



Improved protactinium spike calibration method applied to ^{231}Pa – ^{235}U age-dating of certified reference materials for nuclear forensics

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Abstract

The application of multiple radiochronometers in a forensic investigation of bulk uranium provides increased confidence for interpreting age-dating results. We have developed a streamlined method for the purification of Pa and Th from bulk uranium and have applied this method in analyzing uranium certified reference materials (CRMs) IRMM-1000 and CRM U100, using the ^{231}Pa – ^{235}U and ^{230}Th – ^{234}U radiochronometers. Our improved ^{233}Pa spike calibration technique has replaced the time-intensive, conventional calibration using geologic rock standards. Paired Pa–U and Th–U age-dating analyses of CRM U100 produce concordant results. In contrast, analyses of IRMM-1000 demonstrate reproducibly-discordant Th–U and Pa–U age-dates.

Keywords Radiochronometry · Protactinium · Thorium · Age-dating

Introduction

Nuclear forensic investigations of known or unknown nuclear material commonly involve determining the production history of that material. The material's production date can in many cases be determined empirically, with a 'model age' of that material (i.e., the time elapsed since last chemical purification) measurable by radiochronometry. Model age information is an important signature in reconstructing a material's provenance and processing history, both of which are critical components in a nuclear forensic investigation. To determine the model age of a nuclear material, the relative amounts of a parent isotope and the decay product of that parent isotope, a daughter isotope, are measured by mass spectrometry methods.

Calculating the model age of a nuclear material requires two primary assumptions: (1) the daughter isotope was completely purified from the parent isotope, and (2) the sample has not lost or gained either parent or daughter isotopes, except by radioactive decay (i.e., the sample is effectively a closed system). The most common radiochronometer used in forensic investigations of bulk uranium is the ^{230}Th – ^{234}U daughter–parent decay system. Model ages of many uranium certified reference materials (CRMs) have been measured using this system [1–8]. In some cases, other daughter–parent and even granddaugher–daughter–parent radiochronometers may be applied to CRMs and other nuclear materials, [e.g., 2, 4]. Using multiple radiochronometers can lead to greater confidence in the interpretation of age-dating results and provide insight into processes that lead to concordant or discordant ages. For example, the ^{231}Pa – ^{235}U (Pa–U) and ^{230}Th – ^{234}U (Th–U) radiochronometers can be applied in tandem to better elucidate sample production histories. Importantly, discordant model ages for a given sample from multiple radiochronometers demonstrate that the two major assumptions described above can be violated.

In 2013, the mass spectrometry group at Lawrence Livermore National Laboratory (LLNL) published analysis methods for ^{231}Pa – ^{235}U age-dating and presented results

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for CRMs (U005A, U030A, U630, CRM 125A) with concordant ^{230}Th – ^{234}U and ^{231}Pa – ^{235}U model ages [9]. Since that time, we have improved our ^{231}Pa – ^{235}U age-dating capability by modifying our ^{233}Pa spike preparation and calibration methods, improving our sample purification chemistry, and refining our data reduction algorithms. We have streamlined our chemical purification procedures to quantify both daughter isotopes, ^{230}Th and ^{231}Pa , from single aliquots of dissolved bulk uranium material. One advantage of determining ^{230}Th and ^{231}Pa assay from the same aliquot is for the scenario where one is sample-limited, e.g., samples are low concentration; young, low enriched or depleted uranium; or limited availability. Taken together, our improved process has resulted in increased throughput of ^{231}Pa – ^{235}U model age determinations of CRMs, nuclear materials, and samples for international round robin exercises (i.e., 4, 9).

The most significant improvement to our radiochronometry methods is the use of an in-house ^{231}Pa standard to calibrate ^{233}Pa spikes, which are produced as-needed approximately 4–5 times per year. By utilizing an in-house ^{231}Pa standard solution as a spike calibrant, we have eliminated the complex chemical separation procedures required to produce ^{231}Pa secular equilibrium reference solutions from geologic matrices, as described in [9, 10]. This advance permits rapid spike calibration on the order of approximately 2 days compared with previous calibration methods which can take up to 2 weeks. This rapid spike calibration facilitates the application of multiple radiochronometers to nuclear forensic samples in a timely manner. In this contribution we present radiochronometry results for CRMs U100 and IRMM-1000, and compare the ^{230}Th – ^{234}U model dates to ^{231}Pa – ^{235}U model dates for each material.

Theory

To review, in applying daughter–parent radiochronometers to nuclear materials, the following two criteria must be met if a model age records the time elapsed since last chemical purification: (1) the material was completely purified of daughter isotopes, and (2) no loss or gain of daughter isotope has occurred (i.e., closed system). The daughter–parent isotope age-dating equation (Eq. 1) is used to calculate the age, t , of the material. The decay constants (λ) used for calculating model ages are from [11–13]. The ^{230}Th half-life = $7.569 \times 10^4 \pm 115$ years, and the ^{234}U half-life = 2.4525×10^5 years. The ^{231}Pa half-life = $32,713 \pm 110$ years, and the ^{235}U half-life = $7.0381 \times 10^8 \pm 4.8 \times 10^5$.

$$t = \left(\frac{1}{\lambda_{\text{parent}} - \lambda_{\text{daughter}}} \right) \times \ln \left(1 - \left(\frac{N_{\text{daughter}}}{N_{\text{parent}}} \times \frac{\lambda_{\text{daughter}} - \lambda_{\text{parent}}}{\lambda_{\text{parent}}} \right) \right). \quad (1)$$

Generalized daughter–parent isotope age-dating equation.

All model ages are calculated relative to a reference date, usually the date of Th and/or Pa chemical separation from bulk U in the laboratory during sample purification. If the purification process completely separates the daughter isotope, ^{230}Th or ^{231}Pa , from the parent isotope, ^{234}U or ^{235}U , respectively, then the measured model age subtracted from the reference date results in a ‘model date’. This model date could represent the complete purification date of the daughter from the parent. However, if the purification of daughter from parent is incomplete, the model date will be older than the incomplete purification date. This potential discordance can provide insight into the chemical processes used to purify nuclear material and their separation efficiencies.

Experimental

Age-dating of uranium reference materials by the Th–U and Pa–U radiochronometers requires accurate uranium (U) assay. Uranium isotope dilution by mass spectrometry (IDMS) methods are not given in detail in this study as they are described in other publications [e.g., 5, 8]. Daughter/parent ratio were determined using multi-collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) at LNL.

