

## Dual Chronometer Measurements of Uranium Particles by LG-SIMS

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### Abstract

Large geometry secondary ion mass spectrometry (LG-SIMS) has been widely used for isotopic measurements of uranium particles for many years. In recent years, it has been demonstrated it is possible to perform chronometry (a.k.a. age-dating) measurements of single uranium-containing, micrometer-sized particles using LG-SIMS. For these chronometry measurements, the analytes measured are the  $^{234}\text{U} - ^{230}\text{Th}$  mother-daughter pair. This initial measurement protocol was developed using the mono-collector electron multiplier (EM) configuration on a LG-SIMS instrument with the preponderance of the counting time of an analysis cycle being on the  $^{230}\text{Th}$  to maximize measurement precision. In addition to the  $^{234}\text{U} - ^{230}\text{Th}$  pair, the  $^{235}\text{U} - ^{231}\text{Pa}$  chronometer pair has frequently been measured as a secondary chronometer for uranium-based materials in several scientific fields. The  $^{235}\text{U} - ^{231}\text{Pa}$  pair could have analytical value for some uranium particle sample types, such as highly-enriched uranium. Most LG-SIMS instruments have a multi-collector system configured with five EM detectors, which allows simultaneous measurement of up to five isotopes, typically improving measurement precision and detection limits over mono-collector peak hopping protocols. The multi-collector configuration allows the simultaneous counting of both  $^{230}\text{Th}$  and  $^{234}\text{U}$ , with the added advantage of allowing the collection of  $^{231}\text{Pa}$ ,  $^{232}\text{Th}$ , and  $^{235}\text{U}$  isotopes as well. We present results on the development of our multi-collector system protocol for dual chronometer ( $^{234}\text{U} - ^{230}\text{Th}$  and  $^{235}\text{U} - ^{231}\text{Pa}$ ) measurements. Data presented will focus on results from a commonly available U-series Certified Reference Material (CRM) and from a natural uranium-containing mineral. We also discuss how limitations due to background from peak tailing — often referred to as abundance sensitivity — can negatively impact measurement detection limits for the multi-collector configuration. The reason for abundance sensitivity potentially having negative consequences for age-dating measurements is increased scattering from peak tails in multi-collector systems versus the mono-collector system for LG-SIMS.

### 1. INTRODUCTION

Particle and bulk mass spectrometry measurements are widely used for precise isotopic measurements of uranium and trans-uranic materials for nuclear safeguards and treaty monitoring missions.<sup>1,2,3</sup> Particle measurements offer the added advantage — over bulk measurements — in that they can provide more information from collected samples by providing discrete data sets at the particulate level. Secondary ion mass spectrometry (SIMS) is one method for mass spectrometry-based particulate analysis.<sup>4,5</sup>

Chronometry, or age-dating (AD), of uranium-based materials provides additional value to

conventional uranium isotopic measurements, in that it can reveal a processing timeline of materials because many anthropogenic processes affect, and often reset, observable chronometer ratios. AD measurements are typically constrained by low abundance of target radionuclide decay products (daughter isotopes), which has made extending these measurements to individual particles challenging.<sup>6</sup> Due to this limitation, AD measurements have historically been restricted to bulk measurement techniques where sufficient material mass is available per sample analysis.<sup>7,8</sup> Details describing a methodology for age-dating of individual uranium particles by large geometry secondary ion mass spectrometry (LG-SIMS) were discussed by Szakal *et al.*<sup>9</sup> That paper describes using the  $^{234}\text{U} - ^{230}\text{Th}$  parent-daughter chronometer pair for the age-dating of U-containing particles, and specific statistical considerations for interpreting the  $^{230}\text{Th}/^{234}\text{U}$  ratio in low  $^{230}\text{Th}$  count regimes which are often observed for many U-containing particles.

In prior work, we discussed our efforts to adapt the above-mentioned uranium particle age-dating method, which was developed for the mono-collector electron multiplier (EM) configuration,<sup>9</sup> to the multi-collector configuration of a LG-SIMS instrument.<sup>10</sup> Most LG-SIMS instruments have a multi-collector system equipped with five EM detectors, which allows for simultaneous measurement of up to five isotopes, typically improving measurement precision and detection limits over peak-hopping mono-collector protocols. An advantage, which was previously noted, for the multi-collector configuration is that in addition to measuring the  $^{234}\text{U} - ^{230}\text{Th}$  mother-daughter chronometer pair, a multi-collector AD analysis is easily configured to measure the  $^{235}\text{U} - ^{231}\text{Pa}$  chronometer pair. The  $^{235}\text{U} - ^{231}\text{Pa}$  chronometer pair has frequently been measured as a secondary chronometer for uranium-based materials in several scientific fields,<sup>10,11,12</sup> often to check for concordance with the  $^{234}\text{U} - ^{230}\text{Th}$  chronometer pair which can provide insight into how materials have been affected by both natural and anthropogenic processes. Concordance can provide confidence that model ages are accurate, and discordance can provide insight into processing history.<sup>2</sup>

