



# Evaluating uranium radiochronometry by single-collector mass spectrometry for nuclear forensics: a multi-instrument investigation

Kerri C. Treinen<sup>1</sup> · Kyle M. Samperton<sup>1</sup> · Rachel E. Lindvall<sup>1</sup> · Josh B. Wimpenny<sup>1</sup> · Amy M. Gaffney<sup>1</sup> · Marta Bavio<sup>2</sup> · Eva J. Baransky<sup>1</sup> · Ross W. Williams<sup>1</sup>

Received: 31 July 2019 / Published online: 10 October 2019  
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## Abstract

Radiochronometric data, a key signature in evaluating the provenance and process history of nuclear material out of regulatory control, are conventionally acquired via multi-collector mass spectrometry. Here we explore the potential of age-dating by single-collector mass spectrometry. To evaluate model age accuracy/precision across different instrument designs, we performed  $^{230}\text{Th}$ – $^{234}\text{U}$  and  $^{231}\text{Pa}$ – $^{235}\text{U}$  radiochronometry of CRM 125-A using two single-collector and one multi-collector plasma source mass spectrometers. Single-collector instruments produce accurate model ages for this uranium standard and thus hold promise for nuclear forensics radiochronometry. Increased acquisition of age information via multiple instrument designs will bolster the global response to nuclear interdictions.

**Keywords** Radiochronometry · Single-collector mass spectrometry · Multi-collector mass spectrometry · Uranium · Thorium · Protactinium · Age-dating

## Introduction

Radiochronometry can provide powerful constraints on the history of nuclear material during a nuclear forensic examination. The application of isotope radiochronometers (e.g.,  $^{230}\text{Th}$ – $^{234}\text{U}$  and  $^{231}\text{Pa}$ – $^{235}\text{U}$ ) for characterizing bulk uranium can assist investigators in determining the date of sample production, purification and/or processing (see [1] and references therein). Well-characterized reference materials with known purification ages serve a critical quality control role in validating chemical purification and mass spectrometric methods for radiochronometry [i.e., 2–10]. We have previously developed a streamlined method for purification of protactinium (Pa) and thorium (Th) from bulk uranium (U) and have applied this method to analyze U radiochronometry

certified reference materials (CRMs), including CRM 125-A, U630 and IRMM-1000 [2, 3, 5].

Nuclear forensic laboratories around the world have a variety of isotope dilution spike materials and mass spectrometers (both single-collector and/or multi-collector instruments) that may in theory be utilized for age-dating. In general, single-collector plasma source mass spectrometers are less expensive, with a wider range of applications, and therefore are more common than multi-collector mass spectrometers. While there are a number of technical considerations that make multi-collector–inductively coupled plasma–mass spectrometers (MC-ICP-MS) ideal for isotope ratio measurements required for radiochronometry, single-collector ICP-MS designs may also be capable of accurate and sufficiently-precise U, Th and Pa isotope ratio characterization. If this can be demonstrated, single collector ICP-MS may represent a robust and widely-available alternative to MC-ICP-MS for radiochronometry, thereby expanding significantly the number of potential radiochronometry practitioners.

To evaluate the feasibility of single-collector ICP-MS radiochronometry analyses, we performed a multi-instrument intercomparison experiment in which single- and multi-collector ICP-MS instruments were used to characterize radiochronometry reference material CRM 125-A.

✉ Kerri C. Treinen  
treinen1@llnl.gov

<sup>1</sup> Nuclear and Chemical Sciences Division, Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA

<sup>2</sup> National Atomic Energy Commission, Av. Gral. Paz 1499, Partido Gral., B1650KNA San Martín, Bs. As. Province, Argentina

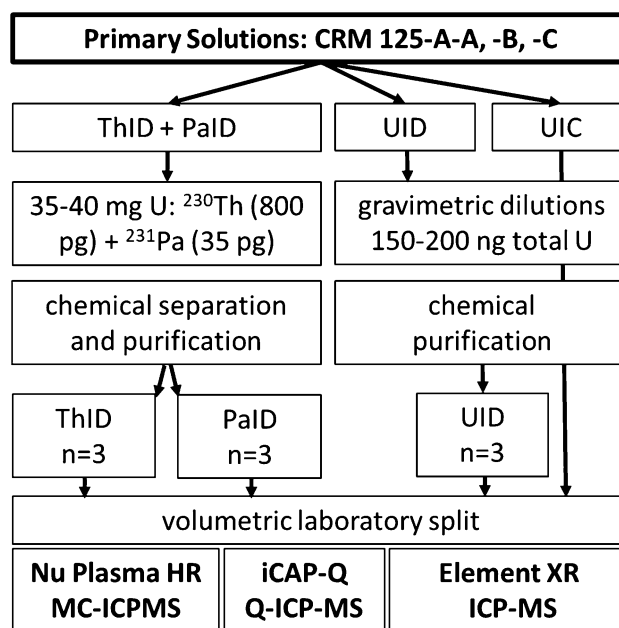
We performed  $^{230}\text{Th}$ – $^{234}\text{U}$  and  $^{231}\text{Pa}$ – $^{235}\text{U}$  analyses on CRM 125-A using three different instruments at Lawrence Livermore National Laboratory (LLNL): (1) ThermoScientific iCAP-Q quadrupole single-collector inductively coupled plasma–mass spectrometer (Q-ICP-MS), (2) ThermoScientific Element XR high resolution single-collector ICP-MS (HR-ICP-MS), and (3) Nu Plasma HR multi-collector ICP-MS (MC-ICP-MS). The same sample aliquots, isotopic tracers, QC reference materials, and data reduction algorithms were employed in the generation and processing of data generated by each instrument, allowing for direct comparison of age-dating results amongst the various mass spectrometer designs.

While single-collector instruments have previously been used to measure parent and daughter isotope concentrations in certified radiochronometry standards [10], the current study is the first to directly compare age-dating results across different ICP-MS platforms. The goal of this multi-instrument approach is to evaluate whether the entire radiochronometric analysis process can be performed using a single-collector plasma source instrument, including: (1) isotopic composition determination, (2) spike calibrations for isotope dilution, and (3) parent and daughter isotopic assay quantification, for an independent and stand-alone single-collector instrument technique. Successful demonstration of radiochronometry analyses by single-collector ICP-MS is of benefit to the international nuclear forensic community as it would permit age-dating measurements to be performed by countries that do not have access to MC-ICP-MS for nuclear forensics.

### Sample purification

Radiochronometry standard CRM 125-A is an enriched uranium dioxide pellet ( $\text{UO}_2$ ; 4.2% enrichment) that is certified for uranium isotopic composition, assay, and model purification date based on  $^{230}\text{Th}$ – $^{234}\text{U}$  chronometry [11]. In order to evaluate the accuracy and precision of age-dating results from the two single-collector and one multi-collector instruments used in this study, CRM 125-A aliquots were prepared following the sample workflow displayed in Fig. 1. Three aliquots of CRM 125-A were dissolved, chemically separated and purified, and split to provide chemically-identical aliquots for each mass spectrometric technique. Calculation of  $^{230}\text{Th}$ – $^{234}\text{U}$  and  $^{231}\text{Pa}$ – $^{235}\text{U}$  model ages requires analyses of the isotopic composition of uranium in the CRM 125-A aliquots, in conjunction with  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  assay (concentration) determination by isotope dilution mass spectrometry (IDMS), referred to hereafter as UID, ThID and PaID, respectively.

First, three solid CRM 125-A  $\text{UO}_2$  pellet aliquots, labeled CRM 125-A-A, -B and -C, were dissolved following LLNL's standard operating procedure for U, Th, and



**Fig. 1** CRM 125-A aliquot preparation and splitting workflow for multi-instrument radiochronometric intercomparison study

Pa determination by IDMS [2]. Dissolved CRM 125-A aliquots, or ‘primary solutions’, were prepared in clean, dry 30-mL Savillex® Teflon vials and stored in 4 M  $\text{HNO}_3$  + 0.05 M HF for further processing.

Following digestion, gravimetric dilution series of the aforementioned primary solutions were prepared for parent isotopic assay determination (i.e.,  $^{234}\text{U}$  and  $^{235}\text{U}$ ). Dilution aliquots were spiked with an in-house, ultra-high purity, calibrated  $^{233}\text{U}$  isotope dilution spike (see spike calibration section below). These UID dilution series were made to target a final U concentration of approximately 80–100 ppb. Approximately 160–200 ng total U of each solution (CRM 125-A-A, -B, -C) were weighed into clean Savillex® Teflon vials and spiked with approximately 10–15 ng  $^{233}\text{U}$  spike. Each UID cross was then split into separate aliquots for analysis using each mass spectrometer.