Determination of ^{231}Pa (and ^{230}Th) assay by IDMS includes three steps: (1) production of a ^{233}Pa spike material to use as a tracer in unknown samples; (2) calibration of that spike using either geologic materials, e.g., Table Mountain Latite or BCR-2 (USGS), or a ^{231}Pa standard material, e.g., that can be milked from highly enriched uranium; and (3) spiking the sample with a calibrated ^{233}Pa spike (and ^{229}Th spike), separating and purifying the Pa and Th from the sample matrix, and measurement by MC-ICP-MS. Each of the chemical separation and purification steps outlined below utilize ultra-high purity reagents, i.e., Seastar Chemicals.

^{233}Pa spike production

Due to the relatively short half-life of ^{233}Pa (26.967 ± 0.004 days [14]), a ^{233}Pa spike has a useful life of a few months, and therefore generally must be produced as-needed. Pa^{233} is sourced at LLNL by milking ^{237}Np aliquots that are sufficiently old to be in secular equilibrium

with ^{233}Pa (Fig. 1). The Np stock used in this study has approximately 20–30 mg ^{237}Np . The ^{237}Np stock material is dried in 20 μL HClO_4 to eliminate residual HF that may be present, as this inhibits Pa sorption to anion exchange resin used in Np–Pa separation. The Np stock is sequentially dried down with a few drops of concentrated HNO_3 , followed by a few drops of concentrated HCl, and finally 0.25 mL concentrated HCl and 0.25 mL 1 M hydroxylamine hydrochloride. These dry-down steps first oxidize and then reduce the oxidation state of Np, converting the ^{237}Np stock to Np(IV) required to sorb Np to the anion exchange resin medium. The dried Np stock should be a bright emerald green color when adequately reduced; critically, Np–Pa separation efficiency is highly dependent on the oxidation state of Np. The Np stock material is then dissolved in (1 mL) 5:1 parts 10 M HCl: 1 M hydroxylamine hydrochloride; heated (capped) to dissolve the Np stock; ultrasonicated; and allowed to cool for at least 10 min.

The first Np–Pa separation step is accomplished by anion exchange chemistry with AG-MP-1 resin (BioRad, 100–200 mesh). A 2-mL resin bed is loaded in a labeled BioRad PolyPrep column and conditioned with 8 mL 10 M HCl. A cleaned, labeled, Teflon vial is placed to catch the load and the vial rinses using 10 M HCl (0.5 mL; 1 mL) of the Np stock. Minor loss of Pa and Np(V) may occur during the initial load and rinse of the column bed with 10 M HCl. Np(IV) should be visible as a bright green band at the top of the resin bed and should remain throughout successive additions of rinse acid. Np sorption can also be monitored using a beta–gamma probe to track activity or measured directly by gamma spectrometry. If necessary, these initial rinses can be combined with the recovered Np later. Subsequent rinses (a total of 9 mL) with 10 M HCl should be activity-free, with Pa and Np fully sorbed to the anion resin. A clean, labeled vial is then placed to collect

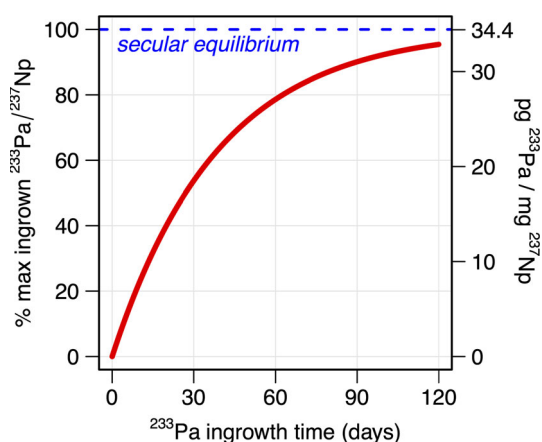


Fig. 1 ^{233}Pa ingrowth curve relative to secular equilibrium between ^{233}Pa and ^{237}Np

the Pa elution, accomplished using 8 mL 10 M HCl + 0.05 HF; the ^{233}Pa elution is then dried down on a hotplate following addition of trace ($\sim 20 \mu\text{L}$) HClO_4 . Additional ^{233}Pa elution dry-downs are performed using a few drops of concentrated HNO_3 , concentrated HCl, and finally, concentrated HCl + 1 M hydroxylamine hydrochloride as described above. The Pa fraction is then ready for an additional Np–Pa separation. A Teflon vial is positioned under the column, and the Np eluted with 10 mL 1 M HCl + 0.5 M HF (combined with the load and rinse of the Np stock material). This can be dried down and used for future ^{233}Pa spike production. The separation and recovery of Np and Pa can be monitored before proceeding to the next anion column. The second Np–Pa separation is done on a smaller volume, 1-mL AG-MP-1 (BioRad, 100–200 mesh) anion exchange resin bed using proportionately smaller load and rinse volumes (relative to the resin volume); again, the load and rinses are collected and combined with the Np recovery after Pa elution. The ^{233}Pa spike can now be dried in a few drops of concentrated HNO_3 + trace HClO_4 to remove residual HF present before the final chemical purification step.

The final purification step for the ^{233}Pa spike preparation is done using silica gel resin (Supelco, 75–200 μm particle size; see [10], for the suggested cleaning procedure). A 1.8-mL resin bed is constructed in a BioRad PolyPrep column and conditioned with 4 mL 5% HNO_3 . The dried ^{233}Pa fraction is dissolved in 0.5 mL 5% HNO_3 and 50 μL saturated H_3BO_3 ; heated (capped) on a hotplate; sonicated; and allowed to sit for 15 min. A waste beaker or Teflon vial is positioned under the column, and the sample is loaded onto the silica gel resin bed. All Pa should be sorbed to the silica gel, the efficiency of which can again be monitored with a beta–gamma probe. Following incremental rinsing (0.5 mL; 1 mL) of the ^{233}Pa vial with 5% HNO_3 , the column is rinsed with 8 mL 5% HNO_3 . These rinses should continue to flush residual ^{237}Np from the ^{233}Pa spike. The tip of the column is then rinsed with ultrapure water to remove trace ^{237}Np that may remain on the tip of the column. It is also important to note the date and time of final ^{233}Pa separation from ^{237}Np in the following elution steps, as this is an important factor when reconstructing the spike calibration after ^{233}Pa has fully decayed to ^{233}U after many months. The ^{233}Pa is eluted into a cleaned, labeled, Teflon vial (i.e., 30-mL capacity) that can be used as a working spike vial with 6 mL 5% HNO_3 + 0.1 M HF. A small aliquot can be taken from this solution and screened by MC-ICP-MS to determine the Np/Pa separation factor, as well as to approximate the ^{233}Pa concentration from the known sensitivity of the instrument. If Np/Pa < 1000, the spike is sufficiently pure. If not, the silica gel purification step is repeated, again, noting the time of separation of ^{233}Pa from ^{237}Np . Once sufficiently

pure, the spike solution can be diluted with 5% HNO₃ to an appropriate volume and/or concentration for use as a working spike.

