2.98
13899	5.9	0.5766	2.10
23399	2.94	0.4197	3.55
18481	3.42	0.4996	2.41
20165	3.11	0.4977	3.76
21060	2.90	0.4320	3.02
18253	3.25	0.4972	2.63
14899	3.11	0.5511	1.62
17203	3.15	0.5132	2.23
17445	3.31	0.5124	2.43
24598	2.86	0.3727	2.35
19235	2.57	0.4676	2.00
25069	4.26	0.3450	3.20
19341	4.79	0.3377	3.16
20458	3.20	0.3177	3.03
26498	3.19	0.3374	3.86
26579	2.96	0.3567	2.23
18087	9.09	0.4691	2.99
22788	2.38	0.3372	2.77
18114	3.21	0.3921	3.07
21711	5.38	0.4084	2.27
Assumptions:			
Initial $^{231}\text{Pa} = 0$, initial $^{226}\text{Ra} = 0$			
$^{238}\text{U}/^{235}\text{U}_{\text{init}} = 137.82$			

3. SEPARATE CHRONOMETERS

U-Pb dates, which make use of the decay of uranium to its stable daughter product, Pb, can be calculated using the "conventional" age equation. For instance, for the decay of ^{238}U to ^{206}Pb ,

$$t_{206/238} = \frac{1}{\lambda_{238}} \log \left[\left(\frac{^{206}\text{Pb}}{^{238}\text{U}} \right)_{\text{rad}} + 1 \right] \quad (1)$$

For phases such as zircon or monazite that start out with a deficit in or excess of ^{230}Th , this equation can be modified to make a "Th correction."

$$\left(\frac{^{206}\text{Pb}}{^{238}\text{U}} \right)_{\text{rad}} = e^{\lambda_{238} t} \frac{^{230}\text{Th}}{^{238}\text{U}}_{\text{init}} - 1 - \left(\frac{^{230}\text{Th}}{^{238}\text{U}} \right)_{\text{eqbm}} \quad (2)$$

U-Th carbonate dates utilize disequilibrium at the beginning of the ^{238}U decay chain, in the isotopes ^{238}U - ^{234}U - ^{230}Th . For instance, carbonates often crystallize incorporating an excess of ^{234}U and negligible ^{230}Th . The subsequent predictable return to secular equilibrium over time can be used to date the carbonate using a solution to equations first proposed by H. Bateman (1910).

$$e^{-\lambda_{230} t} \left[\left(\frac{^{234}\text{U}}{^{238}\text{U}} \right) - 1 \right] \left(\frac{\lambda_{230}}{\lambda_{238} - \lambda_{234}} \right) \left(1 - e^{(\lambda_{234} - \lambda_{230}) t} \right) = 1 - \left(\frac{^{230}\text{Th}}{^{238}\text{U}} \right) \quad (3)$$

The U-Pb equation includes radiogenic Pb ingrowth, but does not account for disequilibrium ^{234}U . Work by Bateman (1910) does not include radiogenic ingrowth of a stable daughter isotope. And neither set of equations incorporate the relatively long-lived isotopes ^{231}Pa and ^{226}Ra , whose addition adds factorially more terms to solutions using Bateman's approach.

To create a system of equations that incorporates how the relative abundance of each nuclide in Figure 1 changes through time, it's easiest for first write out the linear system of differential equations that describes each isotope's abundance through time. The following example includes only the

^{238}U - ^{234}U - ^{230}Th - ^{206}Pb isotopes, but can easily be generalized to include ^{226}Ra and the ^{235}U - ^{231}Pa - ^{207}Pb system.

$$\begin{aligned} d/dt(n_{238}) &= -\lambda_{238} n_{238} \\ d/dt(n_{234}) &= \lambda_{238} n_{238} - \lambda_{234} n_{234} \\ d/dt(n_{230}) &= \lambda_{234} n_{234} - \lambda_{230} n_{230} \\ d/dt(n_{206}) &= \lambda_{230} n_{230} \end{aligned} \quad (4)$$

4. THE MATRIX EXPONENTIAL

The system of equations (4) can be expressed as a single matrix equation. The relative abundances of the isotopes is captured in a vector \mathbf{n} .

$$\frac{d}{dt} \begin{bmatrix} n_{238} \\ n_{234} \\ n_{230} \\ n_{206} \end{bmatrix} = \begin{bmatrix} -\lambda_{238} & 0 & 0 & 0 \\ \lambda_{238} & -\lambda_{234} & 0 & 0 \\ 0 & \lambda_{234} & -\lambda_{230} & 0 \\ 0 & 0 & \lambda_{230} & 0 \end{bmatrix} \begin{bmatrix} n_{238} \\ n_{234} \\ n_{230} \\ n_{206} \end{bmatrix} \quad (5)$$

$$\frac{d}{dt} \mathbf{n} = \mathbf{A} \mathbf{n} \quad (6)$$

Just like a linear differential equation can be solved by an exponential, a linear system of differential equations can be solved by a matrix exponential. Here, \mathbf{n}_0 represents the initial abundances and \mathbf{n}_t the abundances after a time t has elapsed, and \mathbf{A} is a decay constant matrix.