In this work, we will discuss results from the development of our multi-collector system protocol for dual chronometer ( $^{234}\text{U} - ^{230}\text{Th}$  and  $^{235}\text{U} - ^{231}\text{Pa}$ ) measurements. Comparison of results from measurements of  $^{234}\text{U} - ^{230}\text{Th}$  and  $^{235}\text{U} - ^{231}\text{Pa}$  from a commonly available U-series Certified Reference Material (CRM) and a natural mineral will be discussed. It should be noted that there is no certified  $^{231}\text{Pa}$  standard for uranium-based particulates. How this potentially limits interpretation and precision of data obtained from  $^{235}\text{U} - ^{231}\text{Pa}$  chronometer measurements will be discussed. We will also discuss how limitations from increased background from peak tailing — often referred to as abundance sensitivity — can negatively impact measurement detection limits for the multi-collector configuration. Abundance sensitivity can have potentially negative consequences for age-dating measurements with the multi-collector configuration due increased scattering in multi-collector systems versus the mono-collector system for LG-SIMS.

## 2. MATERIALS AND EQUIPMENT

CRM and natural mineral samples were dispersed onto 25 mm diameter carbon planchettes to create particle samples. The density of the dispersions was kept low to allow for sufficient space between particles so that single particle measurements could be made without contributions from adjacent particles. The CRM used for this study is U900.<sup>13</sup> The natural mineral is uraninite from Topsham, Maine USA.

The LG-SIMS instrument used for this work is a CAMECA IMS-1270E7/1280 (Cameca

Instruments INC., 5470 Nobel Dr, Fitchburg, WI, USA).<sup>14</sup> This instrument was originally acquired as an IMS 1270, and was upgraded with electronics and other hardware to be nearly identical to the IMS 1280 in terms of performance and capability. Specific instrument parameters and results described here — while specific to the instrument at NIST — are broadly applicable to other LG-SIMS instruments.

### 3. INSTRUMENT CONFIGURATION FOR AD MEASUREMENTS

Specific instrument operating parameters, with a focus on AD measurements, have been previously described in detail for both the mono-collector and multi-collector configurations.<sup>9,10</sup> To be consistent with the prior published methodology, this work has not meaningfully deviated from the published instrument configurations. Key instrument parameters are summarized in Table 1, reproduced from Ref 10 here.

**Table 1.** Instrument Operation Parameters

	Mono-collector Configuration	Multi-collector Configuration
Primary Beam	13 kV O-	13 kV O-
Primary Beam Mode	Köhler	Köhler
Sample HV	+10000 V	+10000 V
Ent. Slit	175 $\mu\text{m}$	125 $\mu\text{m}$
Contrast Aperture (CA)	400 $\mu\text{m}$	400 $\mu\text{m}$
Field Aperture (FA)	6000 $\mu\text{m}$	6000 $\mu\text{m}$
Energy Slit bandpass	50 eV	50 eV
Max Field of view (MA)	50 $\mu\text{m}$ x 50 $\mu\text{m}$	50 $\mu\text{m}$ x 50 $\mu\text{m}$
Beam Shaping Mode	XY	CIRC
EM Threshold	75 mV	75 mV
Exit Slit	250 $\mu\text{m}$	250 $\mu\text{m}$ (S2)

