Uranium oxide interference correction algorithms

Measurement of the uranium isotopic composition of double-spiked (^{233}U-^{235}U) samples as UO_2^+ species requires the subtraction of the isobaric interference of ^{18}O-bearing $^{233}UO_2$ on the predominant target $^{235}U^{16}O_2$ peak at mass 267. The probability of forming a double ^{17}O-bearing uranium dioxide molecule is so low as to make a $^{233}U^{17}O_2$ interference of negligible importance for this measurement. The probability of an ^{18}O dioxide substitution is estimated by the relative abundance of ^{18}O, also safely approximated by $^{18}O/^{16}O$, which is assigned a value of 0.002 (IUPAC, 1997). Both possible ^{18}O substitutions into the dioxide molecule must be considered. The maths for the correction of the two measured U isotope ratios are given below.

For correcting the $^{235}U/^{233}U$ (or $^{233}U/^{235}U$) ratio:

$$\left(\frac{267}{265}\right)_{meas} = \frac{^{235}U^{16}O^{16}O + {}^{233}U^{18}O^{16}O + {}^{233}U^{16}O^{18}O}{^{233}U^{16}O^{16}O} \tag{1}$$

$$^{233}U^{18}O^{16}O = {}^{233}U^{16}O^{18}O = {}^{233}U^{16}O^{16}O\left(\frac{^{18}O}{^{16}O}\right) \tag{2}$$

$$\left(\frac{267}{265}\right)_{meas} = \frac{^{235}U^{16}O^{16}O + {}^{233}U^{16}O^{16}O\left(\frac{^{18}O}{^{16}O}\right) + {}^{233}U^{16}O^{16}O\left(\frac{^{18}O}{^{16}O}\right)}{^{233}U^{16}O^{16}O} \tag{3}$$

$$\left(\frac{267}{265}\right)_{meas} = \frac{^{235}U^{16}O^{16}O + {}^{233}U^{16}O^{16}O\left[\left(\frac{^{18}O}{^{16}O}\right) + \left(\frac{^{18}O}{^{16}O}\right)\right]}{^{233}U^{16}O^{16}O} \tag{4}$$

$$\left(\frac{267}{265}\right)_{meas} = \frac{^{235}U^{16}O^{16}O}{^{233}U^{16}O^{16}O} + \left[\left(\frac{^{18}O}{^{16}O}\right) + \left(\frac{^{18}O}{^{16}O}\right)\right] \tag{5}$$

$$\frac{^{235}U^{16}O^{16}O}{^{233}U^{16}O^{16}O} = \left(\frac{267}{265}\right)_{true} \tag{6}$$

$$\left(\frac{267}{265}\right)_{meas} = \left(\frac{267}{265}\right)_{true} + \left[\left(\frac{^{18}O}{^{16}O}\right) + \left(\frac{^{18}O}{^{16}O}\right)\right] \tag{7}$$

$$\left(\frac{^{18}O}{^{16}O}\right) = 0.002 \quad \text{(IUPAC 1997)} \tag{8}$$

$$\left(\frac{267}{265}\right)_{meas} = \left(\frac{267}{265}\right)_{true} + [0.002 + 0.002] = \left(\frac{267}{265}\right)_{true} + 0.004 \quad (9)$$

$$\left(\frac{267}{265}\right)_{true} = \left(\frac{267}{265}\right)_{meas} - 0.004 \quad (10)$$

$$\left(\frac{^{233}U}{^{235}U}\right) = \left(\frac{265}{267}\right)_{true} = \frac{1}{\left(\frac{267}{265}\right)_{true}} = \frac{1}{\left(\frac{267}{265}\right)_{meas} - 0.004} = \frac{1}{\frac{1}{\left(\frac{265}{267}\right)_{meas}} - 0.004} \quad (11)$$

The final form of eqn. 11 accommodates those accustomed to both measuring and then entering the $^{233}U/^{235}U$ ratio into data reduction software.

For correcting the $^{238}U/^{235}U$ ratio:

$$\left(\frac{270}{267}\right)_{true} = \left(\frac{270}{265}\right)_{meas} \times \left(\frac{265}{267}\right)_{true} \quad (12)$$

$$\left(\frac{270}{267}\right)_{true} = \left(\frac{270}{265}\right)_{meas} \times \left(\frac{265}{267}\right)_{true} \quad (13)$$

Combining with eqn. 11…

$$\left(\frac{^{238}U}{^{235}U}\right) = \left(\frac{270}{267}\right)_{true} = \left(\frac{270}{265}\right)_{meas} \times \frac{1}{\frac{1}{\left(\frac{265}{267}\right)_{meas}} - 0.004} \quad (14)$$

For those used to measuring the $^{238}U/^{235}U$ and $^{233}U/^{235}U$ ratios…

$$\left(\frac{270}{265}\right)_{meas} = \frac{\left(\frac{270}{267}\right)_{meas}}{\left(\frac{265}{267}\right)_{meas}} \quad (15)$$

$$\left(\frac{^{238}U}{^{235}U}\right) = \left(\frac{270}{267}\right)_{true} = \frac{\left(\frac{270}{267}\right)_{meas} \Big/ \left(\frac{265}{267}\right)_{meas}}{\frac{1}{\left(\frac{265}{267}\right)_{meas}} - 0.004} \quad (16)$$

This last form accommodates those accustomed to both measuring and entering the $^{238}U/^{235}U$ and $^{233}U/^{235}U$ ratios into data reduction software. For Sector-54 users measuring on Faraday cups, the corrections (eqns. 11 and 16) can be simply added as functions to static multi-collection ADS files set up in parallel with existing U metal files but measuring masses 265, 267, and 270. For single collector Daly measurements, these corrections can be done off-line (for example as a group of cells within the 'Reduce Data' page of Pb-MacDat).

These algorithms, including the assumed ^{18}O abundance were confirmed empirically at MIT by splitting large spiked sample U loads and running as both metal and oxide. When combined with the sample Pb isotope abundances, there was excellent agreement (better than 0.1%) in calculated Pb/U ratios between the metal and corrected oxide uranium isotope measurements.

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