²³³Pa calibration

Currently, there is no ²³¹Pa certified reference material that can be used to calibrate a ²³³Pa spike. Given this lack of a ²³¹Pa reference material, laboratories have conventionally relied on using geologic ²³¹Pa secular equilibrium materials, e.g., Table Mountain Latite (TML) and BCR-2 (USGS basalt standard), or, alternatively, ²³¹Pa milked from highly enriched uranium, to calibrate ²³³Pa spike spikes. However, there are numerous complications in using geologic matrices to calibrate ²³³Pa spikes, including low and variable Pa recovery; incomplete dissolution of rock standards; and imprecise U assay of rock standards [9, 10]. Legacy ²³¹Pa material that resided at LLNL has been purified and calibrated to use as an in-house standard solution for ²³³Pa spike calibration. Utilization of an in-house ²³¹Pa standard solution to calibrate ²³³Pa spikes therefore represents a significant advance in ²³¹Pa–²³⁵U radiochronometry. We note that while this ²³¹Pa standard is not certified, it has been calibrated using a ²³³Pa spike that was itself calibrated using TML and BCR-2; therefore, the current ²³¹Pa standard calibration is pinned to geologic secular equilibrium standards. Once calibrated, we have used this in-house ²³¹Pa standard to calibrate a dozen spikes and compared this calibrant to rock matrix calibrations on the same ²³³Pa spikes. Results of this comparison demonstrate good correlation using multiple calibrants for ²³³Pa spikes (Fig. 3). Moreover, we have also demonstrated that use of the in-house ²³¹Pa standard as the single calibrant for a ²³³Pa spike yields correct model ages for CRMs, including NBL U100, CRM 125A, and NBL U630. We have also calibrated our ²³³Pa spikes after they have decayed entirely to ²³³U to confirm original calibrations (see “[Pa²³³ Spike calibration comparison: decayed spike \(ingrown ²³³U\) by IDMS](#)” section). We are therefore confident in the current calibration and use of our in-house ²³¹Pa standard for ²³¹Pa–²³⁵U radiochronometry.

Pa spike calibration using rock standards

The procedure for ²³³Pa calibration using rock standards has been updated since publishing our methods in 2013 [9]. We sought to improve Pa recovery by adopting the first bulk matrix separation step described in [10]. Aliquots of fully dissolved TML and/or BCR-2 are weighed into Teflon vials and ²³³Pa spike was added to achieve ²³¹Pa/²³³Pa ~ 0.5. Typically, multiple aliquots are made to facilitate a calibration check weeks after the initial calibration is made. Following bulk matrix separation with

4 M HF [10], samples are dried down with 20 μL HClO₄. This dry down is followed by using a few drops of concentrated HNO₃, and then a few drops of concentrated HCl. Repeated dry downs help to eliminate any fluorine that impedes Pa sorption on the following anion exchange column. Next, a 1.0-mL AG1X8 (BioRad, 100-200 mesh) anion exchange resin bed is prepared in a BioRad Poly-Prep column, then conditioned with 4 mL 9 M HCl. The Pa sample is dissolved in 1 mL 9 M HCl, trace (15 μL) concentrated HNO₃, and trace (10 μL) saturated H₃BO₃; heated (capped) on a hotplate; cooled by sonication; and allowed to sit for 10 min. The sample is loaded on the conditioned anion resin bed and the sample vial rinsed with 0.5 mL and then 1 mL 9 M HCl. The column is rinsed with 2 mL 9 M HCl, with Pa remaining sorbed to the resin. The Pa is then eluted with 4 mL 9 M HCl + 0.05 M HF (note: U will be remain sorbed to the resin). The Pa elution is sequentially dried down with 20 μL HClO₄, then concentrated HNO₃. Now that the bulk of the rock matrix has been removed from the calibration fractions, the final silica gel purification step is described in the following section.

Pa spike calibration using ²³¹Pa standard

The calibration technique using ²³¹Pa is relatively straightforward and rapid. Multiple aliquots are prepared with the same amount of ²³¹Pa and varying amount of prepared ²³³Pa spike; depending on the concentration of the ²³³Pa spike, the prepared aliquots target ²³¹Pa/²³³Pa ranging from ~ 0.5 to 2. These same aliquots will be measured at a later date to confirm calibration. The mixtures are dried on a hotplate with 20 μL HClO₄ and then concentrated HNO₃. The sample is dissolved in 0.5 mL 5% HNO₃ and trace (10 μL) saturated H₃BO₃; heated (capped) on a hotplate; cooled in a sonicator; and allowed sit for 15 min. A 1-mL silica gel resin bed is prepared in a BioRad column and conditioned with 4 mL 5% HNO₃. The sample is loaded on the resin bed and the sample vial is rinsed with 0.5 mL and then 1 m 5% HNO₃ followed by a column rinse using 4 mL 5% HNO₃. Protactinium will sorb to the column, with ingrown ²³³U eluting during these load and rinse steps. Pa is then eluted using 4 mL 2% HNO₃ + 0.05 M HF. Note the time and date of this final Pa from (ingrown) U purification for calculations. Mass spectrometry should be performed on these aliquots immediately following separation from ingrown U (see “[U/Pa spike sensitivity](#)” section below). Once the spike has been prepared and calibrated, it can be used to make IDMS measurements of ²³¹Pa in unknown samples for approximately 3–6 months before nearly all ²³³Pa has decayed to ²³³U.