In this project CRM 125-A was analyzed as if it were an unknown sample; hence, it was necessary to characterize its uranium isotopic composition (UIC). This value and associated uncertainty were included in all age-dating calculations, and thus affect the final results from each instrument. The corresponding  $^{235}\text{U}/^{238}\text{U}$  ratios influence the final age-dating results through isotope dilution calculations for each instrument. Some isotopic composition results are outside expanded uncertainty envelope of the certified isotopic composition (Table 1). While this may reflect residual instrumental bias, we note that we have previously observed uranium isotopic heterogeneity between individually dissolved CRM 125-A pellets.

**Table 1** CRM 125-A-A, -B, -C isotopic composition and certificate value for reference

Instrument	Sample ID	$^{234}\text{U}/^{238}\text{U}$	Uncert.	$^{235}\text{U}/^{238}\text{U}$	Uncert.	$^{236}\text{U}/^{238}\text{U}$	Uncert.
Nu Plasma HR	125-A-A	0.0003948	0.0000013	0.042318	0.000043	0.000003860	0.000000035
Nu Plasma HR	125-A-B	0.0003936	0.0000013	0.042358	0.000043	0.000003834	0.000000037
Nu Plasma HR	125-A-C	0.0003927	0.0000013	0.042347	0.000043	0.000003849	0.000000035
Element XR	125-A-A	0.0003873	0.0000025	0.04337	0.00025	0.00000532	0.000000022
Element XR	125-A-B	0.0003878	0.0000025	0.04339	0.00025	0.00000519	0.000000022
Element XR	125-A-C	0.0003870	0.0000024	0.04329	0.00024	0.00000531	0.000000024
iCAP-Q	125-A-A	0.0003921	0.0000043	0.04224	0.00042	n.d.	n.d.
iCAP-Q	125-A-B	0.0003914	0.0000042	0.04198	0.00042	n.d.	n.d.
iCAP-Q	125-A-C	0.0003898	0.0000041	0.04180	0.00041	n.d.	n.d.
Certificate	125-A	0.00039130	0.00000038	0.042301	0.000025	0.0000040754	0.0000000047

All uncertainties are reported at the  $2\sigma$ -level. *n.d.* no data (not collected)

Small aliquots (i.e., ~50  $\mu\text{g}$  U) of dissolved primary solutions for CRM 125-A-A, -B, and -C were dissolved in 3 mL 2%  $\text{HNO}_3$ . Each mass spectrometric technique required different dilutions of these prepared UIC fractions for isotopic composition determination, contingent upon operating conditions (e.g., sensitivity) of each instrument at the time of analysis.

Three individual (CRM 125-A-A, -B, -C) aliquots were spiked with both  $^{229}\text{Th}$  and  $^{233}\text{Pa}$  spikes, and then chemically separated and purified for a ‘paired’ daughter ( $^{230}\text{Th}$  and  $^{231}\text{Pa}$ ) assay determination by IDMS (ThID and PaID; Fig. 1). All aliquots (30–40 mg bulk U) were spiked with approximately 30 pg of freshly-prepared and calibrated  $^{233}\text{Pa}$  spike (see spike calibration section below) and 5–10 ng of NFRM  $^{229}\text{Th}$  spike [12]. These ‘paired’ aliquots were separated into ThID and PaID fractions by performing a bulk U separation using Eichrom<sup>®</sup> AG 1-X8 (100–200 mesh) anion exchange resin. ThID aliquots were further purified with Eichrom<sup>®</sup> TEVA resin and another Eichrom<sup>®</sup> AG 1-X8 anion resin column. PaID aliquots were further purified from bulk U and ingrown  $^{233}\text{U}$  with a second Eichrom<sup>®</sup> AG 1-X8 anion exchange resin column, followed by a final purification using Supelco<sup>®</sup> Silica Gel Resin [2, 5].

Final purified aliquots of Th, Pa, and U were dissolved and split volumetrically for each instrument. All U fractions (both UID and UIC aliquots) were dissolved in 2%  $\text{HNO}_3$ , fluxed on a hoptate to equilibrate, and analyzed soon after preparation. Spiked Pa fractions (PaID) were eluted from the final Si-gel purification column in 2%  $\text{HNO}_3$  + 0.05 M HF and analyzed the same day as final purification chemistry [2]. Spiked Th fractions (ThID) were dissolved in 2%  $\text{HNO}_3$  + 0.005 HF, fluxed to equilibrate, and analyzed.

### Multi-instrument spike calibrations

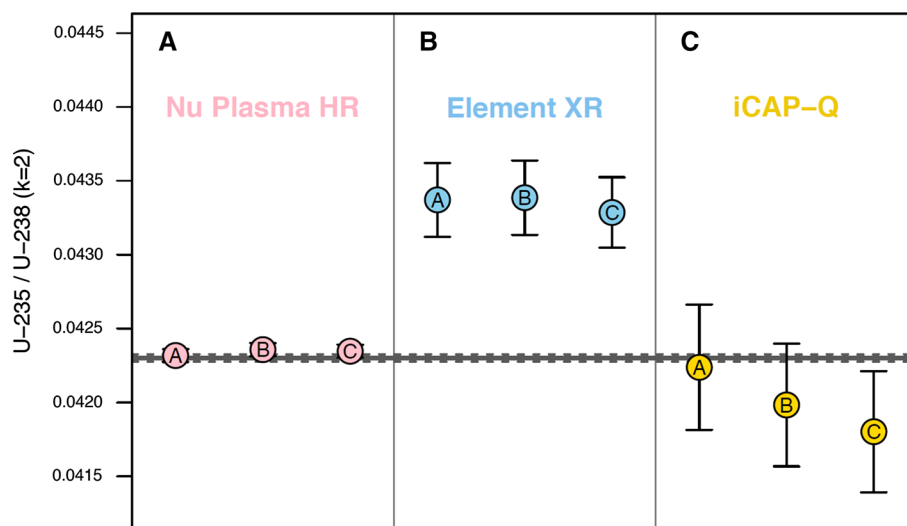
Accurate model ages require properly calibrated isotopic tracers, or “spikes” (e.g.,  $^{229}\text{Th}$ ,  $^{233}\text{U}$  and  $^{233}\text{Pa}$ ),

for concentration determination by isotope dilution. All spiked aliquots for isotopic assay determination were prepared using a freshly prepared and calibrated  $^{233}\text{Pa}$  spike; nuclear forensics reference material (NFRM)  $^{229}\text{Th}$  spike [12]; and a very-high purity (99.9877%)  $^{233}\text{U}$  spike. Each instrument was used to determine an independent  $^{233}\text{U}$  and  $^{233}\text{Pa}$  spike calibration by IDMS, with the resulting spike concentrations and uncertainties being incorporated into final age calculations. The  $^{229}\text{Th}$  spike was not independently calibrated for each instrument, as this solution is certified by mass [12]; as such, the certificate NFRM  $^{229}\text{Th}$  calibration was used in all Th IDMS calculations (Fig. 2).

LLNL’s in-house, ultra-high purity  $^{233}\text{U}$  spike was calibrated using two separately prepared gravimetric standard solutions of CRM 112-A (SRM 960), a U isotopic and assay standard, in 4 M  $\text{HNO}_3$  and 0.05 M HF. Eight spike-sample crosses were prepared, each consisting of approximately 10 ng of  $^{233}\text{U}$  spike and 200–800 ng CRM 112-A. Spike calibration crosses 1–4 were prepared with a CRM 112-A solution dissolved in October 2016. Spike calibration crosses 5–8 were prepared with another CRM 112-A solution dissolved in November 2017. The calibration crosses were designed to have a large dynamic range in  $^{238}\text{U}/^{233}\text{U}$  and  $^{235}\text{U}/^{233}\text{U}$ , with these ratios being measured subsequently by mass spectrometry. The known concentration of  $^{238}\text{U}$  and  $^{235}\text{U}$  from CRM 112-A was used to calibrate the unknown  $^{233}\text{U}$  concentration in the spike, for a final calculated average value and uncertainty (Table 2). Results for all three instrument approaches are summarized in Fig. 3.

A weighted-mean  $^{233}\text{U}$  spike calibration was determined using data produced by each instrument independently and the numerical algorithm of Lyons et al. (1988). As shown in Fig. 3, all three independently-calculated  $^{233}\text{U}$  spike calibrations agree within uncertainty ( $k=2$ ); the Nu Plasma HR yielded the most precise spike calibration, followed by the Element XR and iCAP-Q.

