Different representations of the relative abundances of uranium series isotopes

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There are three ways that geochemists use to communicate the relative abundance of two radioactive species: an atom ratio, an activity ratio, and delta (δ) notation. The examples below are formulated for the isotopes ^{234}U and ^{238}U, but could be used for any such pair. ^{238}U decays to ^{234}U with a half-life of 4.5 billion years, and ^{234}U decays to ^{230}Th with a half-life of 246,000 years.

1. **Atom ratios** are the simplest: If there are 60 atoms of ^{234}U and 10^6 atoms of ^{238}U in a sample, then the atom ratio of ^{234}U to ^{238}U is

$$^{234}\mathrm{U}/^{238}\mathrm{U} = 6 \times 10^{-5}. \tag{1}$$

   Atom ratios will always be greater than or equal to zero. They have the advantage over other forms in that they are absolute values, and not formulated relative to a reference value.

2. **Activity ratios** are the ratios of the activities of the two isotopes. The activity of a sample is the number of decays per unit time it is undergoing. To determine the activity of an isotope, multiply the number of atoms present (N) by its decay constant.

$$A = -\frac{\mathrm{d}N}{\mathrm{d}t} = \lambda N \tag{2}$$

   Decay constants are usually represented by the greek letter lambda (λ) and are related to the more commonly known half-life $t_{1/2}$ by the equation

$$t_{1/2} = \frac{\ln(2)}{\lambda} \tag{3}$$

   For the example above with 60 atoms of ^{234}U and 10^6 atoms of ^{238}U, the activity ratio is

$$\left[^{234}\mathrm{U}/^{238}\mathrm{U}\right] = \frac{\lambda_{234}N_{234}}{\lambda_{238}N_{238}} \approx \frac{(2.82206 \times 10^{-6})(60)}{(1.55125 \times 10^{-10})(10^6)} \approx 1.0915 \tag{4}$$

Activity ratios are often denoted with square brackets, or some other mechanism that is explained nearby, to distinguish them from atom ratios. Activity ratios are often more convenient than atom ratios for geochemists to understand because they are directly related to the radioactive processes that have taken place to create the sample. Unfortunately, we do not know the uranium series decay constants perfectly. When make better measurements of the decay constants and revise their values, all activity ratios that were calculated from atom ratios must be recalculated.

3. When the two isotopes being compared are a parent and daughter pair, an activity ratio of 1 indicates a special condition called *secular equilibrium* where both isotopes are decaying at the same rate. Over long periods of time as a closed system (for U-series, a million years or more), daughter isotopes like ^{234}U radioactively decay (to ^{230}Th) just as fast as they are produced (from ^{238}U). Geologic processes – like those that form of a speleothem or coral – can perturb that state of secular equilibrium, for instance by enriching the sample in ^{234}U. Then the sample's return to secular equilibrium will happen in a predictable, time-dependent way that we can use to date when that sample again became a closed system.

   A $\left[^{234}\mathrm{U}/^{238}\mathrm{U}\right]$ activity ratio greater than 1 indicates that there is more ^{234}U than ^{238}U relative to secular equilibrium, and the ^{234}U will decrease over time, since its activity and therefore decay rate is greater than decay rate of the ^{238}U that is producing it. A $\left[^{234}\mathrm{U}/^{238}\mathrm{U}\right]$ activity ratio less than 1 will likewise increase over time, as ^{238}U decays to ^{234}U. In these examples, we are interested in the often small difference between a measured activity ratio and the ratio at secular equilibrium.

   To express small differences between the atom or activity ratio of a reference ratio – a sample and a standard or known value – geochemists often use **delta (δ) notation**. A delta value has units of per mil (‰), or parts per thousand, an analog to percent or parts per hundred. The general formula for calculating a delta value for two isotopes x and y is

$$\delta x = \left(\frac{(x/y)_{sample}}{(x/y)_{reference}} - 1 \right) \times 1000 \tag{5}$$

   For uranium series measurements, by convention we use activity ratios in equation (6), and all ratios have ^{238}U in the denominator, since it's the parent isotope. So the formula for δ^{234}U is

$$\delta^{234}\mathrm{U} = \left(\frac{\left[^{234}\mathrm{U}/^{238}\mathrm{U}\right]_{sample}}{\left[^{234}\mathrm{U}/^{238}\mathrm{U}\right]_{reference}} - 1 \right) \times 1000 \tag{6}$$

   Since we use a secular equilibrium activity ratio of 1 as our reference value, we can simplify this to

$$\delta^{234}\text{U} = \left(\left[{}^{234}\text{U}/{}^{238}\text{U} \right]_{sample} - 1 \right) \times 1000 \tag{7}$$

For our example above, with 60 atoms of ^{234}U and 10^6 atoms of ^{238}U,

$$\delta^{234}\text{U} = (1.0915 - 1) \times 1000 = 91.5‰ \tag{8}$$

Like activity ratios, if you calculate a delta value from an atom ratio, the delta value must be revised when the decay constant values are revised.

A few final points.

- You can use equations (5) and (8) to calculate activity ratios from atom ratios and delta values from activity ratios, and solve each equation to do the reverse. These are three ways of expressing the exact same information, and many plots are created with either activity ratios or a delta values, according to users' preferences. Redux should give users the ability to make these choices.
- Sometimes people write the curly 'd' used for a partial derivative (∂) instead of the Greek letter δ in delta notation. This is incorrect.
- Equation (7) is useful if a lab is using a standard that was thought to be in secular equilibrium but has recently been shown to be variable, such as the Harwell uraninite (HU-1) reference material. Andrea and I will talk to you about how to make this correction in practice.