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International cooperation in age-dating uranium standards for nuclear forensics using the $^{231}Pa/^{235}U$ radiochronometer

Joanna S. Denton[1] · Kerri C. Treinen[2] · Yan Chen[3] · Eva Baransky[2] · Amy M. Gaffney[2] · Sheng-Hui Huang[3] · Theresa M. Kayzar-Boggs[1] · Kyle Samperton[2] · Robert E. Steiner[1] · Allison M. Wende[1] · Ross W. Williams[2] · Yong-Gang Zhao[3]

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Abstract

During 2017–2018 Los Alamos National Laboratory, Lawrence Livermore National Laboratory and the China Institute of Atomic Energy collaborated in an interlaboratory $^{231}Pa/^{235}U$ radiochronometry exercise. The laboratories used different analytical methods to obtain a consensus model purification date for CRM U010 of December 28, 1958 ± 198 days and for CRM U850 of May 20, 1958 ± 363 days. These results agree with previously reported model dates using the $^{230}Th/^{234}U$ radiochronometer as well as the production histories of these materials. The concordance of interlaboratory data confirms the ability of laboratories to make reproducible radiochronometry measurements using distinct analytical approaches.

Keywords Radiochronometry · Protactinium · Certified reference material · Nuclear forensics · Uranium

Introduction

The aim of a nuclear forensics investigation is to establish the origin and history of nuclear materials of unknown origin. This can be achieved through the physical, chemical, and isotopic analysis of material found out of regulatory control or with an unknown history [1–5]. Radiochronometry, or the science of age-dating radioactive materials using parent and progeny isotopes, is a fundamental research area addressing the 'when was a material produced or purified' question within the field of nuclear forensics [6–10].

When a nuclear material is purified during production, impurities are removed (including progeny isotopes). Following purification, progeny isotopes will be produced at a rate governed by radioactive decay (the Bateman equations). The time elapsed since purification can be calculated by combining (1) the Bateman equations, with (2) the known half-lives of the radionuclides in question, and (3) accurate and precise measurements of the parent-to-progeny ratios in the present-day material. For the radiochronometric age to be an accurate representation of the production date a number of conditions have to be met: (1) there was complete separation of progeny isotopes from the parent during material production, and (2) the sample has remained a 'closed' system since production (i.e. no gain or loss of parent or progeny isotopes except through radioactive decay). In radiochronometry, these conditions are assumed to be true and the resulting age is termed a model age since purification.

There are many potential radiochronometers applicable to nuclear materials and ideally, numerous model purification dates would be obtained from the same sample using multiple radiochronometers. If the model ages determined using different radiochronometers agree (are concordant), then confidence that the model age of the sample represents the purification age is increased. If the model ages disagree (are non-concordant) then this information can be used to interpret a sample's process history as well as its maximum age [7, 9–11].

For uranium materials, $^{230}Th/^{234}U$ is the most commonly used radiochronometer due to the relatively high abundance

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✉ Joanna S. Denton
jdenton@lanl.gov

[1] Nuclear and Radiochemistry Group, Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

[2] Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94551, USA

[3] Department of Radiochemistry, China Institute of Atomic Energy, Xinzhen Fangshan District, P.O. Box 275-8, Beijing 102413, China

of the ^{230}Th radionuclide and the wide availability of tracers e.g. ^{229}Th and ^{232}Th. Recently, many laboratories have focused efforts on developing analytical methods to date nuclear materials using the ^{231}Pa/^{235}U radiochronometer. Protactinium-231 is the daughter of ^{235}U and, depending on the enrichment and age of the uranium material, can be present in measurable quantities (pg level). The use of the ^{231}Pa/^{235}U radiochronometer is, however, complicated by the following:

(a) the short half-life (~ 27 days) of the ^{233}Pa tracer rendering each freshly produced tracer obsolete in a few months;
(b) until recently there were no protactinium standards against which to calibrate a freshly produced ^{233}Pa tracer;
(c) there are no reference materials certified for age using the ^{231}Pa/^{235}U chronometer.

Due to the short half-life of ^{233}Pa, the usefulness of each tracer can be maximized by preparing fresh tracer for each imminent age-dating campaign. The lack of a protactinium standard for ^{233}Pa tracer calibrations (issue (b) above) was remedied recently when a ^{231}Pa Reference Material (NFRM ^{231}Pa) was produced by the National Institute of Standards and Technology (NIST, USA) in collaboration with Lawrence Livermore National Laboratory (LLNL, USA), the National Research Council, (NRC, Canada), and the National Physical Laboratory (NPL, UK) [12]. It is possible to address the lack of reference materials certified for ^{231}Pa/^{235}U radiochronometry [issue (c) above] by the international nuclear forensics community conducting interlaboratory comparison ^{231}Pa/^{235}U measurements. The goal of these exercises is to obtain consensus ^{231}Pa/^{235}U model purification dates of commercially available certified uranium isotopic reference materials as well as those certified for purification date by the ^{230}Th/^{234}U radiochronometer. Interlaboratory studies have been conducted using the ^{230}Th/^{234}U radiochronometer [6, 8] establishing that reproducible ages can be obtained by laboratories around the world.