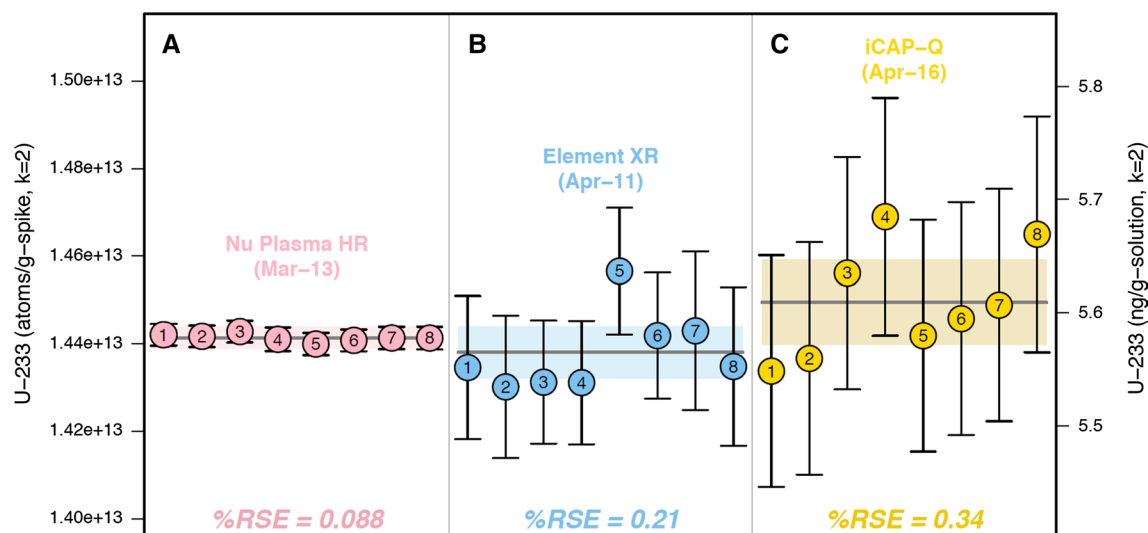
**Fig. 2** Multi-instrument uranium isotopic composition results ( $^{235}\text{U}/^{238}\text{U}$ ) for the three plasma source ICP-MS instruments. A) Nu Plasma HR (MC-ICP-MS) UIC results. B) Element XR (ICP-MS) UIC results. C) iCAP-Q (ICP-MS) UIC results. The horizontal dark grey line and dashed lines are the certified  $^{235}\text{U}/^{238}\text{U}$  isotopic composition and associated uncertainty [11]. Uncertainties are displayed at the  $k=2$  level



**Table 2** Final  $^{233}\text{U}$  spike calibration results for each instrument

Instrument	Sample ID	Atoms- $^{233}\text{U}$ /g-Spike 917	Expanded uncert.	ng- $^{233}\text{U}$ /g-Spike 917	Expanded uncert.	%RSE ( $k=1$ )
Nu Plasma	Cal-1	1.4421E+13	2.5E+10	5.5805	0.0096	0.086
Nu Plasma	Cal-2	1.4417E+13	2.5E+10	5.5791	0.0096	0.086
Nu Plasma	Cal-3	1.4428E+13	2.5E+10	5.5833	0.0096	0.086
Nu Plasma	Cal-4	1.4411E+13	2.7E+10	5.5765	0.0104	0.093
Nu Plasma	Cal-5	1.4400E+13	2.5E+10	5.5723	0.0098	0.088
Nu Plasma	Cal-6	1.4408E+13	2.5E+10	5.5755	0.0097	0.087
Nu Plasma	Cal-7	1.4414E+13	2.5E+10	5.5777	0.0098	0.088
Nu Plasma	Cal-8	1.4413E+13	2.6E+10	5.5776	0.0100	0.090
Nu Plasma	Avg. Calib.	1.4414E+13	2.5E+10	5.5778	0.0098	0.088
ElementXR	Cal-1	1.435E+13	1.6E+11	5.552	0.063	0.57
ElementXR	Cal-2	1.430E+13	1.6E+11	5.534	0.063	0.57
ElementXR	Cal-3	1.431E+13	1.4E+11	5.539	0.054	0.49
ElementXR	Cal-4	1.431E+13	1.4E+11	5.538	0.055	0.49
ElementXR	Cal-5	1.457E+13	1.4E+11	5.637	0.056	0.50
ElementXR	Cal-6	1.442E+13	1.4E+11	5.580	0.056	0.50
ElementXR	Cal-7	1.443E+13	1.8E+11	5.584	0.070	0.63
ElementXR	Cal-8	1.435E+13	1.8E+11	5.552	0.070	0.63
ElementXR	Avg. Calib.	1.438E+13	5.9E+10	5.565	0.023	0.21
iCAP-Q	Cal-1	1.434E+13	2.6E+11	5.548	0.102	0.92
iCAP-Q	Cal-2	1.437E+13	2.7E+11	5.560	0.103	0.92
iCAP-Q	Cal-3	1.456E+13	2.7E+11	5.635	0.103	0.91
iCAP-Q	Cal-4	1.469E+13	2.7E+11	5.685	0.105	0.92
iCAP-Q	Cal-5	1.442E+13	2.6E+11	5.580	0.102	0.92
iCAP-Q	Cal-6	1.446E+13	2.7E+11	5.595	0.103	0.92
iCAP-Q	Cal-7	1.449E+13	2.7E+11	5.607	0.103	0.91
iCAP-Q	Cal-8	1.465E+13	2.7E+11	5.669	0.104	0.92
iCAP-Q	Avg. Calib.	1.449E+13	9.7E+10	5.609	0.038	0.34

Uncertainties are expanded,  $k=2$ , except where noted explicitly



**Fig. 3**  $^{233}\text{U}$  spike calibration; Panel A: Nu Plasma HR MC-ICP-MS, Panel B: Element XR ICP-MS, and Panel C: iCAP-Q Q-ICP-MS. Error bars,  $k=2$ , represent the combined uncertainty for each inde-

pendent cross and analysis. The shaded colored bars in each panel represent the weighted mean and 2RSE for the calculated average

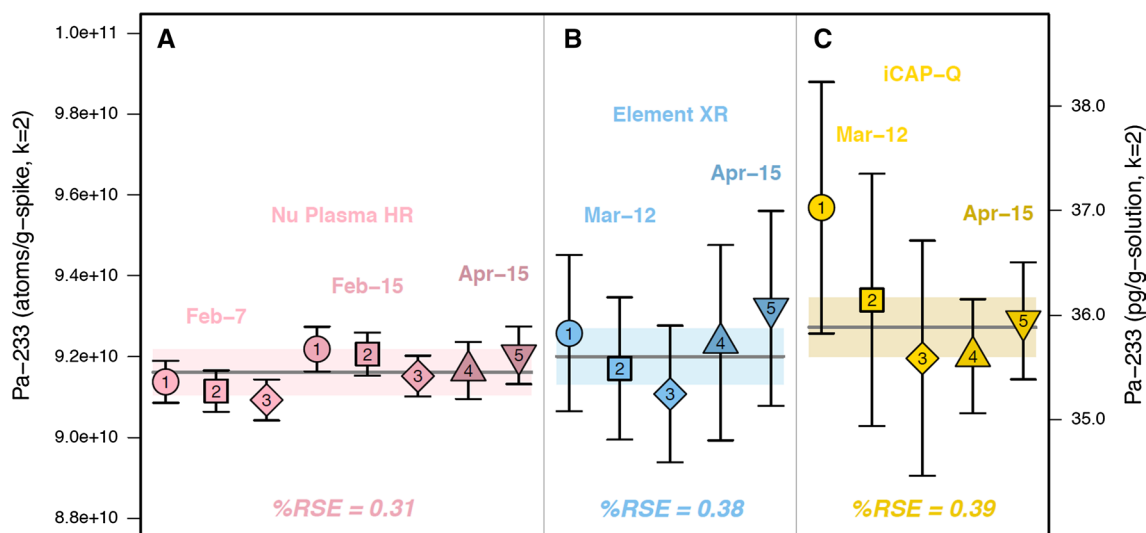
Calibration analyses of the  $^{233}\text{Pa}$  spike were also performed using data from each instrument independently. Analyses were made on the same day with all three instruments, directly following final purification chemistry. In total, five calibration crosses and a chemistry blank were prepared using an in-house  $^{231}\text{Pa}$  calibration solution of known concentration, spiking each calibration cross with approximately 10 pg  $^{231}\text{Pa}$ . The calibration crosses had a range of concentrations, from 10 to 35 pg  $^{233}\text{Pa}$  per sample. Methods used for the  $^{233}\text{Pa}$  spike preparation and calibration are described in [2]. The  $^{233}\text{Pa}$  spike used for this study was initially calibrated in February 2019. The initial calibration analyses of the  $^{233}\text{Pa}$  spike were performed using the Nu Plasma HR MC-ICP-MS (calibration samples 1–3). One week later, these three calibration crosses were re-prepared for analysis by drying the crosses and performing a purification column to remove any ingrown  $^{233}\text{U}$  before reanalysis by MC-ICP-MS. These calibration crosses (1–3) were then dried down and stored for future additional calibration measurements by single-collector instruments. The original three calibration crosses were purified a third time for analysis by the Element XR and iCAP-Q ICP-MS in March 2019. Two additional  $^{233}\text{Pa}$  spike calibration crosses were prepared in April 2019 and analyzed by all three instruments on the same day (calibration samples 4–5). The results are shown in Fig. 4, with symbols representing individual, gravimetrically prepared calibration crosses. Results for  $^{233}\text{U}$  and  $^{233}\text{Pa}$  spike calibrations by each instrument and the corresponding relative standard errors are summarized in Table 3. As with the  $^{233}\text{U}$  spike calibration, the  $^{233}\text{Pa}$  spike calibration was determined for each instrument independently using the numerical algorithm of Lyons et al., 1988 [13].