$$\begin{bmatrix} n_{238} \\ n_{234} \\ n_{230} \\ n_{206} \end{bmatrix}_t = \exp \left(\begin{bmatrix} -\lambda_{238} & 0 & 0 & 0 \\ \lambda_{238} & -\lambda_{234} & 0 & 0 \\ 0 & \lambda_{234} & -\lambda_{230} & 0 \\ 0 & 0 & \lambda_{230} & 0 \end{bmatrix} t \right) \begin{bmatrix} n_{238} \\ n_{234} \\ n_{230} \\ n_{206} \end{bmatrix}_0 \quad (7)$$

$$n_t = e^{\mathbf{A}t} \mathbf{n}_0 \quad (8)$$

In this system, the n only need to be proportional to the number of atoms of each isotope, and atom and activity ratios can be calculated using the ratio of the vectors' components. This matrix exponential equation is complete, and makes none of the simplifying assumptions used to write equations (1-3). The equation can also be turned around to case the initial abundances as a function of the (measured) modern-day relative isotope abundances.

$$\begin{bmatrix} n_{238} \\ n_{234} \\ n_{230} \\ n_{206} \end{bmatrix}_0 = \exp \left(- \begin{bmatrix} -\lambda_{238} & 0 & 0 & 0 \\ \lambda_{238} & -\lambda_{234} & 0 & 0 \\ 0 & \lambda_{234} & -\lambda_{230} & 0 \\ 0 & 0 & \lambda_{230} & 0 \end{bmatrix} t \right) \begin{bmatrix} n_{238} \\ n_{234} \\ n_{230} \\ n_{206} \end{bmatrix}_t \quad (9)$$

$$\mathbf{n}_0 = e^{-\mathbf{A}t} \mathbf{n}_t \quad (10)$$

5. EVALUATING THE MATRIX EXPONENTIAL

The matrix \mathbf{A} of decay constants controls the ingrowth and radioactive decay of each isotope. Some insight into the system, and a simpler way to evaluate the matrix exponential, can be gained with an eigendecomposition of \mathbf{A} ,

$$\mathbf{A} = \mathbf{Q} \mathbf{A}^{-1} \mathbf{Q}^{-1}, \quad e^{\mathbf{A}t} = \mathbf{Q} e^{\mathbf{A}t} \mathbf{Q}^{-1} \quad (11)$$

\mathbf{A} is a diagonal matrix that contains the eigenvalues of \mathbf{A} , and \mathbf{Q} contains, as its columns, the corresponding eigenvectors. For \mathbf{A} in equation (5),

$$\mathbf{A} = \begin{bmatrix} -\lambda_{238} & 0 & 0 & 0 \\ 0 & -\lambda_{234} & 0 & 0 \\ 0 & 0 & -\lambda_{230} & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad (12)$$

$$e^{\mathbf{A}t} = \begin{bmatrix} e^{-\lambda_{238}t} & 0 & 0 & 0 \\ 0 & e^{-\lambda_{234}t} & 0 & 0 \\ 0 & 0 & e^{-\lambda_{230}t} & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad (13)$$

$$\mathbf{Q} = \begin{bmatrix} -((\lambda_{238} - \lambda_{234})(\lambda_{238} - \lambda_{230})) / (\lambda_{234}\lambda_{230}) & 0 & 0 & 0 \\ \lambda_{238} - \lambda_{234} - \lambda_{230} / (\lambda_{234}\lambda_{230}) & 0 & 0 & 0 \\ -\lambda_{238} / \lambda_{230} & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix} \quad (14)$$

$$\mathbf{Q}^{-1} = \begin{bmatrix} -(\lambda_{234}\lambda_{230}) / ((\lambda_{238} - \lambda_{234})(\lambda_{238} - \lambda_{230})) & 0 & 0 & 0 \\ (\lambda_{238}\lambda_{230}) / ((\lambda_{238} - \lambda_{234})(\lambda_{238} - \lambda_{230})) & \lambda_{230} / (\lambda_{234} - \lambda_{230}) & -1 & 0 \\ -\lambda_{238} / \lambda_{230} & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix} \quad (15)$$

Using the method above, the matrix exponentials in equations (7) and (9) can be reframed as matrix products and very accurately evaluated with modern math software (e.g., Moler and Van Loan, 2003).

6. PLOTTING DISEQUILIBRIUM CONCORDIA

A larger version of equations (7) and (9), which include ^{226}Ra and the 235