^{231}Pa and ^{230}Th assay by IDMS in U-bearing materials

Often age-dating efforts require that both radiochronometers, ^{230}Th – ^{234}U and ^{231}Pa – ^{235}U , are performed on the same material. As such, we have combined efforts to attain ^{230}Th and ^{231}Pa from a single aliquot, PaID + ThID (Fig. 2). The process for determining ^{230}Th and ^{231}Pa assay in U-bearing materials is described below. The first chemical separation step separates the bulk U from the ThID and PaID fractions. Each of those fractions is further processed for analysis by MC-ICP-MS.

The following method assumes that a fully dissolved primary solution has been prepared. An important addition to this dissolved primary solution is HF. The presence of HF will keep the Th and Pa in solution and ideally inhibit these elements from adhering to the walls of the Teflon vial. First, a paired Pa isotope dilution (PaID) and Th isotope dilution (ThID) aliquot of primary solution is prepared and weighed so as to yield the desired amount of ^{231}Pa and ^{230}Th for measurement based on either a priori knowledge or an estimate about the sample, e.g., a certified reference material with a known purification age, U isotopic composition, or an unknown. Additional information, such as a pre-screening of the material by gamma or mass spectrometry may also be used to determine aliquot volumes. The process described here also assumes that the U assay has been determined by IDMS as a separate aliquot described in other publications [e.g., 1, 2, 3, 5, 8]. The desired amount of primary sample for ^{231}Pa + ^{230}Th assay is gravimetrically transferred to a cleaned, labeled Teflon

vial, followed by gravimetric addition of the appropriate amounts of calibrated ^{229}Th (or ^{232}Th) spike and calibrated ^{233}Pa spike so as to yield a sample/spike ratio of ~ 0.5–10. This mixture is then equilibrated by heating (capped) on a hotplate for several hours, followed by drying to completion with 20 μL HClO_4 to ensure elimination of fluorine complexes. Chemical separations and purifications of ThID and PaID aliquots follow a series of chemistries described below.

The first step is to chemically separate bulk U from the desired ^{231}Pa and ^{230}Th . This is accomplished with a 1.0-mL AG1X8 (BioRad, 100-200 mesh) anion exchange resin bed in an Environmental Express[®] column. Thorium has been observed to sorb to the frit of BioRad Poly prep columns, whereas Environmental Express columns enable higher Th recovery, an important distinction for Th-limited samples. The dried sample is dissolved in 1 mL 9 M HCl + trace (25 μL) H_3BO_3 + trace (15 μL) concentrated HNO_3 , and the column conditioned with 3 mL 9 M HCl. A clean Teflon vial is placed to catch the ThID fraction, which will not sorb to the anion exchange resin in 9 M HCl. The vial is then rinsed with 0.5 mL and then 1 mL 9 M HCl, followed by a column rinse with 3 mL 9 M HCl. This ThID fraction is dried down, dried in concentrated HCl, and is ready for the second chemical purification of Th from U. The PaID fraction is then eluted into a cleaned Teflon vial with 3 mL 9 M HCl + 0.05 M HF and dried down with 30 μL HClO_4 . The dried PaID fraction is then dried with concentrated HNO_3 , followed by concentrated HCl. This fraction is ready for the second chemical separation of Pa from U matrix.

The next separation chemistry for the ThID fraction is performed using a 1-mL TEVA (Eichrom) resin bed. The ThID fraction is dissolved in 0.5 mL 4 M HNO_3 . The resin is conditioned with ultrapure 3 mL H_2O followed by 4 mL 4 M HNO_3 . The sample is loaded on the resin bed, with both U and Th sorbing to TEVA resin. The vial is rinsed with 0.5 mL and then 1 mL 4 M HNO_3 , followed by a 4 mL 4 M HNO_3 column rinse. A cleaned vial is placed to catch the Th elution, and the ThID fraction eluted, first, with 2 mL 9 M HCl, and then with 5 mL 0.1 M HCl + 0.005 HF. This elution is dried down, and then again with concentrated HCl. The last Th purification step for the ThID fraction is done using another 1-mL AG1x8 anion exchange resin (BioRad, 100-200 mesh) bed, conditioned with 3 mL 9 M HCl + 0.01 M HF. The sample is dissolved in 1 mL 9 M HCl + 0.01 M HF + trace (25 μL) concentrated HNO_3 . A new vial is placed to collect the sample load, and the vial and column rinsed with a total of 3.5 mL 9 M HCl + 0.01 HF. This aliquot is then dried down with concentrated HNO_3 and dissolved in 2% HNO_3 + 0.005 HF for mass spectrometry by MC-ICP-MS.

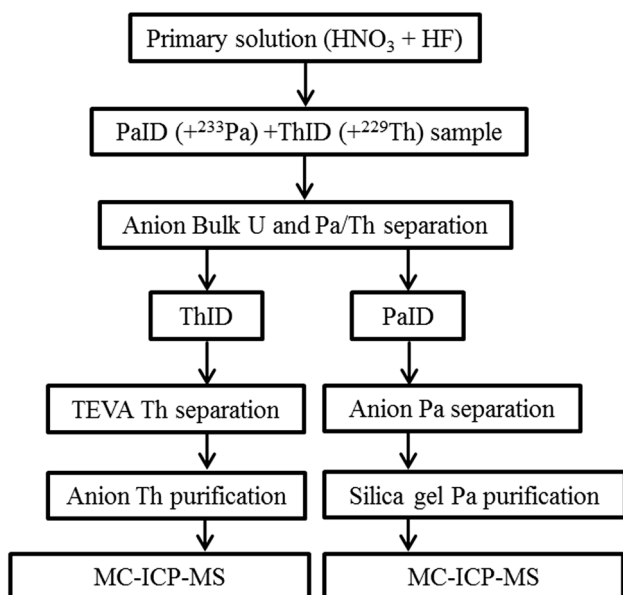
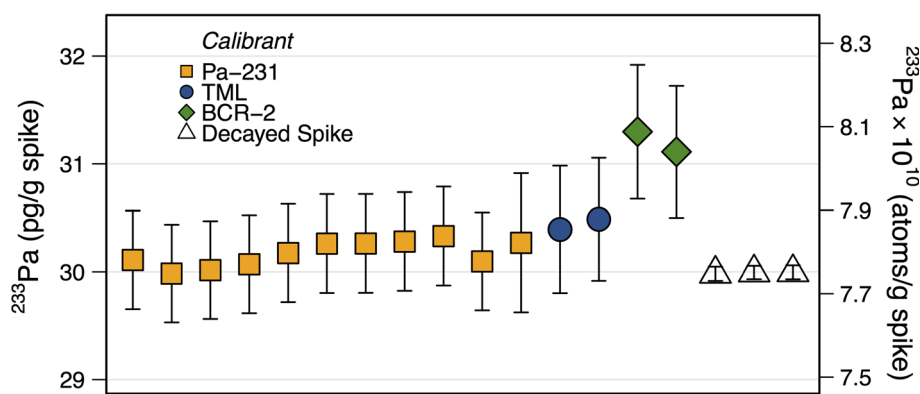