Results from the Nu Plasma represent two analytical sessions for Pa-233-Cal-1, -2, -3 and one analytical session for Pa-233-Cal-4, -5. The iCAP-Q and Element XR each analyzed Pa-233 Cal-1-5 once during two analytical sessions each. The average of the results is given with expanded uncertainties,  $k=2$ .

### Mass spectrometry methods

Each mass spectrometric technique used in this study is described in detail below: (1) ThermoScientific iCAP-Q quadrupole single-collector ICP-MS, (2) ThermoScientific Element XR single-collector ICP-MS, and (3) Nu Plasma HR multi-collector ICP-MS. For all instruments the reference material CRM U010 was used to monitor instrumental mass-dependent fractionation in each analytical session (see “*Mass Spectrometry Data Reduction and Assessment*” below). In addition, for all instruments CRM U005A was analyzed over the course of each analytical session as a QC material to ensure the accuracy of isotope ratio measurement and data reduction corrections (e.g., blank, mass bias, etc.). The U isotopic results for CRM U005A for all analytical sessions across all instrument platforms were consistent with certificate values.

The protactinium (PaID) aliquot for both single-collector instruments was first centrifuged at 3000 rpm for 15 min and the supernate was split into two separate fractions (one for each instrument). The decision to centrifuge was based on a previous clogging event of the sample introduction system with  $\text{SiO}_2$  particles from silica gel resin used to purify the sample immediately prior to analysis. In the March 2019 analytical session, each single-collector instrument had a



**Fig. 4** Multi-instrument  $^{233}\text{Pa}$  spike calibration; Panel A: Nu Plasma HR MC-ICP-MS, Panel B: Element XR ICP-MS, and Panel C: iCAP-Q ICP-MS. Numbered data points indicate the same measured spike calibration aliquots. Error bars,  $k=2$ , represent the combined

uncertainty for each independent cross and analysis. The shaded colored bars in each panel represent the weighted mean and 2RSE for the calculated average

**Table 3** Final  $^{233}\text{Pa}$  spike calibration results for all three instruments

Instrument	Sample ID	Atoms- $^{233}\text{Pa/g-Spike}$	Expanded uncert.	$\text{pg-}^{233}\text{Pa/g-Spike}$	Expanded uncert.	%RSE ( $k=1$ )
Nu Plasma	Pa-233-Cal-1_1	9.138E+10	5.2E+08	35.36	0.20	0.28
Nu Plasma	Pa-233-Cal-2_1	9.115E+10	5.1E+08	35.27	0.20	0.28
Nu Plasma	Pa-233-Cal-3_1	9.093E+10	5.1E+08	35.19	0.20	0.28
Nu Plasma	Pa-233-Cal-1_2	9.219E+10	5.5E+08	35.67	0.21	0.30
Nu Plasma	Pa-233-Cal-2_2	9.207E+10	5.3E+08	35.63	0.21	0.29
Nu Plasma	Pa-233-Cal-3_2	9.152E+10	5.0E+08	35.42	0.19	0.28
Nu Plasma	Pa-233-Cal-4	9.166E+10	7.1E+08	35.47	0.27	0.38
Nu Plasma	Pa-233-Cal-5	9.204E+10	7.1E+08	35.62	0.28	0.39
Nu Plasma	Avg. Calib.	9.162E+10	5.7E+08	35.45	0.22	0.31
ElementXR	Pa-233-Cal-1	9.258E+10	9.7E+08	35.83	0.37	0.52
ElementXR	Pa-233-Cal-2	9.171E+10	8.8E+08	35.49	0.34	0.48
ElementXR	Pa-233-Cal-3	9.108E+10	8.5E+08	35.24	0.33	0.46
ElementXR	Pa-233-Cal-4	9.234E+10	1.2E+09	35.73	0.47	0.65
ElementXR	Pa-233-Cal-5	9.319E+10	1.2E+09	36.06	0.47	0.65
ElementXR	Avg. Calib.	9.2006E+10	6.92E+08	35.60	0.27	0.38
iCAP-Q	Pa-233-Cal-1	9.569E+10	1.6E+09	37.03	0.60	0.81
iCAP-Q	Pa-233-Cal-2	9.340E+10	1.6E+09	36.14	0.60	0.84
iCAP-Q	Pa-233-Cal-3	9.196E+10	1.5E+09	35.59	0.56	0.79
iCAP-Q	Pa-233-Cal-4	9.201E+10	7.1E+08	35.61	0.27	0.38
iCAP-Q	Pa-233-Cal-5	9.288E+10	7.2E+08	35.94	0.28	0.39
iCAP-Q	Avg. Calib.	9.2731E+10	7.3E+08	35.88	0.28	0.39

total of 1 mL purified sample solution with approximately 3–6  $\text{pg } ^{233}\text{Pa}$  available for the Pa spike calibrations. The prepared CRM 125-A aliquots, in 2 mL of solution had approximately 25  $\text{pg Pa}$  was available for analysis. In the April 2019

analytical session, the Pa spike calibration crosses contained approximately 6  $\text{pg } ^{233}\text{Pa}$ . The  $^{233}\text{Pa}$  spike calibration and samples were analyzed in the eluted 2%  $\text{HNO}_3$  + 0.05 M HF. The U010 mass bias solution was prepared in 2%  $\text{HNO}_3$ .



## ThermoScientific iCAP-Q quadrupole single-collector ICP-MS

The Pa, Th and U analyses were performed using a ThermoScientific iCAP-Q quadrupole ICP-MS with a single secondary electron multiplier (Bremen, Germany). The chosen sample introduction system components varied depending on the required sensitivity for a given analysis.

Protactinium (PaID) and thorium (ThID) analyses were measured using an APEX IR Desolvating Nebulizer (Elemental Scientific) with a self-aspirating APEX PFA ST-1970 variable flow nebulizer (flow rate 0.4 mL/min) and high-sensitivity cones. The combination of the APEX with the high-sensitivity cones provided an approximate 10-fold improvement in sensitivity for a total of  $\sim 7 \times 10^6$  counts per second per ppb (cps/ppb)  $^{238}\text{U}$  with an oxide production  $< 2\%$ . Samples were introduced in the eluted matrix of 2%  $\text{HNO}_3$  and 0.05 M HF. The mass bias solution, CRM U010, and the QA/QC solution, CRM U005A, were prepared at a concentration of 100–150 pg/g in 2%  $\text{HNO}_3$  and 0.005 M HF. Data were collected using time resolved analysis and solely within counting mode of the detector. Standard-sample bracketing was utilized in all analysis sequences.

The March 2019 analytical session included  $^{229}\text{Th}$ ,  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$ ,  $^{232}\text{Th}$ ,  $^{233}\text{Pa}$ ,  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  intensities. Dwell times of 50 ms and 10 ms were assigned to Pa and U masses, respectively. Total analysis time for each pass was 0.16 s; 400 passes were collected for each sample/standard corresponding to a measurement time of approximately 1.5 min. Average total Pa measured for both isotopes was  $\sim 0.35$  pg in the spike calibration solutions and 0.9 pg in the CRM 125-A-A-C sample solutions. The U005 QA/QC solution had a sensitivity of  $\sim 7.4 \times 10^6$  cps/ppb U.

In the April analytical session,  $^{228}\text{Th}$  was added to the acquired masses, and a dwell time of 100 ms was assigned to all masses to produce 0.90 s per pass. For the Pa spike calibration analyses, 99 passes were collected for a total measurement time of 1.5 min for each calibration analysis. Average total Pa measured for both isotopes was 2.5 pg. In the Th ID analysis, 198 passes were collected for a total measurement time of 3 min per analysis. Average total Th measured in CRM125-A-C for  $^{229}\text{Th}$  and  $^{230}\text{Th}$  was 13 pg and 50 pg, respectively.