In this paper we report the results of a ^{231}Pa/^{235}U radiochronometry interlaboratory comparison exercise between Los Alamos National Laboratory (LANL), LLNL and the Chinese Institute of Atomic Energy (CIAE). All three laboratories applied the ^{231}Pa/^{235}U radiochronometer to age date certified reference material (CRM) U010 and CRM U850 produced by New Brunswick National Laboratory (NBL) in the United States. A record of the production of these materials is available providing known purification dates for each material [13]. Data reported here are compared to previously reported results from a ^{230}Th/^{234}U radiochronometry interlaboratory comparison exercise between these laboratories for CRM U010 and CRM U850 [8].

Experimental

LANL, LLNL and CIAE obtained and dissolved CRM U010 and CRM U850 independently. Each laboratory measured ^{231}Pa and ^{235}U assay by isotope dilution mass spectrometry (IDMS) using ^{233}Pa and ^{233}U isotopic tracers. Well-characterized tracers are required for accurate and high-precision measurements and details of the tracers and calibrations can be found in the following sections. Table 1 contains a summary of the analytical methods for each laboratory as well as the half-lives used by each laboratory in the age-dating equation.

LANL analytical methods

CRM dissolution

Primary dissolutions of U010 and U850 were made by dissolving each CRM powder in 8 M HNO_3 on a hot plate. Following dissolution each solution was diluted and HF added to generate a final solution for storage of between 4 M HNO_3 + 0.01 M HF and 4 M HNO_3 + 0.05 M HF. The concentration of uranium in each primary solution was ~ 728 µg U/g for CRM U010 and ~ 285 µg U/g for CRM U850. Two serial dilutions were made in order to measure ^{235}U concentration. These dilutions were made gravimetrically to yield a final secondary dilution uranium concentration of approximately 30 ng U/g for U850 and 3 ng U/g for U010.

Uranium assay and isotope composition measurements

Aliquots containing ~ 2 ng of uranium were taken for ^{235}U assay measurements from the secondary dilution of each CRM and were traced with ^{233}U tracer (LANL legacy material). The LANL ^{233}U tracer was calibrated using National Bureau of Standards (NBS) Standard Reference Material (SRM) 960. Following tracer-sample equilibration the uranium in CRM U850 was purified using 1 mL of UTEVA resin where the samples were loaded in 3 M HNO_3 and the uranium eluted in 0.1 M HCl. Aliquots containing ~ 50 ng of uranium were also taken from the secondary dilution to measure the uranium isotope composition. The samples were purified using the same chemistry as the uranium assay samples. To quantify background contamination, process blanks (4 M HNO_3 + 0.05 M HF) were processed alongside the samples using the same chemistry. Chemical purification of uranium aliquots was not performed for CRM U010 due to the high-purity of the CRM and tracer materials.

Uranium measurements were performed on a ThermoScientific™ Neptune Plus Multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) using static

Table 1 Summary of different methods used by LANL, LLNL, and CIAE

	LANL	LLNL	CIAE
^{235}U			
Tracer	^{233}U (legacy material)	^{233}U (legacy material)	^{233}U (IRMM051)
Tracer calibration material	NBS SRM 960	NBS SRM 960	None
Sample chemistry	UTEVA	UTEVA	None
Mass spectrometry	ThermoScientific™ Neptune Plus MC-ICP-MS	Nu Plasma HR MC-ICP-MS	ThermoScientific™ Element XR ICP-MS
^{231}Pa			
Tracer	^{233}Pa (from legacy ^{237}Np)	^{233}Pa (from legacy ^{237}Np)	^{233}Pa (from ^{237}Np in tributyl phosphate waste)
Tracer calibration material	In-house ^{231}Pa solution and ^{231}Pa reference material	In-house ^{231}Pa solution and rock standards	NBL CRM U100
Tracer production	Silica gel Silica gel	AG MP-1 AG MP-1 Silica gel	TRU TRU Silica gel Silica gel Silica gel
Tracer calibration chemistry	Silica gel	Silica gel	AG1-X8 anion AG1-X8 anion Silica gel
Sample chemistry	AG1-X8 anion Silica gel Silica gel	AG1-X8 anion AG1-X8 anion Silica gel	AG1-X8 anion AG1-X8 anion Silica gel
Mass spectrometry	ThermoScientific™ Neptune Plus MC-ICP-MS	Nu Plasma 3 MC-ICP-MS	ThermoScientific™ Element XR ICP-MS
Nuclear data			
^{235}U half-life (years)	$7.04\times10^{8}\pm0.005\times10^{8}$ [18]	$7.04\times10^{8}\pm0.005\times10^{8}$ [18]	$7.04\times10^{8}\pm0.01\times10^{8}$ [19]
^{231}Pa half-life (years)	32,713 ± 110 [20]	32,760 ± 110 [21]	32,760 ± 110 [19]
^{233}Pa half-life (days)	26.697 ± 0.004 [22] [e]	26.967 ± 0.004 [22]	26.975 ± 0.013 [19]