Fig. 2 Analytical flow diagram showing the path for U-bearing materials processing for ^{230}Th and ^{231}Pa assay

Fig. 3 ^{233}Pa spike prepared in April 2017 using multiple calibrants: TML, BCR-2, ^{231}Pa , and ^{238}U (decayed spike method)



The next separation step for PaID involves further separating Pa from matrix elements. This second separation chemistry uses a 1-mL anion AG1x8 (BioRad, 100-200 mesh) resin bed. This second purification chemistry is the same chemistry as the first U matrix from ThID and PaID chemistry, omitting the elution of the ThID fraction. The PaID elution fraction is dried down with 30 μL HClO_4 for the final silica gel resin purification. This final chemistry step is the silica gel chemistry that is described above in the “Pa spike calibration using ^{231}Pa ” section. The final elution in 2 M HNO_3 + 0.05 M HF is ready for mass spectrometry by MC-ICP-MS. Empirical study in our lab has shown removal of > 99.8% of U matrix using silica gel resin procedure as described above.

Mass spectrometry methods

Both Pa and Th IDMS measurements were performed using a Nu Plasma HR MC-ICP-MS. Protactinium IDMS fractions were eluted in 2 M HNO_3 + 0.05 M HF and Th samples dissolved in 2% HNO_3 + 0.005 HF. Protactinium IDMS aliquots were analyzed using a one-cycle, static multicollection routine in which ^{231}Pa and ^{233}Pa are simultaneously measured on separate ion counters (ICs). Comparatively, thorium IDMS aliquots were analyzed using a two-cycle, dynamic multicollection routine in which ^{232}Th is measured continuously on a Faraday collector and ^{229}Th and ^{230}Th are peak-hopped onto the same IC. Peak-hopping ^{229}Th and ^{230}Th with simultaneous ^{232}Th Faraday measurement permits calculation of more precise $^{229}\text{Th}/^{230}\text{Th}$ by crossing $^{229}\text{Th}/^{232}\text{Th}$ (cycle #1) and $^{230}\text{Th}/^{232}\text{Th}$ (cycle #2), as uncertainties associated with Faraday/IC gain are obviated by this approach. Instrumental mass-dependent fractionation (mass bias) and Faraday/IC gain corrections for Pa and Th measurements were made using CRM U010 in the same analytical batch run by standard–sample–standard bracketing. Time-interpolation of mass bias and Faraday/IC gain factors for samples analyzed between bracketing CRM U010

measurements, in addition to a conservative expansion of uncertainties affiliated with interpolated correction factors, cumulatively yield more accurate and rigorous Pa and Th radiochronometric results. For complementary analytical details, see also [1, 2, 8, 9].

Pa^{233} Spike calibration comparison: decayed spike (ingrown ^{233}U) by IDMS

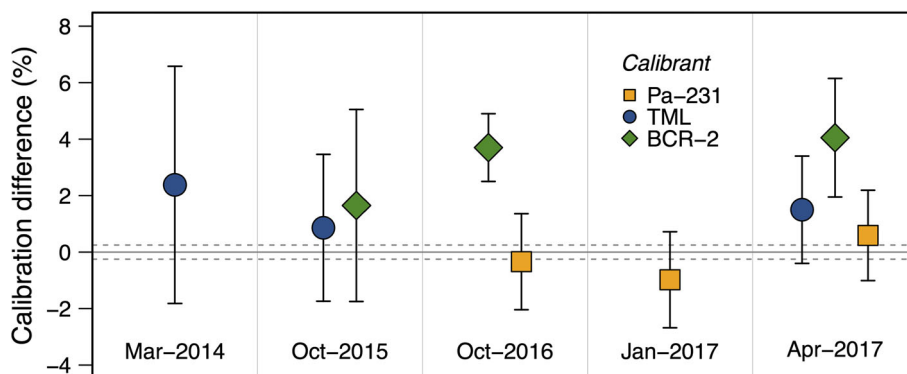
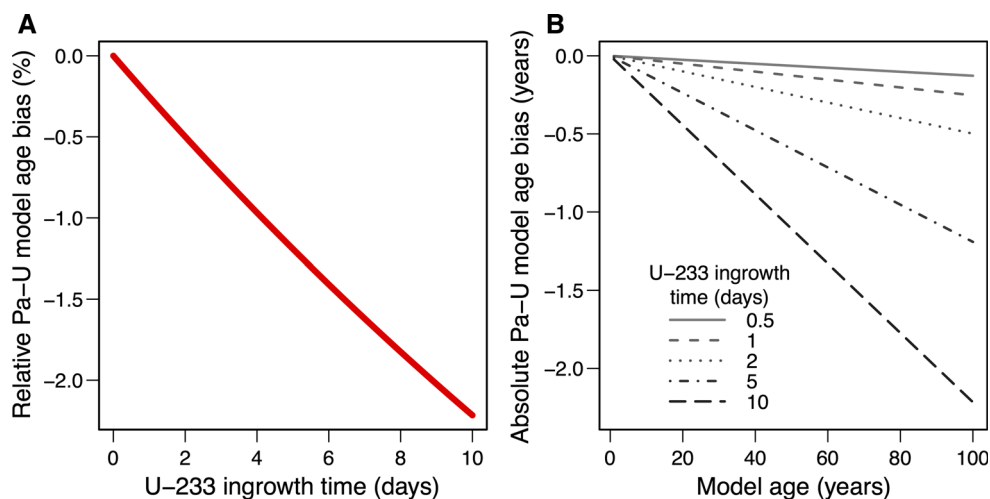
To assess the relative accuracy and precision of various materials (including the ^{231}Pa standard) used for calibrating ^{233}Pa spikes at LLNL, we have measured decayed ^{233}Pa spikes (as ^{233}U) using a natural U assay standard (NBS 960). The half-life of ^{233}Pa is 26.967 ± 0.004 days [14], which through beta decay creates ^{233}U . Therefore, after approximately 6 months, ^{233}Pa has near-fully decayed to ^{233}U . To check the original calibration of our ^{233}Pa spikes, we looked at previously produced spikes using this decayed spike IDMS method. Five independently prepared and calibrated ^{233}Pa spikes are shown in Table 2 (Fig. 3).