Sample UID, UIC and  $^{233}\text{U}$  spike calibration analyses were performed with a traditional “wet plasma” using a standard quartz introduction system, including a cyclonic spray chamber; a self-aspirating Sea Spray U series nebulizer, 0.5 mm autosampler probe (flow rate  $\sim 0.36$  mL/min); and standard extraction cones. Instrument optimization yielded a sensitivity of 520,000 cps/ppb U and cerium oxide production of  $< 2\%$ . Data were collected using time resolved analysis and standard-sample bracketing was utilized in all analysis sequences. The mass bias solution (CRM

U010) and QC solution (CRM U005A) were prepared in 2%  $\text{HNO}_3$  at concentrations to match the concentration of U in the samples. UID samples were measured at  $\sim 2$  ng U/g solution to keep both the  $^{233}\text{U}$  and  $^{238}\text{U}$  signals in the pulse counting mode of the detector to avoid any uncertainty that could result from crossing into analog mode. The  $^{233}\text{U}$  spike calibration analyses had different 233:238 ratios and concentrations and were measured at approximately 2 ng U/g solution and 8 ng U/g solution to have sufficient  $^{233}\text{U}$  signal for measurement. UIC samples were analysed at  $\sim 75$  ng U/g solution in order to have a  $^{234}\text{U}$  signal greater than 10,000 cps (Table 4).

Critical Limit Lc was calculated based on uranium sensitivity and using the standard deviation of 3 process blanks and multiplied by the student t factor 9.925 for 2 degrees of freedom at the 99% CI. Only 2 process blanks were analyzed in the 15-April-2019 run and therefore the standard deviation was multiplied by 63.657 for 1 degree of freedom at the 99% CI.

## ThermoScientific Element XR single-collector ICP-MS

The Element XR is a magnetic sector single-collector ICP-MS instrument with high resolving power designed for trace element concentration measurements. Here, it was utilized to make Pa, Th and U isotope ratio measurements following the procedures outlined below.

Protactinium (PaID) and ThID: Samples were dissolved in 2%  $\text{HNO}_3$  + trace HF and introduced to the plasma using an ESI ST variable flow Teflon nebulizer connected to an ESI Apex IR introduction system, which partially desolvates the sample and reduces oxide formation. The Element XR was fitted with the standard ‘H’ skimmer cone and high sensitivity ‘Jet’ sample cone, achieving a sensitivity of  $1.2 \times 10^7$  cps/ppb for  $^{238}\text{U}$  and an oxide production rate of  $< 2\%$ . The analytical method involved collecting data for  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$ ,  $^{232}\text{Th}$ ,  $^{233}\text{Pa}$ ,  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  intensities. During each pass the total sampling time for each isotope was between 5 and 20 ms. Each individual sample or standard measurement consisted of a total of 200 passes, which corresponds to a sampling time of approximately 7 min. Mass bias standard CRM U010 was measured at a concentration of 50 ppt, which produced a  $^{238}\text{U}$  signal of  $\sim 500$  k cps. All isotopes in standards and samples were analyzed using counting mode on the secondary electron multipliers, preventing complications associated with detector cross-calibration. To assess the accuracy of these measurements, the standard U005A was analyzed alongside the samples as an unknown.

Uranium (UID) and UIC: Samples and standards were diluted in 2%  $\text{HNO}_3$  and introduced to the instrument in ‘wet plasma’ mode using a cyclonic spray chamber. Typical sensitivity using this setup was  $1.7 \times 10^6$  cps/ppb  $^{238}\text{U}$ .

**Table 4** iCAP-Q ICP-MS parameter summary table

Date	3/12/2019		4/15/2019		4/15/2019		4/16/2019	
Inlet system	APEX IR		APEX IR		APEX IR		Wet plasma	
Uptake rate (ml/min)	0.40		0.40		0.40		0.36	
Total analysis time (min)	3.0		2.5		4.0		2.5	
Total solution used (ml)	0.86		1.0		1.6		1.3	
Analysis	Pa Spike Cal		PaID Sample		Pa Spike Cal		ThID Sample	
							UID, U233 Spike Cal, UIC	
Isotope	231	233	231	233	231	233	229	230
critical limit (Lc) (ppt)	0.000077	0.00019	0.00034	0.00072	0.0013	0.0046	-	-
Chemistry blank (ppt)	0.0018	-	0.00083	-	-	-	-	0.0034
Analyte (pg/g)	0.86	0.62	2.5	1.5	2.5	2.5	8.0	31
AVG total analyte consumed (pg)	0.39	0.28	1.1	0.68	2.5	2.5	13	50
Mass bias (U010 ng/g)	0.1				0.15		0.15	
QC (U005-A ng/g)	0.1				0.15		0.15	
acid matrix	2% HNO <sub>3</sub> +0.05 M HF				2% HNO <sub>3</sub> +0.05 M HF		2% HNO <sub>3</sub> +0.005 M HF	

Both UIC and UID samples were bracketed by a 10 ppb dilution of the U010 standard, with <sup>238</sup>U analyzed in analog mode and <sup>233</sup>U, <sup>234</sup>U, <sup>235</sup>U and <sup>236</sup>U analyzed in counting mode. Uranium was measured at relatively high level in order to obtain a high <sup>234</sup>U signal. Typical <sup>234</sup>U intensities for unknowns were ~8000 cps. The standard U005A was analyzed alongside the uranium samples for QC purposes and, as mentioned above, results are consistent with certified values [14].

### Nu Plasma HR multi-collector ICP-MS

The U, Th and Pa mass spectrometry methods by Nu Plasma multi-collector ICP-MS are described below. UID and spike calibration samples were analyzed by measuring the <sup>233</sup>U, <sup>235</sup>U, and <sup>238</sup>U isotopes simultaneously on Faraday collectors (Fig. 5, routine ‘U-ID-234-IC0’). UIC fractions were measured with the <sup>235</sup>U and <sup>238</sup>U beams on Faraday collectors, and <sup>234</sup>U on an ion counter (Fig. 5, routine ‘U-Static’). The Nu Plasma HR MC-ICP-MS sample introduction consisted of a CETAC® Aridus II desolvating nebulizer system and autosampler equipped with a Savillex® PFA C-Flow nebulizer (100 µL/min). Average instrument sensitivity over the course of this study was equivalent to ~0.5 V/ppb. This setup was used for all U, Th and Pa isotope ratio analyses, as a ‘dry plasma’ optimizes Nu Plasma HR sensitivity for such actinide measurements. Given this sensitivity and instrument configuration, the <sup>233</sup>U spike calibration samples ran between 4–6 V <sup>238</sup>U and between 30 and 135 mV <sup>233</sup>U. CRM 125-A samples were measured with a <sup>238</sup>U signal intensity between 300 and 500 mV and 25–35 mV <sup>233</sup>U.

ThID aliquots were analyzed using a two-cycle, dynamic multi-collection routine in which <sup>232</sup>Th is measured continuously on a Faraday collector and <sup>229</sup>Th and <sup>230</sup>Th are sequentially analyzed on the same ion counter by peak-jumping (Fig. 5, routine ‘Th-Jump’). Because <sup>229</sup>Th and <sup>230</sup>Th analyses are performed contemporaneous with Faraday <sup>232</sup>Th measurements, the <sup>229</sup>Th/<sup>230</sup>Th ratio can be calculated by crossing <sup>229</sup>Th/<sup>232</sup>Th (cycle #1) with <sup>230</sup>Th/<sup>232</sup>Th (cycle #2). This approach results in more precise <sup>229</sup>Th/<sup>230</sup>Th data, as the uncertainties associated with Faraday/IC gains are eliminated. ThID samples were measured at a <sup>229</sup>Th ion beam intensity between 55,000 and 110,000 cps and a <sup>230</sup>Th signal intensity between 125,000 and 450,000 cps. High-purity <sup>232</sup>Th spike was added to each sample prior to mass spectrometry to yield an intensity of approximately 30 mV <sup>232</sup>Th on a Faraday collector.

Protactinium (PaID) aliquots were analyzed using a one-cycle, static multi-collection routine in which <sup>231</sup>Pa and <sup>233</sup>Pa are simultaneously measured on separate ion counters (Fig. 5, routine ‘Pa-Pulse’). Pa-233 intensities for CRM 125-A-A-C were between 10,500 and 32,000 cps; corresponding <sup>231</sup>Pa intensities ranged 47,000–54,000 cps.