multi-ion counting methods. For uranium assay measurements, ^{233}U, ^{235}U, and ^{238}U were measured on Faraday detectors with IRMM 074/1 used for mass bias corrections and IRMM 074/2 used as a quality control standard. For uranium isotope composition measurements, ^{238}U and ^{235}U were measured on Faraday detectors and ^{234}U and ^{236}U were measured on full-size secondary electron multiplier (SEM) detectors equipped with retarding potential quadrupole (RPQ) lenses. For U010 uranium measurements, CRM U200 was used for mass bias and gain corrections and a separate dissolution of U010 was used as a quality control standard. For U850 uranium measurements, CRM U500 was used for mass bias and gain corrections. The CRMs U930 and IRMM 074/9 were used as quality control standards. Other corrections applied to the final data included tailing, acid blank subtractions, and hydride corrections (^{235}U + ^{1}H on mass ^{236}U).

Protactinium assay measurements

For protactinium isotope dilution measurements LANL purified a ^{233}Pa tracer from ~ 5 mg of ^{237}Np using silica gel (high purity, 63–200 μm particle size). The ^{237}Np solution was loaded onto 2 mL of silica gel in 2% HNO_3 and the ^{237}Np was washed from the resin using 2% HNO_3. The ^{233}Pa was then eluted in 2% HNO_3 + 0.01 M HF. This column purification was performed twice and the resulting elution screened using a ThermoScientific™ Element 2 High Resolution Inductively Coupled Plasma Mass Spectrometer (ICP-MS) to confirm adequate Np/Pa purification. If necessary, the silica gel column was repeated until adequate purification was achieved. The resulting spikes were diluted to a working tracer concentration of ~ 1 pg ^{233}Pa/g solution in 4 M HNO_3 + 0.05 M HF. The ^{233}Pa tracers used in this study were calibrated using (a) the NFRM ^{231}Pa reference material and (b) an in-house ^{231}Pa solution, itself characterized by a ^{233}Pa spike calibrated using the NFRM ^{231}Pa reference material. Prior to the calibration analytical session, the ^{233}U present from ^{233}Pa decay was removed using a single silica gel column purification described above. The ^{231}Pa to ^{233}Pa ratio was measured by the MC-ICP-MS method described below. Each tracer was calibrated twice during its lifetime and the average calibration was used for data reduction. For sample ^{231}Pa assay measurements, aliquots containing ~ 5 pg of ^{231}Pa were taken from the primary solution. This represented ~ 100 µg of uranium for U850 and ~ 7300 µg of uranium for U010. These aliquots were traced with ~ 2 pg of ^{233}Pa. Following tracer-sample equilibration the protactinium was purified using a three step process: (1) a column containing 2 mL of BioRad anion exchange resin (AG1-X8, 100–200 mesh) where the sample was loaded in 9 mL HCl with trace HNO_3 and H_3BO_3 and Pa eluted in 9 M HCl + 0.05 M HF, (2) a column containing 2 mL of silica gel where the sample was loaded in 2% HNO_3 with trace H_3BO_3 and Pa eluted in 2% HNO_3 + 0.05 M HF, and (3) a repeat of column (2). To quantify background contamination, process blanks (4 M HNO_3 + 0.05 M HF) were processed alongside the samples using the same chemistry.

All protactinium measurements were performed the same day of the final column purification to minimize the isobaric interferences from the decay of ^{233}Pa to ^{233}U. Protactinium measurements were performed on a ThermoScientific™ Neptune Plus MC-ICP-MS using static multi-ion counting methods with ^{231}Pa and ^{233}Pa measured on full-size SEM detectors. Faraday detectors are also used to measure ^{235}U (to confirm purification) and ^{232}Th (to monitor hydride interference at mass 233). As no certified isotopic Pa reference materials are available, uranium CRM U010 was used for mass bias and gain corrections and CRM U005A was used as a quality control standard. These CRMs were measured as described above for uranium isotope measurements. It was assumed that the instrumental mass bias correction derived from uranium is appropriate for Pa. Other corrections applied to the final data included tailing and acid blank subtractions as well as a subtraction of ^{232}Th + ^{1}H hydride interference on mass 233.

LLNL analytical methods

CRM dissolution

Primary dissolutions of U010 and U850 were made by dissolving each CRM powder in concentrated HNO_3 in precleaned quartz crucibles on a hotplate at 120 °C for at least 4 h. Following dissolution each solution was diluted and HF added to generate a final solution for storage of 2 M HNO_3 + 0.05 M HF. The concentration of uranium in each primary solution was ~ 1 mg U/g for U010 and ~ 56 µg U/g for U850. Two serial dilutions were made gravimetrically in order to measure ^{235}U concentration.