Aliquots of decayed ^{233}Pa spike were gravimetrically transferred to clean, dry Teflon vials. Aliquot sizes were determined to achieve $^{235}\text{U}/^{233}\text{U}$ of ~ 1 . The same amount of natural U (NBS 960) of known concentration was added to each spike aliquot. When possible, multiple aliquots of each spike were analyzed. The decayed spike crosses were dried down, dried down again with concentrated HNO_3 , and dissolved in 2% HNO_3 for analysis by MC-ICP-MS. The multicollection analysis method is the same as that used for measuring U by IDMS, where ^{238}U , ^{235}U , and ^{233}U are all measured on Faraday collectors (^{234}U is measured on an IC) (Table 1).

Figure 4 shows the relative difference between the decayed spike calibration (^{233}U by IDMS) as compared with the original ^{233}Pa assay determined by the calibrants: TML, BCR-2, and ^{231}Pa . The difference is calculated as the percent difference between the original calibration as compared to the decayed spike calibration. The calculated uncertainty on the % difference is the combined

Table 1 Protactinium spikes used in calibration check by reverse IDMS using NBS 960

| Spike | Calibrant | Original calibration ^{233}Pa atoms/g-spike | Uncertainty ($1 - \sigma$) | Decayed calibration value | Uncertainty ($1 - \sigma$) | % Difference | Combined uncertainty ($2 - \sigma$) |
|--------------|-------------------|--|------------------------------|---------------------------|------------------------------|--------------|---------------------------------------|
| March 2014 | TML | 2.407E+10 | 5.0E+08 | 2.35E+10 | 5.4E+07 | 2.38 | 4.20 |
| October 2015 | TML | 2.580E+10 | 3.3E+08 | 2.56E+10 | 2.8E+07 | 0.86 | 2.60 |
| | BCR-2 | 2.600E+10 | 4.4E+08 | | | 1.65 | 3.40 |
| October 2016 | BCR-2 | 4.033E+10 | 2.3E+08 | 3.89E+10 | 4.8E+07 | 3.70 | 1.20 |
| | ^{231}Pa | 3.876E+10 | 3.2E+08 | | | -0.34 | 1.70 |
| January 2017 | ^{231}Pa | 7.832E+10 | 6.7E+08 | 7.91E+10 | 1.2E+08 | -0.98 | 1.70 |
| April 2017 | TML | 7.866E+10 | 7.5E+08 | 7.75E+10 | 8.3E+07 | 1.50 | 1.90 |
| | BCR-2 | 8.064E+10 | 8.0E+08 | | | 4.05 | 2.10 |
| | ^{231}Pa | 7.796E+10 | 6.1E+08 | | | 0.59 | 1.60 |

Fig. 4 Decayed ^{233}Pa spike (measured as ^{233}U) by IDMS using natural U (NBS 960)**Fig. 5** ^{231}Pa - ^{235}U model age bias effect from U^{233} ingrowth and contribution to mass-233 during PaID mass spectrometric analysis, assuming a relative U/Pa sensitivity of +10%. **a** Relative (%) model age bias as a function of ^{233}U ingrowth time (days). **b** Absolute (years) model age bias as a function of a sample's true model age (years). Lines indicate a given ^{233}U ingrowth time (i.e., time elapsed between final PaID purification and mass spectrometric analysis)

uncertainty from both the decayed spike and original spike calibration. The uncertainty on the Faraday measurement of the $^{238}\text{U}/^{233}\text{U}$ ratio used to calculate the ^{233}U assay is shown (Fig. 4) as a $\pm 0.25\%$, expanded uncertainty, $k = 2$.

U/Pa sensitivity

Another consideration for accurate PaID analysis is accounting for relative U/Pa sensitivity during mass