Instrumental mass-dependent fractionation and Faraday/IC gain corrections for U measurements were made using CRM U010 in the same analytical batch run by standard–sample–standard bracketing (see below). For complementary analytical details, see also [2–8].

### Mass spectrometry data reduction and assessment

For all instruments, mass spectrometric data reduction/evaluation; isotopic assay and model age calculations; figure



high mass ← → low mass										Collector Block	Analysis Routine	
H3	H2	H1	Ax	L1	L2	IC0	L3	IC1	IC2			
				<i>238</i>		<b>236</b>	<i>235</i>	<b>234</b>	<b>233</b>	U-Static	URANIUM	
<i>238</i>		<i>236</i>	<i>235</i>	<i>234</i>	<i>233</i>					U-Faraday		
		<i>238</i>		<i>236</i>	<i>235</i>	<b>234</b>	<i>233</i>			U-ID-234-IC0		
				<i>238</i>		<b>236</b>	<i>235</i>	<b>234</b>	<b>233</b>	U-Jump (C1)	URANIUM	
			<i>238</i>		<i>236</i>	<b>235</b>	<i>234</i>	<b>233</b>		U-Jump (C2)		
						<b>232</b>		<b>230</b>	<b>229</b>	Th-Pulse	THORIUM	
				<i>232</i>		<b>230</b>	<i>229</i>			Th-230-IC0		
		<i>232</i>		<i>230</i>	<i>229</i>					Th-Faraday		
				<i>232</i>		<b>230</b>	<i>229</i>			Th-Jump (C1)	THORIUM	
			<i>232</i>		<i>230</i>	<b>229</b>				Th-Jump (C2)		
						<b>233</b>		<b>231</b>		Pa-Pulse	PROTACTINIUM	
			<i>233</i>		<i>231</i>					Pa-Faraday		
						<b>233</b>		<b>231</b>		Pa-Jump (C1)		
				<i>233</i>		<b>231</b>				Pa-Jump (C2)	PROTACTINIUM	

**Fig. 5** Schematic of collector–isotope analysis routines used for Nu Plasma HR MC-ICP-MS U (blue), Th (pink) and Pa (blue) radiochronometric measurements. “Jump” indicates a two-cycle (C1 and C2)

dynamic analysis routine. Italicized isotopic masses indicate Faraday measurements; bold isotopic masses indicate ion counter (IC) measurements

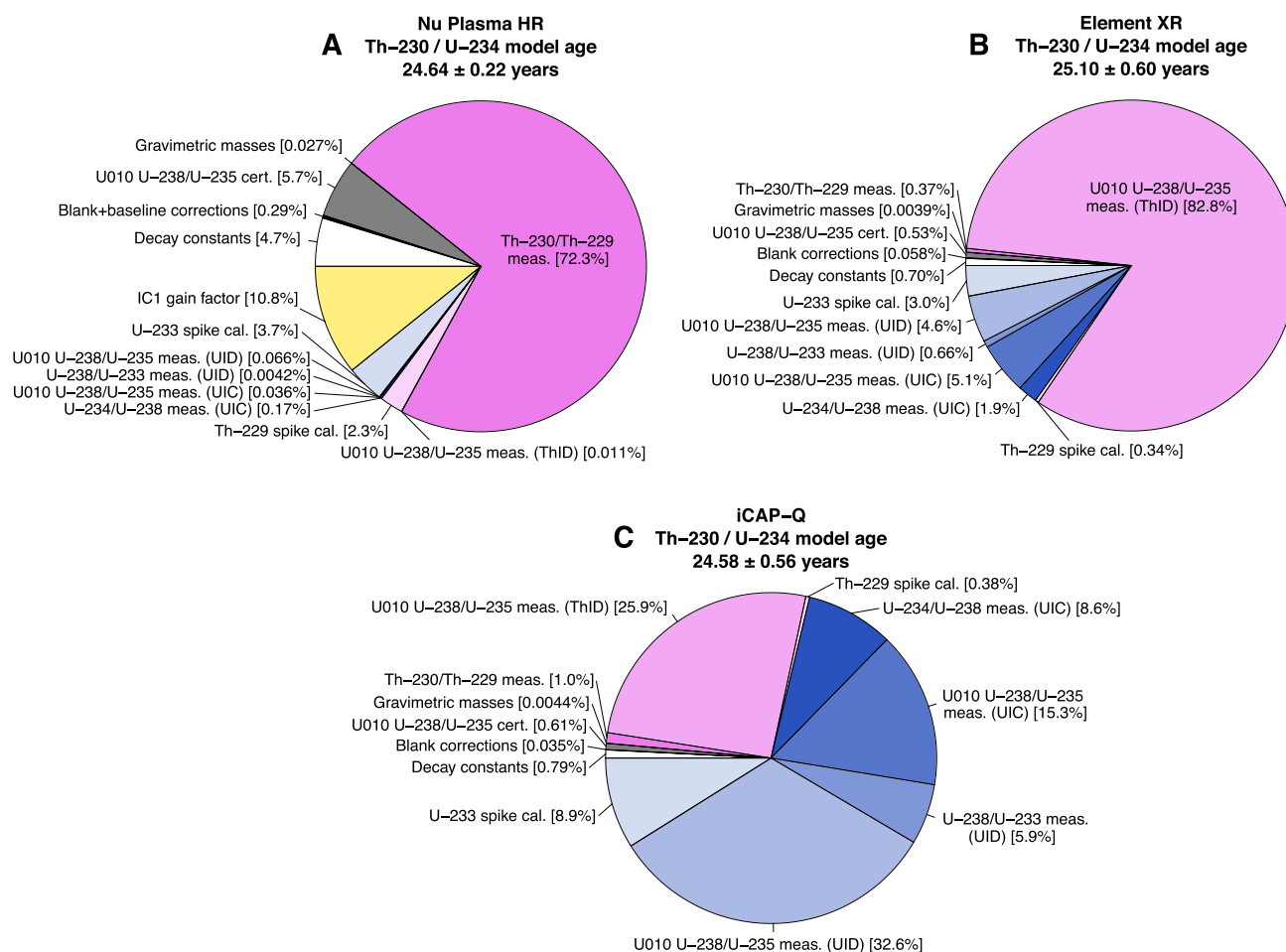
generation; and uncertainty propagation/uncertainty budget construction (see below) were performed using the R statistical programming environment [15]. The application of a common data reduction approach to all mass spectrometric analyses removes potential complications arising from disparate, instrument-specific data reduction algorithms, thereby permitting direct comparison of radiochronometric results from these instruments. As described earlier, instrumental mass-dependent fractionation (mass bias) was quantified on all instruments by repeat monitoring of CRM U010  $^{238}\text{U}/^{235}\text{U}$  during each analytical session, with applied mass bias factors ( $\beta$ ) determined by (1) interpolation of bracketing CRM U010 analyses, and (2) assuming an exponential mass fractionation law [e.g., 16]. A conservative expansion of uncertainties affiliated with interpolated correction factors was applied to yield more robust isotope ratio results. Quantitative blank corrections were made for all instruments; additional quantitative corrections for detector baseline and Faraday/ion counter (IC) gain (as needed) were made for Nu Plasma HR analyses.

### Uncertainty propagation, budgets and evaluation

As described above, uncertainty propagation and uncertainty budget construction for all radiochronometric model ages were implemented in the R statistical programming

environment (Figs. 6, 7). Uncertainty propagation was performed via the Monte Carlo method [17, 18], a computational alternative to the more common, partial derivative-based linear uncertainty propagation method [19]. One million ( $10^6$ ) samplings were performed for each Monte Carlo calculation, which was more than sufficient to obtain convergence of all calculated model ages to the level of two significant figures in the uncertainty associated with each age.