Uranium assay and isotope composition measurements

Aliquots containing ~ 40 ng uranium for CRM U010 and ~ 50 ng uranium for CRM U850 were taken for ^{235}U assay measurements from the secondary dilutions of each CRM. Each aliquot was traced with ultra-high purity ^{233}U (LLNL legacy material). The LLNL ^{233}U tracer was calibrated using NBS SRM 960. Following tracer-sample equilibration the uranium was purified using 1 mL of UTEVA resin where the samples were loaded in 4 M HNO_3 and the uranium eluted in 0.1 M HCl. Aliquots were taken from the primary solutions and diluted to approximately 10 ng of uranium to measure the uranium isotope composition. The samples were purified using the same chemistry as the uranium assay samples. To quantify background contamination, process blanks were processed alongside the samples through CRM dissolution and chemistry.

Uranium assay measurements for U010 and U850, as well as uranium isotope composition measurements for U850 were performed on a Nu Plasma HR MC-ICP-MS. Uranium isotope composition measurements for U010 were performed on a Nu Plasma 3 MC-ICP-MS. For uranium assay measurements, Faraday detectors were used to measure ^{238}U, ^{235}U, and ^{233}U, ^{234}U was measured on an ion counter. For uranium isotope composition measurements, ^{238}U and ^{235}U were measured on Faraday detectors and ^{236}U, ^{234}U, and ^{233}U were measured on ion counters. In both cases static multi-ion counting methods were employed with a 10 s integration time. CRM U010 was used for mass bias and Faraday-ion counter gain corrections, and the measured isotopic compositions of U010 and U850 were used for IDMS calculations. The CRMs 112A, 129A, and U005-A were used as quality control standards. Other corrections applied to the final data include peak tailing and acid blank subtractions.

Protactinium assay measurements

For protactinium isotope dilution measurements, LLNL purified a ^{233}Pa tracer from a stock solution containing ~ 25 mg ^{237}Np using a three column procedure. The ^{237}Np solution was loaded onto a 2 mL AG MP-1 resin column in 10 M HCl. The ^{233}Pa was eluted in 10 M HCl + 0.05 M HF and the ^{237}Np was recovered using 1 M HCl + 0.5 M HF. This column was repeated using only 1 mL of AG MP-1 resin. Final purification was achieved by loading the ^{233}Pa tracer onto 2 mL of silica gel in 5% HNO_3 and eluting the ^{233}Pa in 5% HNO_3 + 0.1 M HF. Two separately prepared ^{233}Pa tracers were produced during the course of this study. Final spikes were screened by MC-ICP-MS to verify final Np/Pa ratios of < 1000. The final tracer solutions were diluted to between

16 and 28 pg ^{233}Pa/g solution. The ^{233}Pa tracers used in this study were calibrated using an in-house ^{231}Pa solution. The ^{231}Pa concentration of this in-house solution was previously measured using a ^{233}Pa tracer calibrated using the United States Geological Survey (USGS) BCR-2 rock standard and the Table Mountain Latite (TML) material that has been well-characterized by the geological community [14, 15]. Protactinium-233 tracer calibration methods using geological materials have been previously described [16, 17]. Following tracer-sample equilibration, the ^{233}U present from the decay of ^{233}Pa was removed using a single silica gel column purification described above. The ^{231}Pa to ^{233}Pa ratio was measured by the MC-ICP-MS method described below.

For sample ^{231}Pa assay measurements aliquots containing ~ 6.5–7 pg Pa were taken, which contained ~ 125 µg of uranium for U850 and ~ 12 mg of uranium for U010. These aliquots were traced with ~ 2 pg ^{233}Pa. Protactinium was purified from the bulk uranium matrix using a three column procedure. The first column consisted of a 1 mL BioRad AG1-X8 resin bed. Samples were dried and dissolved in 9 M HCl + trace H_3BO_3 + trace HNO_3 and loaded onto the column. Protactinium was eluted with 9 M HCl + 0.05 M HF. The second column was a smaller resin column volume using the same dissolution, rinsing, and elution solutions. The final column was a 1 mL silica gel (high purity, 75–200 µm particle size) column conditioned with 5% HNO_3. The sample was loaded onto the silica gel with 5% HNO_3 and protactinium was eluted using 2% HNO_3 + 0.05 M HF. To quantify background contamination, process blanks were processed alongside the samples through CRM dissolution and chemistry.

All protactinium measurements were performed the same day of the final column purification to minimize the isobaric interferences from the decay of ^{233}Pa to ^{233}U. Protactinium measurements were performed on a Nu Plasma HR MC-ICP-MS using static multi-ion counting methods with ^{231}Pa and ^{233}Pa collected on ion counters with a 10–15 s integration. CRM U010 was used for mass bias and gain corrections, CRM 005-A was used as a quality control standard. Other corrections applied to the final data include peak tailing and blank subtraction.

CIAE analytical methods

CRM dissolution

Primary dissolutions of U010 and U850 were made by dissolving each CRM powder in 6 M HNO_3 on a hotplate at 90 °C for 24 h. Following dissolution each solution was diluted and HF added to generate a final solution for storage of 6 M HNO_3 + 0.05 M HF. The concentration of the uranium in each primary solution was 1–4 mg U/g. Two serial dilutions were made in order to measure ^{235}U concentrations.