Table 2 Results for Th-U and Pa-U model ages for U100 and IRMM-1000

| Sample ID | Reference date | ^{230}Th – ^{234}U (atom ratio) | Expanded uncertainty, $k = 2$ | Model age (y) | Model date | Expanded uncertainty, days, $k = 2$ | |
|----------------------------|----------------|--|----------------------------------|---------------|-------------|---|--------------------------------------|
| U100-1 ^b | 22-Jun-2017 | 1.6713E–04 | 1.2E–06 | 59.15 | 30-Apr-1958 | 157 | |
| U100-2 ^b | 22-Jun-2017 | 1.6666E–04 | 1.2E–06 | 58.98 | 30-Jun-1958 | 157 | |
| U100-3 ^b | 22-Jun-2017 | 1.6773E–04 | 1.4E–06 | 59.36 | 12-Feb-1958 | 181 | |
| IRMM-1000-1 ^{a,c} | 22-Jan-2014 | 4.3460E–06 | 4.0E–08 | 1.54 | 9-Jul-2012 | 4 | |
| IRMM-1000-2 ^{a,d} | 12-Feb-2014 | 4.5550E–06 | 4.0E–08 | 1.61 | 3-Jul-2012 | 4 | |
| IRMM-1000-3 ^{a,d} | 12-Feb-2014 | 4.5940E–06 | 4.0E–08 | 1.63 | 28-Jun-2012 | 5 | |
| IRMM-1000-4 ^{a,d} | 10-Mar-2014 | 4.8060E–06 | 4.0E–08 | 1.70 | 26-Jun-2012 | 6 | |
| IRMM-1000-5 ^{a,b} | 27-Oct-2014 | 6.6220E–06 | 1.2E–07 | 2.34 | 23-Jun-2012 | 15 | |
| IRMM-1000-6 ^{a,e} | 24-Mar-2016 | 1.0433E–05 | 1.0E–07 | 3.69 | 14-Jul-2012 | 14 | |
| IRMM-1000-7 ^{a,e} | 7-Jul-2016 | 1.1310E–05 | 1.6E–07 | 4.00 | 6-Jul-2012 | 22 | |
| IRMM-1000-8 ^f | 27-Jan-2017 | 1.3019E–05 | 1.0E–07 | 4.61 | 19-Jun-2012 | 14 | |
| IRMM-1000-9 ^f | 29-Jun-2017 | 1.4105E–05 | 1.2E–07 | 4.99 | 2-Jul-2012 | 15 | |
| IRMM-1000-10 ^f | 29-Jun-2017 | 1.4196E–05 | 1.0E–07 | 5.02 | 20-Jun-2012 | 14 | |
| IRMM-1000-11 ^g | 10-Nov-2017 | 1.5158E–05 | 1.8E–07 | 5.36 | 30-Jun-2012 | 23 | |
| IRMM-1000-12 ^g | 10-Nov-2017 | 1.5090E–05 | 3.4E–07 | 5.34 | 8-Jul-2012 | 44 | |
| IRMM-1000-13 ^g | 10-Nov-2017 | 1.4970E–05 | 2.6E–07 | 5.30 | 23-Jul-2012 | 34 | |
| Sample ID | Reference date | ^{231}Pa – ^{235}U (atom ratio) | Expanded uncertainty, $k = 2$ | Model age (y) | Model date | Expanded uncertainty, days, $k = 2$ | ^{233}Pa spike calibrant |
| U100-1 ^b | 18-Jul-2017 | 5.733E–08 | 1.0E–09 | 58.25 | 18-Apr-1959 | 371 | ^{231}Pa , TML, BCR-2 |
| U100-2 ^b | 18-Jul-2017 | 5.782E–08 | 1.0E–09 | 58.74 | 20-Oct-1958 | 373 | |
| U100-3 ^b | 18-Jul-2017 | 5.749E–08 | 9.9E–10 | 58.41 | 17-Feb-1959 | 370 | |
| IRMM-1000-1 ^{a,d} | 10-Mar-2014 | 1.881E–09 | 5.8E–11 | 1.91 | 11-Apr-2012 | 22 | TML |
| IRMM-1000-2 ^{a,d} | 30-Oct-2014 | 2.469E–09 | 6.0E–11 | 2.51 | 27-Apr-2012 | 22 | TML |
| IRMM-1000-3 ^{a,e} | 24-Mar-2016 | 3.992E–09 | 1.6E–10 | 4.05 | 4-Mar-2012 | 59 | TML, BCR-2 |
| IRMM-1000-4 ^{a,e} | 7-Jul-2016 | 4.112E–09 | 6.2E–11 | 4.18 | 3-May-2012 | 23 | TML |
| IRMM-1000-5 ^f | 27-Jan-2017 | 4.674E–09 | 7.6E–11 | 4.75 | 29-Apr-2012 | 28 | ^{231}Pa |
| IRMM-1000-6 ^f | 18-Jul-2017 | 5.167E–09 | 9.2E–11 | 5.25 | 18-Apr-2012 | 34 | ^{231}Pa , TML, BCR-2 |
| IRMM-1000-7 ^f | 18-Jul-2017 | 5.176E–09 | 9.2E–11 | 5.26 | 15-Apr-2012 | 34 | |
| IRMM-1000-8 ^g | 10-Nov-2017 | 5.352E–09 | 1.1E–10 | 5.43 | 4-Jun-2012 | 42 | ^{231}Pa |
| IRMM-1000-9 ^g | 10-Nov-2017 | 5.387E–09 | 1.1E–10 | 5.47 | 21-May-2012 | 42 | |
| IRMM-1000-10 ^g | 10-Nov-2017 | 5.419E–09 | 1.1E–10 | 5.50 | 10-May-2012 | 42 | |

^aResults from REIMEP-22 [7] interlaboratory exchange material^bU by IDMS analyzed June 2017^cU by IDMS analyzed January 2014^dU by IDMS analyzed February 2014^eU by IDMS analyzed March 2016^fU by IDMS analyzed January 2017^gU by IDMS analyzed September 2017

spectrometry. Differing element-to-element instrumental sensitivity within an analytical session is a long-recognized and ubiquitous phenomenon. Elemental sensitivity tests demonstrate $\sim 10\%$ greater U sensitivity relative to concurrent Pa sensitivity on LLNL's Nu Plasma HR MC-ICP-MS. This observation is crucial due to the relatively rapid ingrowth of isobaric ^{233}U from decay of ^{233}Pa spike ($t_{1/2} \sim 27$ days) in PaID aliquots between final silica gel purification chemistry and analysis by mass spectrometry. The magnitude of bias induced in $^{231}\text{Pa}/^{233}\text{Pa}$ increases with the time elapsed between PaID sample purification and analysis, resulting in increasingly-underestimated

$^{231}\text{Pa}/^{233}\text{Pa}$ (sample/spike) due to the greater contribution of ^{233}U at mass-233. Use of this low-biased $^{231}\text{Pa}/^{233}\text{Pa}$ for $^{231}\text{Pa}-^{235}\text{U}$ age-dating calculations will yield a model age that is too young (Fig. 5a), with the absolute magnitude of bias depending on (1) the time elapsed between chemistry and analysis, and (2) the absolute model age of the sample (Fig. 5b). It is therefore essential that mass spectrometry be performed as soon as PaID aliquots are purified to minimize the ^{233}U isobar effect. Alternatively, U/Pa sensitivity would need to be determined empirically during the same batch run as sample analyses to make a "live" correction if significant time (> 2 days) passed between purification and mass spectrometry.

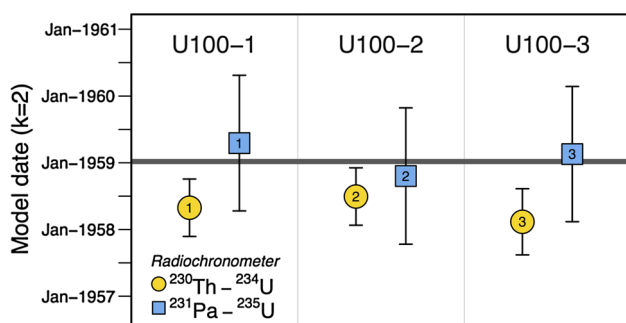


Fig. 6 U100 results for paired ThID and PaID analyses, U100-1, U100-2, and U100-3. The horizontal line represents the number of aliquots of U100. Each pair of results has an individual U concentration by IDMS from the same aliquot. All uncertainties reported are expanded uncertainties, $k = 2$