As visualized in Figs. 6 and 7, both similarities and differences are observed amongst the various ICP-MS platforms regarding their major radiochronometric uncertainty contributors. Firstly, uncertainties arising from decay constants, gravimetric masses (i.e., weights of primary solutions and spikes), and blank and baseline corrections are minor contributors for both the multi-collector and single collector instruments. However, for the Nu Plasma HR MC-ICP-MS the most important uncertainty contributors arise from two distinct sources (Figs. 6, 7). The first source is daughter isotope-related measurement uncertainties: for the  $^{230}\text{Th}$ – $^{234}\text{U}$  chronometer, it is the measured ThID  $^{230}\text{Th}/^{229}\text{Th}$  (sample/spike isotope) value; for the  $^{231}\text{Pa}$ – $^{235}\text{U}$  chronometer, it is the  $^{233}\text{Pa}$  spike calibration, which is ultimately rooted in the  $^{233}\text{Pa}/^{231}\text{Pa}$  measurement precision of the protactinium standard-spike aliquot “crosses” and the assay uncertainty for the 231Pa reference material. The second source is the



**Fig. 6** Comprehensive uncertainty budgets for  $^{230}\text{Th}$ - $^{234}\text{U}$  CRM 125-A model ages for the Nu Plasma HR (a), Element XR (b) and iCAP-Q (c), using results from Aliquot A. Blue and pink uncertainty components correspond to contributions from U and Th analyses,

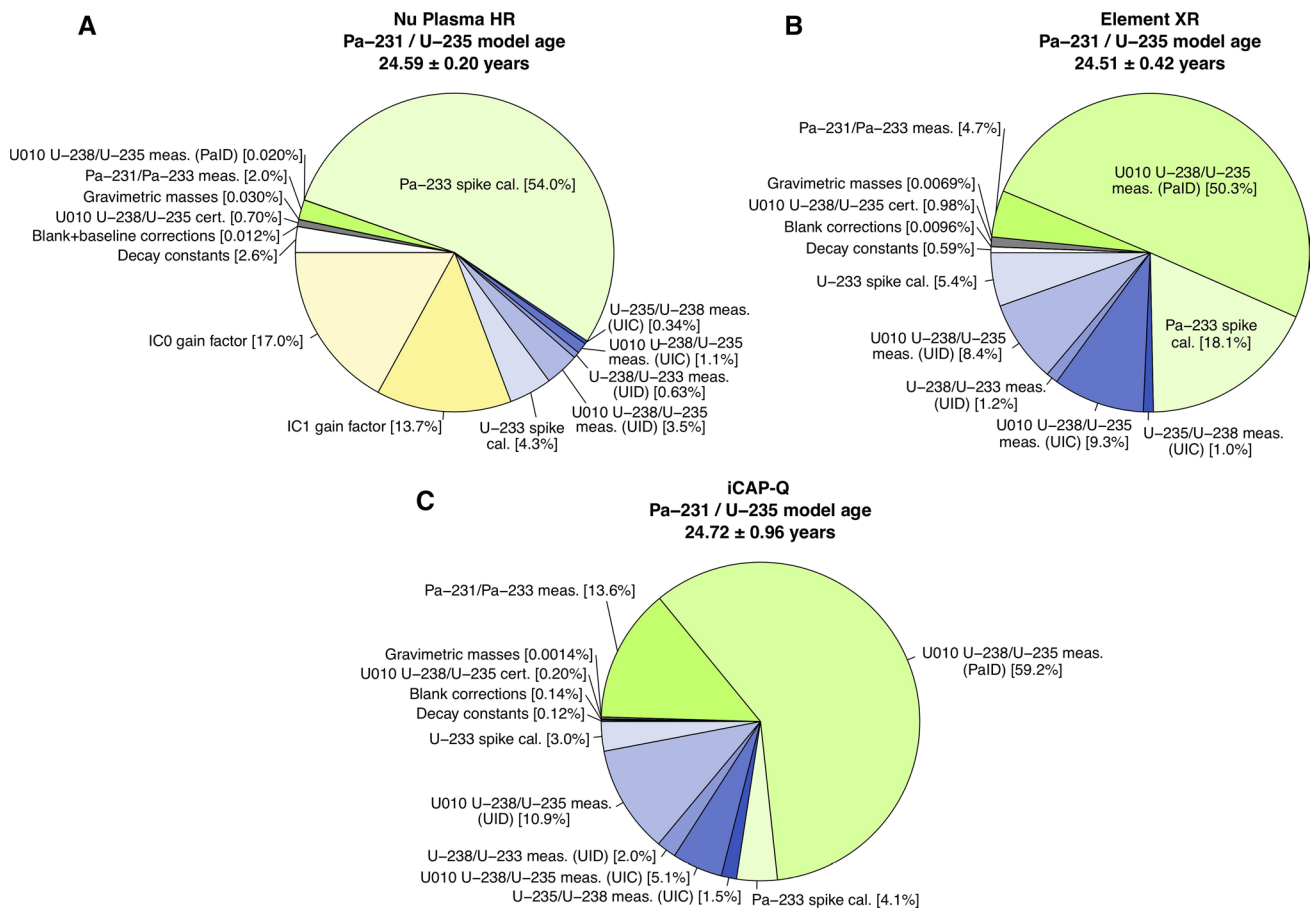
respectively, for all instrument platforms. Yellow uncertainty component for the Nu Plasma HR correspond to Faraday/ion counter (IC) gain factor determination. Model age uncertainties are stated at the  $k=2$  level

Faraday/IC gain factor uncertainties: these are tied to the certified  $^{236}\text{U}/^{235}\text{U}$  and  $^{234}\text{U}/^{235}\text{U}$  values of CRM U010, which are used to empirically determine Faraday/IC0 and Faraday/IC1 gain, respectively, during each analytical session. Notably, these gain intercalibration uncertainties are unique to the Nu Plasma HR in the current study, as the Element XR and iCAP-Q are equipped with only a single detector. Comparatively, the dominant uncertainty for both the Element XR and iCAP-Q arises from the measurement of CRM U010  $^{238}\text{U}/^{235}\text{U}$  for the mass bias correction (Figs. 6 and 7). This observation is partly explained by true day-to-day variability in the precision at which CRM U010  $^{238}\text{U}/^{235}\text{U}$  was measured. However, it is also due to the fact that the mass bias determination using CRM U010  $^{238}\text{U}/^{235}\text{U}$  is an *interpolated* correction using standard-sample bracketing. Thus, while individual CRM U010  $^{238}\text{U}/^{235}\text{U}$  measurements on the single-collector instruments have relative uncertainties generally on par with sample/spike isotope

ratio measurements (e.g.,  $^{230}\text{Th}/^{229}\text{Th}$ ), our data reduction algorithm conservatively expands the uncertainty associated with the mass bias correction applied to samples so as to account for drift in instrumental fractionation over an analytical session. Taken together, the precision of single-collector ICP-MS model ages is expected to improve if subsequent steps can be taken to optimize the measurement of the primary mass bias standard.

## Results and discussion

The certified model purification date of CRM 125-A, August 18, 1994 ( $\pm 116$  days), was determined using the  $^{230}\text{Th}$ - $^{234}\text{U}$  chronometer [11]. Results of the multi-instrument approach are summarized in Table 5 and Fig. 8. The summary of results to follow are average model dates calculated from the three aliquots CRM 125-A-A, -B, -C for each instrument;



**Fig. 7** Comprehensive uncertainty budgets for  $^{231}\text{Pa}$ - $^{235}\text{U}$  CRM 125-A model ages for the Nu Plasma HR (a), Element XR (b) and iCAP-Q (c), using results from Aliquot A. Blue and green uncertainty components correspond to contributions from U and Pa analyses,

respectively, for all instrument platforms. Yellow uncertainty components for the Nu Plasma HR correspond to Faraday/ion counter (IC) gain factor determinations. Model age uncertainties are stated at the  $k=2$  level

the expanded ( $k=2$ ) combined uncertainties are given in days. The average  $^{230}\text{Th}$ - $^{234}\text{U}$  model date from the iCAP-Q is September 5, 1994 ( $\pm 202$  days); the nominal date is less than 1 month younger than the certified age. The average  $^{231}\text{Pa}$ - $^{235}\text{U}$  model date from the iCAP-Q analyses is May 9, 1994 ( $\pm 356$  days), approximately 3 months older than the certified age but in agreement well within the associated uncertainties. The average  $^{230}\text{Th}$ - $^{234}\text{U}$  model date result from the Element XR is February 12, 1994 ( $\pm 221$  days), older than the certified model date, but still within uncertainty. The average  $^{231}\text{Pa}$ - $^{235}\text{U}$  model date result from the Element XR is September 21, 1994 ( $\pm 178$  days), less than 1 month younger than the certified model date. The average  $^{230}\text{Th}$ - $^{234}\text{U}$  model date for the Nu Plasma HR is August 18, 1994 ( $\pm 69$  days). The average  $^{231}\text{Pa}$ - $^{235}\text{U}$  model date for the Nu Plasma HR is September 27, 1994 ( $\pm 76$  days), less than 1 month younger than the certified model date. Paired  $^{231}\text{Pa}$ - $^{235}\text{U}$  and  $^{230}\text{Th}$ - $^{234}\text{U}$  model ages produced by all instruments are concordant, both internally and with the certified age of CRM 125-A, within stated uncertainties.

Certified radiochronometry standard ages and isotopic data from single collector instruments are thus consistent with those from a multi-collector instrument.