Uranium assay and isotope composition measurements

Aliquots containing ~ 3 µg (U850) and ~ 27 µg (U010) of uranium were taken for ^{235}U assay measurements from the second dilution. Each aliquot was traced with ^{233}U (IRMM-051). The IRMM-051 ^{233}U tracer is certified for ^{233}U concentration by mass, therefore no calibration was necessary. Following tracer-sample equilibration, no chemical purification was performed prior to mass spectrometry due to the high-purity of the CRM and tracer materials. Similar aliquot sizes of uranium were also taken for uranium isotope composition measurement. Again, no chemical purification of the sample aliquots was performed. To quantify background contamination, blank acid samples were processed alongside the samples through CRM dissolution and chemistry.

Uranium measurements were performed on a Thermo-Scientific™ Element XR. Dynamic ion counting mode was used with an SEM detector peak-jumping between each isotope with a 2 min integration time. The method involved three runs with twenty passes. Twenty lines were used per peak with the central ten lines used for data calculation. No abundance filter tune was used. CRM IRMM-199 was used for mass bias corrections and the Chinese natural uranium standard reference material GBW04205 was used as a quality control standard.

Protactinium assay measurements

For protactinium isotope dilution measurements CIAE purified a ^{233}Pa tracer from tributyl phosphate waste containing 19.7 mg of ^{237}Np using a five column purification with Eichrom TRU resin and silica gel. This more lengthy purification process was due to the more complex matrix of the CIAE ^{237}Np material than that used by LANL and LLNL. The ^{237}Np solution was loaded onto 1.8 mL TRU resin in 1 M HNO_3 + 0.1 M $NaNO_2$. The resin was rinsed with 1 M HNO_3 + 0.1 M HCl to recover the ^{237}Np and then the ^{233}Pa was eluted in 3 M HCl + 2 M HF. Any residual ^{237}Np was then eluted with high purity water. This column was then repeated. Following elution from the second column, the ^{233}Pa was reconstituted in 3 M HNO_3 and loaded onto a column containing 1.8 mL of silica gel. Any remaining ^{237}Np was recovered with washes of 5% HNO_3 and high purity water. The ^{233}Pa was eluted in 5% HNO_3 + 0.1 M HF. This silica gel column was repeated twice to obtain the ^{233}Pa tracer.

In the absence of a ^{231}Pa standard CIAE calibrated the ^{233}Pa spike using CRM U100. Aliquots of CRM U100 were taken to contain ~ 58 and ~ 53 pg ^{231}Pa and these were traced with ~ 70 pg and ~ 100 pg of ^{233}Pa respectively. Following tracer-sample equilibration for 1 h the samples were reconstituted in 9 M HCl and loaded onto a column containing 1.8 mL BioRad AG1-X8 anion exchange resin. Matrix elements were eluted in 9 M HCl and then Pa was eluted with 9 M HCl + 0.05 M HF. This column was repeated with the subsequent eluted Pa re-constituted in 3 M HNO_3 and loaded onto a column containing 1.8 mL silica gel (high-purity, 70–230 µm particle size). Matrix elements were eluted with 5% HNO_3 and high-purity water. Finally, protactinium was eluted in 5% HNO_3 + 0.05 M HF. The ^{231}Pa to ^{233}Pa ratio was measured by the ICP-MS method described below. For sample ^{231}Pa assay measurements, aliquots containing 2–15 pg of ^{231}Pa were taken which contained ~ 300 µg of uranium for U850 and 1000 µg of uranium for U010. These aliquots were traced with picograms of ^{233}Pa. Following tracer-sample equilibration for an hour the same chemical purification method was performed as described above for the ^{233}Pa tracer calibration. To quantify background contamination, blank acid samples were processed alongside the samples using the same chemistry.

All protactinium measurements were performed within 5 days of the final column purification using a ThermoScientific™ Element XR with the same method and mass bias standards as described above for uranium.

Radiochronometry

The number of atoms of ^{231}Pa and ^{235}U measured by the isotope dilution mass spectrometry methods described above were used in Eq. 1 to calculate the model age of CRMs U010 and U850

$$t = \frac{1}{\lambda_{^{235}\mathrm{U}} - \lambda_{^{231}\mathrm{Pa}}} \ln\left(1 - \frac{N_{^{231}\mathrm{Pa}}}{N_{^{235}\mathrm{U}}} \times \frac{\lambda_{^{231}\mathrm{Pa}} - \lambda_{^{235}\mathrm{U}}}{\lambda_{^{235}\mathrm{U}}}\right) \tag{1}$$

where t is the model age, λ is the decay constant (derived from the half life, Table 1) and N is the number of atoms measured. The model age can be presented as a model purification date relative to a laboratory reference date. This model purification date can then be compared to the known production date of the CRM to assess the validity of the original model assumptions detailed in Sect. 1. The uncertainty on these measurements represents a full error propagation including, but not limited to, components such as half-life uncertainties, spike calibration uncertainties, measurement and weighing uncertainties.

