NEW MEASUREMENTS OF URANIUM DECAY CONSTANTS

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Radioisotopic dating techniques are highly valuable tools for understanding the history of physical and chemical processes in materials related to planetary sciences and nuclear forensics, and rely on accurate knowledge of decay constants and their uncertainties. The decay constants of 238U and 235U are particularly important to Earth science, and often the measured values with lowest reported uncertainties are applied, although they have not been independently verified with similar precision. New direct measurements of λ238U, λ234Th, λ235U, and λ234U are underway, using various approaches. The determination of λ238U involves measurement of 234Th ingrowth in chemically purified, isotopically enriched 238U solutions, by quantitative extraction of the Th and complete decay to 234U. The method relies on a starting material with low 234 content, careful yield tracing, and accurate measurements use the isotope dilution (ID) method with multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). To reduce the uncertainty propagated from the that of λ234Th, 234Th decay curves were measured with both a windowless gas-proportional counter and high-purity Ge (HPGe) gamma detector. For the measurement of λ235U and λ234U, isotopically enriched samples are being chemically purified and analyzed for U concentration and isotopic composition by MC-ICP-MS. Counting sources are prepared with a known quantity of U and the absolute alpha activity measured by alpha-gamma coincidence and low-geometry counting. An overarching goal of the project is to ensure the quality of results including metrological traceability to facilitate implementation across diverse disciplines.

I. INTRODUCTION

It has been widely recognized that accurate and precise decay constants (λ) are critical to radioisotopic dating, particularly the calibration benchmarks λ235U and λ238U.1 Alpha counting experiments2 in 1971 measured λ235U and λ238U with ~0.1% precision, but have never been independently validated at comparable precision and the metrological traceability of these experiments is sub-optimal.3 In past measurements of the 234U, a slight discrepancy exists between values obtained from counting experiments4,5 and those obtained from isotope ratios of geological samples.6-7 The latter are reported with higher precision, but are subject to different systematic biases including reliance upon the accuracy of λ238U. Our α-γ coincidence measurements of 234U sources were further motivated by the need to reduce the high uncertainty in the γ branching ratio of the key 120.9 keV γ-line.

II. EXPERIMENTS

II.A. 234Th ingrowth in 238U

For independent verification of λ238U, we are measuring 234Th ingrowth in aliquots of unique uranium material that is over 99.96% 238, and only 3 ppm 234. Over 40 g 238U in 4 M HNO3/0.005 M HF was doped with 232Th, sub- aliquoted for yield tracing, and divided into 6 aliquots containing 6-8 g U each. Initial Th extractions to establish t = 0 were achieved via LaF3 co-precipitation. The purified uranium aliquots were dried down and again dissolved in 4 M HNO3/0.005 M HF, sub aliquoted for Th yield measurement in the first extraction, then doped with 232Th once more and sub- aliquoted for measurements of U concentration and Th yield in the second extraction. Duplicate sub- aliquots for U assay were successively diluted and spiked with IRMM-3636 for ID analysis performed on a Nu Instruments MC-ICP-MS. Th yield measurements used a relative ID approach, to remove the influence of the uncertainty in Th concentration of the 229Th ID spike. Spiked aliquots of the extracted Th were bracketed by duplicate spiked aliquots of the U cow before separation, all measured at least twice on the same Faraday cup detectors. The Th yield (Y) was calculated by Equation 1, with fTh = aliquot mass fraction of the U cow, fAl = aliquot mass fraction of the milked Th, and STh and SU are the masses of 229Th spike solution in the Th and U, respectively. The second Th extractions occurred after various decay times between 45 and 141 days, and were achieved by a combination of LaF3 coprecipitations and anion exchange, with all extraction steps timed during both separations to allow for full 234Th ingrowth uncertainty propagation. Sub- aliquots of milked Th were weighed
for yield and separation analysis, and the bulk aliquots left to decay so that they can be measured as 234U via ID-MC-ICP-MS using IRMM-3636 spike. The yield-corrected atoms 234U measured (N234) will be used to calculate λ238U with Equation 2, where atoms 238U (N238) are treated as constant on the experimental timescale, and λ234 is the decay constant of 234Th. To lower uncertainty in λ234Th, decay curves are being measured with a windowless gas-proportional counter as well as a HPGe detector, and fitted along with thorough consideration of systematic bias and uncertainty.

\[
Y = \frac{(232/229)_{\text{Th}} \cdot f_{\text{U}}}{(234/229)_{\text{Th}} \cdot f_{\text{U}}} \quad (1)
\]

\[
\lambda_{234} = \frac{N_{234}(t) - N_{234}(0) - e^{-\lambda_{234}t}}{N_{234}(t) - N_{234}(0)e^{-\lambda_{234}t} + 1 - e^{-\lambda_{234}t}} \quad (2)
\]

II.B. Absolute activity measurements of 234U and 238U sources

The decay constants of 234U and 235U are being evaluated by measuring the absolute activities of sources with precisely quantified amounts of isotopically enriched U (99.99% 235U or 99.94% 235U). The techniques used for 234U include α-γ coincidence counting and low-geometry α counting. Purified solutions were assayed by ID-MC-ICP-MS using IRMM-3636 spike, and weighed aliquots used for counting sources. Initially sources were prepared by molecular deposition as in reference (2) but drop-cast sources are also being prepared to avoid uncertainties associated with quantifying the molecular plating yield. Sources are positioned in a vacuum chamber with an ion-implanted surface-barrier Si detector facing the U side (Ortec ULTRA-AS) and an n-type HPGe detector (Ortec, 60% relative efficiency) beneath. Each source is counted for several months in list mode using a FAST ComTec MPA-3 data acquisition system with model 7072 fixed dead-time ADCs. The list data are being evaluated to determine the absolute activity of the sources, and the apparent branching ratio of the 120.9 keV gamma ray. Concurrently, long α counts of additional sources in low-geometry defined solid-angle chambers provide an alternative way to evaluate λ234U with absolute activity measurements. Due to its complex decay scheme, accurate measurement of 235U absolute activities using the α-γ coincidence technique may require a 4π geometry in the α channel, which can be approximated using a liquid scintillation chamber as the α detector. Updated results will be discussed.

III. CONCLUSIONS

Modern measurements of the decay constants of 238U, 234Th, 234U, and 235U are underway to provide additional high-precision data for realistic evaluated values and uncertainties to be applied in radiochronometry. Experimental results and uncertainties will be discussed.

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