Results and discussion

Measured $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ and corresponding expanded uncertainties ($k = 2$), and calculated model ages, model dates and expanded uncertainties ($k = 2$), for radiochronometry standards IRMM-1000 and CRM U100 are given in Table 2. Results for U100 $^{230}\text{Th}-^{234}\text{U}$ and $^{231}\text{Pa}-^{235}\text{U}$ were processed as paired analyses as described above, where the Th and Pa assay originated from a single aliquot. Additionally, each radiochronometer aliquot has a unique U assay. IRMM-1000 results are a combination of analyses of REIMEP-22 from an interlaboratory exchange material [7] and an independently prepared reference unit

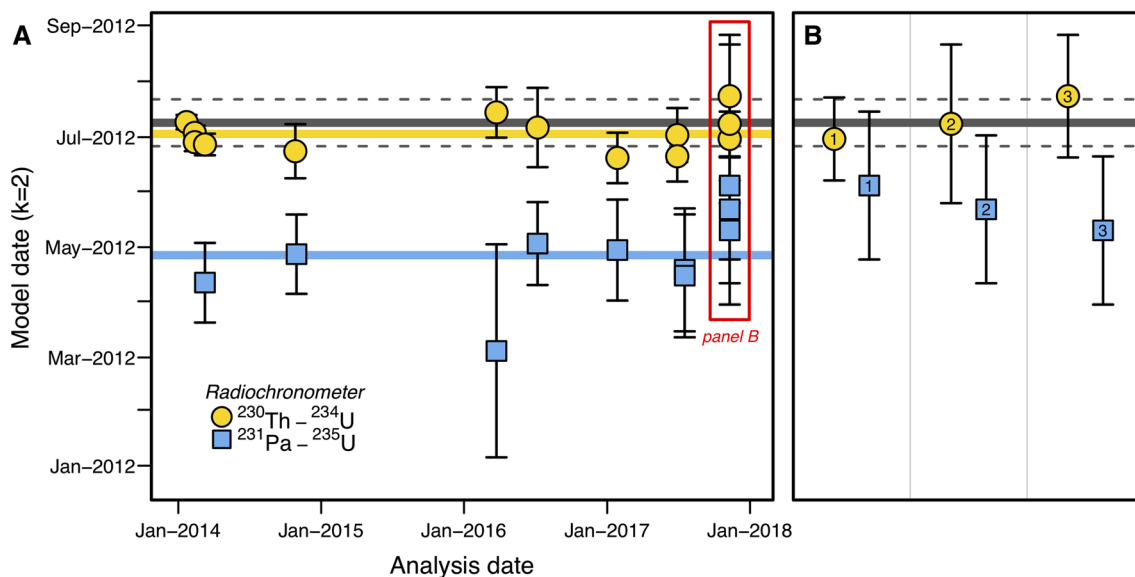


Fig. 7 IRMM-1000 $^{230}\text{Th}-^{234}\text{U}$ and $^{231}\text{Pa}-^{235}\text{U}$ model dates with expanded uncertainties shown relative to reference date. All analyses listed in Table 2 are in **a**. The certified $^{230}\text{Th}-^{234}\text{U}$ production date and combined uncertainty are in grey. The weighted average model dates for both radiochronometers are given in yellow (Th-U) and blue (Pa-U) (errors are stated in text below). Panel B inset shows our most

recent data in finer detail as three separate paired ThID and PaID. U-assay for the paired analyses in **b** were determined using a newly prepared and calibrated in-house high purity ^{233}U spike. All uncertainties reported are expanded uncertainties, $k = 2$. (Color figure online)

of IRMM-1000, purchased from IRMM (Institute of Materials and Measurement) in 2015.

The ^{230}Th – ^{234}U model dates calculated for CRM U100 span February–June 1958, with corresponding ^{231}Pa – ^{235}U model dates ranging from October 1958–April 1959 (Fig. 6). The known production date of CRM U100 is January 8, 1959 [15]. Both radiochronometry daughter–parent pairs agree with one another within uncertainty, and are therefore concordant, in addition to preserving the material’s production date. This CRM can therefore act as a useful quality control standard when processing unknown U materials for age-dating as both chronometers yield similar results, suggesting near-complete purification of ^{230}Th and ^{231}Pa daughters during production, as well as being consistent with the production history of this material.

The reference material IRMM-1000 is a radiochronometry standard certified with a ^{230}Th – ^{234}U production date of July 9th, 2012 \pm 13 days [7]. The ^{230}Th – ^{234}U model dates for this material range from late June–July 2012, with an average model date ($n = 13$) of July 2nd, 2012 \pm 28 days, in agreement with the known production history of IRMM-1000. However, ^{231}Pa – ^{235}U model dates range span April–early June 2012, with an average model date ($n = 10$) of April 26th, 2012 \pm 56 days (Fig. 7). Long-term average IRMM-1000 Th–U and Pa–U model dates and uncertainties ($k = 2$) were calculated by propagating uncertainties from individual analyses. The average ^{231}Pa – ^{235}U model date is therefore ~ 70 days older than the average ^{230}Th – ^{234}U model date, with the two radiochronometers being clearly discordant at the $k = 2$ uncertainty level. This observable difference has been reproduced over time using two different IRMM-1000 stock solutions, one being from the REIMEP-22 interlaboratory exchange, as well as using two different ^{233}U spikes, two different ^{229}Th spikes, and six independently-prepared and -calibrated ^{233}Pa spikes. As this material ages, the discordance becomes more difficult to observe because the absolute precision is a function of the age, thus older samples have larger absolute uncertainties on calculated model ages. This observed discordance between Th–U and Pa–U radiochronometers could be due to incomplete separation of Pa during the production of IRMM-1000 as a radiochronometry standard. Despite the observed model date discordance, we note that IRMM-1000 is still a valuable quality control material in nuclear forensics.

Conclusions

The ^{230}Th – ^{234}U and ^{231}Pa – ^{235}U model dates determined with our updated Pa–U age-dating methods for U100 are concordant and retain the production date of this material. By comparison, ^{230}Th – ^{234}U and ^{231}Pa – ^{235}U model ages for IRMM-1000 are discordant within uncertainties attainable using the improved Pa–U methodology. These methods can be applied to both relatively old (i.e., U100) and young (i.e., IRMM-1000) reference materials and unknowns and yield accurate results. Our improved methods are robust over time, using multiple distinct reference units, independently-prepared and -calibrated spikes, and newly available spikes, i.e., NFRM ^{229}Th spike [16]. This study confirms the utility of calibrating ^{233}Pa spikes with a ^{231}Pa solution and the need for such a reference material for the age-dating community.

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