Results and discussion

The measured ^{231}Pa/^{235}U atom ratios, resulting model ages, and model purification dates (with associated uncertainties) are presented in Table 2. The model purification dates are shown in Fig. 1. For reference the ^{230}Th/^{234}U model purification dates reported by LANL, LLNL and CIAE are also plotted in Fig. 1 [8]. Process blank concentrations for both uranium and protactinium for all three laboratories represent < 0.2% of the aliquot sizes and are therefore insignificant relative to reported measurement uncertainties.

The ^{231}Pa/^{235}U model purification dates calculated by LANL, LLNL and CIAE for CRM U010 range from October 14, 1957 to June 17, 1959. These model purification dates are concordant (agree) within analytical uncertainty. However, all model purification dates from this study, with the exception of one CIAE data point, are biased younger than the June 5, 1958 date in the historical record marking the end of production [13]. CRM U010 is not certified for radiochronometry but there is a detailed record of production published by the NBS and Union Carbide/Oak Ridge [13]. The recorded production of CRM U010 began on April 16, 1958 and concluded on June 5, 1958 [13]. No details of the chemical purification procedure are available in the CRM production history so it is possible that Th and Pa were purified from the bulk uranium at different times. The younger (relative to historical record) calculated model ages measured in this study could result from loss of ^{231}Pa or gain of ^{235}U over time through CRM handling. Conversely there may also be a systematic bias in either tracer calibrations or corrections during mass spectrometry. If systematic biases were the cause they would need to be consistent across the diverse range of analytical methods used.

Using the independent measurements reported from each laboratory, an average, or mean, model purification date can be calculated. The external uncertainty (k = 2) provided for the mean is calculated as the uncertainty of the mean using Eq. 2 below:

$$\textit{uncertainty of the mean} = \bar{x} \pm t_{\left(1-\frac{\alpha}{2}\right),\nu}\left(\sigma\sqrt{N}\right) \tag{2}$$

where N is the number of replicates, $t_{\left(1-\frac{\alpha}{2}\right)}$ is the $100_{\left(1-\frac{\alpha}{2}\right)}$th percentile of the student's t-distribution corresponding to a probability $\alpha = 0.05$, and $\nu = N_r - 1$ degrees of freedom. This calculation provides the uncertainty of the mean of the replicates at the 95% confidence level. It does not incorporate the uncertainty on each individual measurements and therefore represents the variability within the data set. The calculated average ^{231}Pa/^{235}U model purification date for CRM U010 is December 28, 1958 ± 198 days. This ^{231}Pa/^{235}U interlaboratory consensus value for CRM U010 is almost 7 months younger than, but consistent within analytical uncertainty with, the CRM U010 historical production records [13]. As noted by [8], the model purification dates calculated using the ^{230}Th/^{234}U radiochronometer are generally biased older than June 5, 1958 suggesting that perhaps ^{230}Th was not completely purified during the production of CRM U010. However, many of the ^{230}Th/^{234}U model purification dates reported previously are concordant with the ^{231}Pa/^{235}U model purification dates within analytical