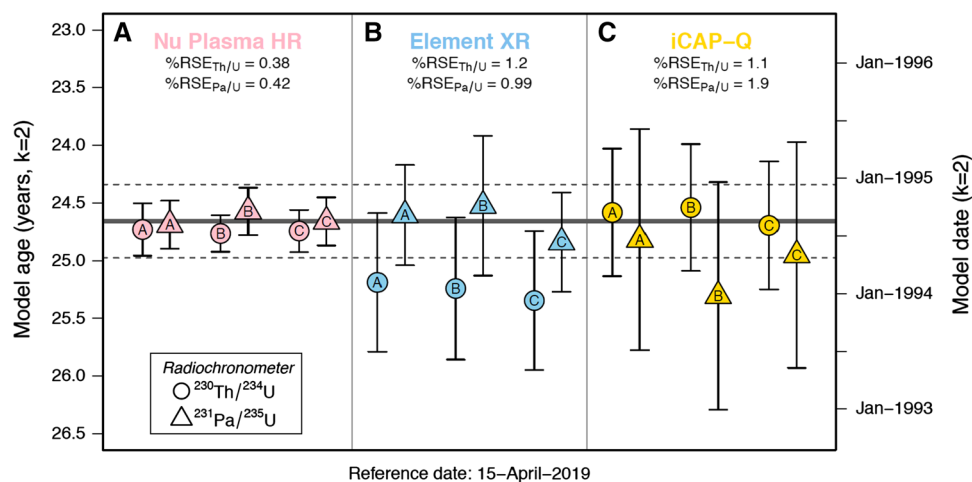
The reference date for all model age calculations is 15-April-2019. Expanded uncertainties are all 2-sigma. The daughter-parent isotope age-dating (Bateman) equation is used to calculate the age,  $t$ , of the material (see Treinen et al., 2018 for equation and discussion). Decay constants ( $\lambda$ ) used for calculating model ages are from [20–23]. The  $^{230}\text{Th}$  half-life =  $7.569 \times 10^4 \pm 115$  years, and the  $^{234}\text{U}$  half-life =  $2.4525 \times 10^5$  years. The  $^{231}\text{Pa}$  half-life =  $32,713 \pm 110$  years, and the  $^{235}\text{U}$  half-life =  $7.0381 \times 10^8 \pm 4.8 \times 10^5$ .

## Future considerations

While results from the present work are promising insofar as the practical utility of single-collector ICP-MS is concerned, we note that subsequent research and analyses are

**Table 5** Final Th–U and Pa–U radiochronometry results for multi-instrument approach

Instrument	Sample ID	Chronometer	Daughter/Parent (atom ratio)	expanded uncertainty, $k=2$	Model age (y)	Model date	expanded uncertainty, days, $k=2$
Nu Plasma HR	125-A-A	$^{230}\text{Th}$ – $^{234}\text{U}$	6.963E–05	6.3E–07	24.64	24-Aug-1994	83
Nu Plasma HR	125-A-B	$^{230}\text{Th}$ – $^{234}\text{U}$	6.973E–05	4.3E–07	24.67	11-Aug-1994	58
Nu Plasma HR	125-A-C	$^{230}\text{Th}$ – $^{234}\text{U}$	6.967E–05	4.9E–07	24.65	19-Aug-1994	66
Nu Plasma HR	125-A-A	$^{231}\text{Pa}$ – $^{235}\text{U}$	2.422E–08	2.0E–10	24.59	10-Sep-1994	76
Nu Plasma HR	125-A-B	$^{231}\text{Pa}$ – $^{235}\text{U}$	2.410E–08	2.0E–10	24.48	21-Oct-1994	75
Nu Plasma HR	125-A-C	$^{231}\text{Pa}$ – $^{235}\text{U}$	2.419E–08	2.0E–10	24.57	20-Sep-1994	76
Element XR	125-A-A	$^{230}\text{Th}$ – $^{234}\text{U}$	7.090E–05	1.7E–06	25.1	9-Mar-1994	219
Element XR	125-A-B	$^{230}\text{Th}$ – $^{234}\text{U}$	7.110E–05	1.7E–06	25.15	18-Feb-1994	225
Element XR	125-A-C	$^{230}\text{Th}$ – $^{234}\text{U}$	7.140E–05	1.7E–06	25.26	11-Jan-1994	220
Element XR	125-A-A	$^{231}\text{Pa}$ – $^{235}\text{U}$	2.414E–08	4.3E–10	24.51	9-Oct-1994	158
Element XR	125-A-B	$^{231}\text{Pa}$ – $^{235}\text{U}$	2.405E–08	5.9E–10	24.43	10-Nov-1994	220
Element XR	125-A-C	$^{231}\text{Pa}$ – $^{235}\text{U}$	2.437E–08	4.2E–10	24.75	16-Jul-1994	157
iCAP-Q	125-A-A	$^{230}\text{Th}$ – $^{234}\text{U}$	6.950E–05	1.6E–06	24.58	14-Sep-1994	201
iCAP-Q	125-A-B	$^{230}\text{Th}$ – $^{234}\text{U}$	6.940E–05	1.5E–06	24.54	29-Sep-1994	200
iCAP-Q	125-A-C	$^{230}\text{Th}$ – $^{234}\text{U}$	6.980E–05	1.6E–06	24.69	4-Aug-1994	203
iCAP-Q	125-A-A	$^{231}\text{Pa}$ – $^{235}\text{U}$	2.434E–08	9.4E–10	24.72	24-Jul-1994	350
iCAP-Q	125-A-B	$^{231}\text{Pa}$ – $^{235}\text{U}$	2.482E–08	9.7E–10	25.21	27-Jan-1994	360
iCAP-Q	125-A-C	$^{231}\text{Pa}$ – $^{235}\text{U}$	2.447E–08	9.6E–10	24.86	6-Jun-1994	357



**Fig. 8** Final model age results for multi-instrument approach. Panel A displays results from the Nu Plasma HR; Panel B displays results from the Element XR; Panel C displays results from the iCAP-Q. The average percent relative standard error (%RSE) for  $^{230}\text{Th}/^{234}\text{U}$  and  $^{231}\text{Pa}/^{235}\text{U}$  radiochronometers for each instruments results are also

displayed. All model age results are calculated with a reference date of 15-April-2019. The certified Th–U model purification date of CRM 125-A is August 18th, 1994 ( $\pm 116$  days). All expanded uncertainties are  $k=2$

required to thoroughly evaluate the “real-world” feasibility of this approach to nuclear forensics. Considerations for the application of this approach should focus on the type of sample being examined, i.e., the uranium concentration and isotopic composition, age, and availability of sample under examination. In addition, the methods presented here require complete chemical purification of the trace quantities of Th and Pa from a bulk U sample. Future method development

may also explore the level of allowable residual U in the Th or Pa isotope dilution aliquots.

Future method development work for single-collector analysis may also focus on optimizing the analysis sequence. In particular, the measurement method for the mass bias calibration standard may potentially be optimized by modifying dwell times. For UIC analyses, this would also include utilizing the  $^{234}\text{U}/^{235}\text{U}$  ratio instead of the  $^{234}\text{U}/^{238}\text{U}$  ratio in

order maintain ion beam signal intensities below the threshold of the analog region of the detector, and thereby avoid the additional uncertainty associated with crossing between detector modes on the single-collector ICP-MS platforms. As discussed previously, additional research to stabilize and improve single-collector ICP-MS mass bias measurement would produce more precise radiochronometric results, as mass bias correction uncertainty dominates single-collector model ages (Figs. 6, 7). Future work could also explore the use of a desolvating nebulizer that is designed for the relatively high HF concentration (0.05 M HF) necessitated by the current Pa purification and analysis method.

Additional multi-instrument age-dating comparison work may explore complimentary techniques of isotopic determination for age-dating, including alpha spectrometry, as was explored in [24]. Improvements in alpha spectrometry instrumentation and chemical purification techniques could allow this method to be a viable choice for laboratories for radiochronometry.

## Conclusions

In this study, single collector ICP-mass spectrometry was used to perform calibrations of isotope dilution tracers, as well as to perform isotope dilution analyses of the samples. Additionally, spiked Th and Pa sample aliquots were purified from the bulk U sample matrix prior to analysis, thus minimizing sample matrix effects and isobaric interferences. While multi-collector mass spectrometers ultimately generate the most precise radiochronometric and isotopic data, single collector mass spectrometers can be used to determine the model age of bulk uranium with respectable precision. Because single-collector mass spectrometers are more widely available than multi-collector mass spectrometers, this approach may enable a greater number of nuclear forensic practitioners to perform radiochronometry analyses.

**Acknowledgements** This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Releasable to external audiences, LLNL-CONF-784319. The authors would like to acknowledge the contributions made by LLNL team members Victoria D. Gentti, Dana L. Drew, and Sam R. Shipman.

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