Synthetic 'age solutions' reference materials for U-Th geochronology

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Over the past 15 years there has been considerable improvement in our ability to measure U and Th isotope ratios and concentrations resulting in a reduction of U-Th age uncertainties by an order of magnitude (age uncertainties are now as low as 0.1%). The accuracy of these dates is dominated by (1) the U/Th tracer calibration; (2) mass spectrometry, (3) various corrections applied, and (4) 'constants' used in the age calculation (secular equlibrium and decay constants, the $^{235}U/^{238}U$ value of natural U etc.). Some of these parameters can be considered as 'systematic' (i.e., decay constant uncertainties) and others either contain a random component or are systematic but 'laboratory' specific (such as tracer calibration).

At present inter-laboratory agreement and intra-laboratory long-term external reproducibility of U-Th Isotope Dilution Isotope Ratio Mass Spectrometry data is assessed through analyses of natural cabonate 'standards'. Though powdered carbonates standard zircons are ideal for assessing the total system (dissolution, purification via anion echange chemistry and mass-spectrometry), these are limited in supply and not widley avaibalbe limiting their use for asessing inter-laboratory agreement. Here we outline a proposal and the initial steps taken for the development the development and calibration of a series of synthetic U-Th 'age solutions' prepared by mixing different amounts of high-purity mono-isotopic solutions (^{234}U, ^{230}Th etc.) in proportions that mimic commonly analysed materials (e.g., a last-interglacial speleothem) so that their analyses closely replicates the analytical protocols employed on normal samples. We believe these solutions will augment natural carbonate standards as a means of interlaboratory comparsion and assessment of long-term external reproducibility, and as such are intended for community use and will be made available. The intercalibration project is part of a broader community effort that has developed out of the PALSEA and EARTHTIME initiatives.

Measuring the isotopic composition of small (<5 ng) U samples by MC-ICP-MS

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Pb-Pb ages have been based on Pb isotopic measurements while assuming that the $^{238}U/^{235}U$ ratio is constant at 137.88. Using a second-generation multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), [1] has documented 3400 ppm variability in the $^{238}U/^{235}U$ ratios of calcium-aluminum-rich inclusions (CAI) in chondrites [1], corresponding to a 5 Myr deviation in calculated Pb-Pb ages. This makes clear the need to measure the U isotopic composition of all meteorites and their components when determining their Pb-Pb ages. The challenge lay in developing analytical protocols to measure the isotopic composition of typically small samples of U (<5 ng) sufficiently precisely to be useful in constraining events that occurred in the first 10 million years of the solar system. With 100 ppm uncertainty corresponding to 0.15 Myr, we must achieve less then 200 ppm uncertainty on $^{238}U/^{235}U$ ratios. We have developed a three stage chemistry starting with Eichrom's UTEVA resin followed by two progressively smaller anion columns that effectively isolates U from the sample matrix elements. U is measured using an Aridus II desolvating nebulizer on a ThermoFisher Neptune with the Jet Cone Interface, a configuration that delivers ~2500 V of signal per 1 ppm concentration of U. Running with an uptake rate of 0.15 ml/min, we analyze 5 ng for a total acquisition time of 15 min with a ^{235}U intensity of ~40 mV. Fractionation correction for the measured $^{238}U/^{235}U$ ratio is controlled by the simultaneous measurement of the synthetic equal-atom ^{233}U-^{236}U tracer IRMM 3636 that was added to samples before dissolution. Blank correction is determined by bracketing runs (of equal time as unknown runs) of the 2% HNO_3 used to dissolve samples. CRM 112a spiked with IRMM 3636 is run as a bracketing standard to monitor within run stability. Using these methods, we are able to routinely determine the isotopic composition of small (<5 ng) amounts of U separated from terrestrial rock standards and doped meteoritic matrices to better than 200 ppm precision and external reproducibility. Analyzing meteorites and their components, we have investigated the $^{238}U/^{235}U$ variability of the inner solar system.

[1] Brennecka *et al.* (2010) *Science* **327**, 449-451.