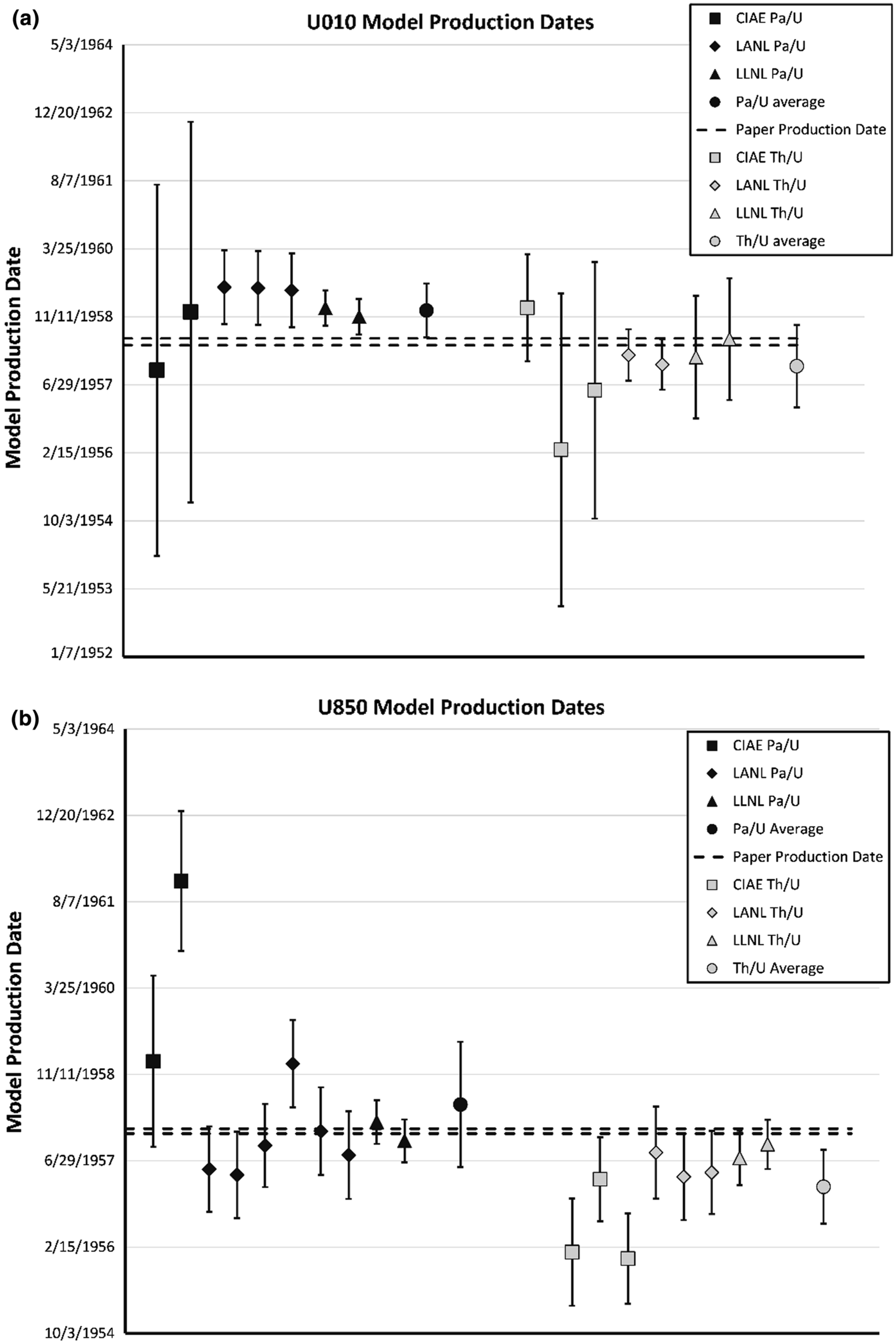
Table 2 Results and calculated model ages and model purification dates for CRM U010 and U850 by CIAE, LANL, and LLNL

Lab	Sample	Reference date	^{231}Pa/^{235}U atom ratio	Uncertainty (k = 2)	Model age (years)[a]	Uncertainty (k = 2, years)	Model purification date	Uncertainty (k = 2, days)
CIAE	U010-1	September 25 2018	6.00×10^{-8}	3.7×10^{-9}	61.0	3.7	October 14, 1957	1364
	U010-2	September 25 2018	5.88×10^{-8}	3.8×10^{-9}	60.0	3.8	December 16, 1958	1399
LANL	U010-1	September 13 2018	5.831×10^{-8}	7.3×10^{-10}	59.24	0.74	June 17, 1959	271
	U010-2	September 13 2018	5.833×10^{-8}	7.3×10^{-10}	59.26	0.74	June 11, 1959	271
	U010-3	September 13 2018	5.838×10^{-8}	7.3×10^{-10}	59.31	0.74	May 24, 1959	271
LLNL	U010-1	September 13 2018	5.872×10^{-8}	3.4×10^{-10}	59.66	0.35	January 14, 1959	129
	U010-2	September 13 2018	5.889×10^{-8}	3.4×10^{-10}	59.84	0.36	November 11, 1958	131
Consensus model purification date	U010						December 28, 1958	198
CIAE	U850-1	July 25 2018	5.85×10^{-8}	1.3×10^{-9}	59.0	1.4	January 26, 1959	496
	U850-2	July 25 2018	5.57×10^{-8}	1.1×10^{-9}	57.0	1.1	December 4, 1961	405
LANL	U850-1	March 16 2017	5.891×10^{-8}	6.6×10^{-10}	59.85	0.68	May 11, 1957	247
	U850-2	March 16 2017	5.899×10^{-8}	6.8×10^{-10}	59.94	0.69	April 8, 1957	251
	U850-3	March 17 2017	5.854×10^{-8}	6.5×10^{-10}	59.48	0.66	September 25, 1957	241
	U850-4	July 26 2017	5.761×10^{-8}	6.8×10^{-10}	58.54	0.69	January 12, 1959	254
	U850-5	August 8 2017	5.870×10^{-8}	6.8×10^{-10}	59.64	0.70	December 17, 1957	254
	U850-6	August 17 2017	5.910×10^{-8}	6.8×10^{-10}	60.05	0.70	August 1, 1957	254
LLNL	U850-1	May 18 2018	5.932×10^{-8}	3.3×10^{-10}	60.27	0.35	February 8, 1958	127
	U850-2	May 18 2018	5.961×10^{-8}	3.2×10^{-10}	60.57	0.34	October 22, 1957	124
Consensus model purification date	U850						May 20, 1958	363

[a] Each model age is calculated from separate aliquots of an independent digestion of the CRM by each laboratory

uncertainty. Additionally, the calculated mean/consensus ^{230}Th/^{234}U model purification date of November 12, 1957 ± 303 days for U010 is concordant with both the known end of production as well as the consensus ^{231}Pa/^{235}U model purification date. The concordant nature of the ^{230}Th/^{234}U and ^{231}Pa/^{235}U results thus give confidence that the radiochronometry model assumptions and recorded production history of CRM U010 are valid.

The interlaboratory model purification dates calculated for CRM U850 range from April 8, 1957 to December 4, 1961. The calculated model purification dates for CRM U850 show larger variation between laboratories than the CRM U010 ^{231}Pa/^{235}U model purification dates, which may result from the calibration methods, materials and instrumentation used. In the case of CRM U850 not all of the model purification dates determined by the laboratories are concordant. There is however, no systematic bias younger or older within these laboratory data than the recorded CRM production date range in the historical record. Similarly to CRM U010, there is a detailed record of production for this CRM published by the NBS and Union Carbide/Oak Ridge [13]. The recorded production began on December 3, 1957 and ended on December 31, 1957 [13] but no details on the chemical purification procedure are available. The calculated mean ^{231}Pa/^{235}U model purification date for CRM U850 is May 20, 1958 ± 363 days. This ^{231}Pa/^{235}U interlaboratory consensus value is approximately 4.5 months younger than but consistent within analytical uncertainty


(a)
U010 Model Production Dates
Model Production Date
5/3/1964
12/20/1962
8/7/1961
3/25/1960
11/11/1958
6/29/1957
2/15/1956
10/3/1954
5/21/1953
1/7/1952
CIAE Pa/U
LANL Pa/U
LLNL Pa/U
Pa/U average
Paper Production Date
CIAE Th/U
LANL Th/U
LLNL Th/U
Th/U average
(b)
U850 Model Production Dates
Model Production Date
5/3/1964
12/20/1962
8/7/1961
3/25/1960
11/11/1958
6/29/1957
2/15/1956
10/3/1954
CIAE Pa/U
LANL Pa/U
LLNL Pa/U
Pa/U Average
Paper Production Date
CIAE Th/U
LANL Th/U
LLNL Th/U
Th/U Average

◂**Fig. 1** Model purification dates calculated for **a** CRM U010, **b** CRM U850. The black symbols are ^{231}Pa/^{235}U model dates calculated in this study by CIAE, LANL, and LLNL. Gray symbols are ^{230}Th/^{234}U model dates previously reported by [8]. The horizontal dashed lines represent the start and end dates of production: April 16, 1958 and June 5, 1958 for U010 and December 3, 1957 and December 31, 1957 for U850 [13]. Error bars represent expanded uncertainties with a coverage factor of 2. The average model purification dates (circle data points) are calculated mean/consensus values of the model purification dates for each radiochronometer. The expanded uncertainty of this consensus value is calculated using Eq. 2

of the recorded end of production. Similarly to CRM U010, the CRM U850 model purification dates calculated using the ^{230}Th/^{234}U radiochronometer are biased older than the known end of production [8]. However, like CRM U010, many of the reported ^{230}Th/^{234}U model purification dates are concordant with the ^{231}Pa/^{235}U model purification dates, within analytical uncertainty. Additionally, the calculated mean/consensus ^{230}Th/^{234}U model purification date for CRM U850 is concordant with the consensus ^{231}Pa/^{235}U model purification date. Therefore these results give confidence that the radiochronometry model assumptions and recorded production history of CRM U850 are also valid. The CIAE U850-2 result is much younger than other model ages. This is due to each U850 model date being derived from different spike calibrations. The lower precision achieved by CIAE is likely due to the use of a single collector mass spectrometer compared to the use of multi-collector instruments at both LANL and LLNL.

Conclusions

The ^{231}Pa/^{235}U model purification dates calculated for CRMs U010 (October 14, 1957 to June 17, 1959) and U850 (April 8, 1957 to December 4, 1961) are generally concordant between laboratories and agree within analytical uncertainty with the production histories of both CRMs. The consistency between the measurements from three different laboratories using different tracers, tracer calibration protocols, purification chemistries and mass spectrometry methods demonstrates the validity of each laboratory's methods. The concordance observed between the ^{231}Pa/^{235}U model purification dates reported by this study and previous ^{230}Th/^{234}U model purification dates for CRM U010 and CRM U850 increases confidence that both ^{230}Th and ^{231}Pa decay products were well-purified during the production of both CRM U010 and CRM U850. Therefore, both CRMs represent good candidate materials to be used for quality control during radiochronometry measurements of unknown uranium materials for nuclear forensics. Through such international collaborations, we validate methods and establish that reproducible ^{231}Pa/^{235}U ages can be obtained by laboratories around the world. This study therefore validates the use of the ^{231}Pa/^{235}U radiochronometer to support radiochronometry measurements in future nuclear forensics investigations and supports the establishment of a global radiochronometry capability that deters nuclear proliferation.

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