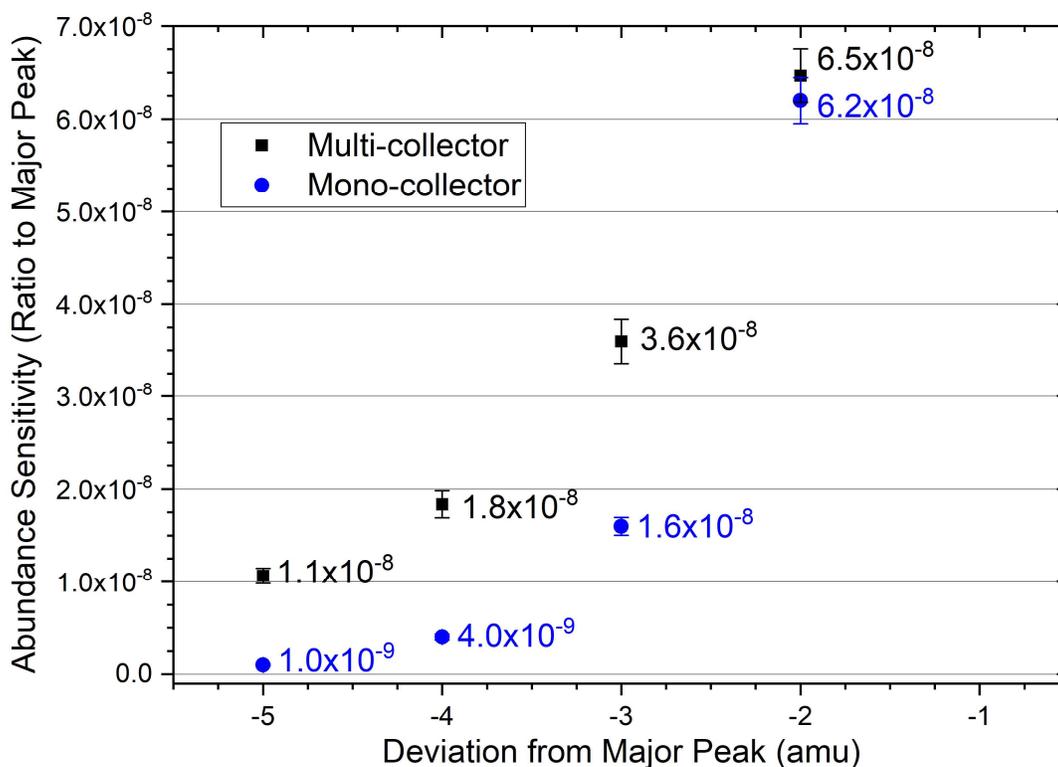
The IMS1280 LG-SIMS multi-collector system has 5 EM detectors, allowing for 5 simultaneous isotopic measurements. The standard configuration for U-isotopic analysis is to align the detectors to measure  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$ ,  $^{238}\text{U}$ , and  $^{238}\text{U}$ - $^1\text{H}$  (which is used as a hydride correction) simultaneously. By adjusting the axial mass of the magnetic sector mass analyzer down 4 u (i.e. amu) from this isotopic configuration while also adjusting a few instrument parameters to account for reduced dispersion<sup>10</sup>, the detectors are aligned to measure  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$ ,  $^{232}\text{Th}$ ,  $^{234}\text{U}$ , and  $^{235}\text{U}$ . This is an appropriate multi-collector configuration for most LG-SIMS AD measurements as it allows for the measurement of both  $^{234}\text{U} - ^{230}\text{Th}$  and  $^{235}\text{U} - ^{231}\text{Pa}$  chronometer pairs. Note, for some enriched U materials such as CRM U900, the signal from  $^{235}\text{U}$  can be too large for an AD measurement with an EM. In such cases the detector positioned for  $^{235}\text{U}$  can be either moved away or its high voltage can be turned off.

Mono-collector configuration measurements are done by peak hopping, which requires adjusting the magnetic field of the mass analyzer and a settling time. A preponderance of counting time is on the low abundance signal of the chronometer isotope of interest, either  $^{230}\text{Th}$  or  $^{231}\text{Pa}$ . Typical AD measurements are done for 20 total cycles with a cycle consisting of a possible nearby interference peak (2.00 s dt, 2.00 s wt), chronometer isotope of interest (20.00 s dt, 0.96 s wt),

and uranium isotope (2.00 s dt, 0.96 s wt). Total cycle time is 28 s, where dt is the dwell time and wt is the wait time. The interference peak is chosen to be 0.0675 u (i.e. amu) below the chronometer isotope of interest. Multi-collector measurements do not require peak hopping, and a static mass (axial mass of  $^{234}\text{U}$ ) is chosen to result in the masses of interest aligned according to the detector configuration described above. To facilitate comparison between the mono- and multi-collector configurations for a typical measurement, a cycle time of 20 s is used for 28 cycles to make the total measurement time identical. Primary beam intensity is tuned such that a particle is mostly consumed during an analysis.

#### 4. ABUNDANCE SENSITIVITY EFFECT ON AD MEASUREMENTS

Abundance sensitivity refers to the effect of the scatter tail of a major peak onto neighboring minor peaks of interest. Scattering of ions following the flight path of the mass spectrometer and their appearance at neighboring mass peaks is a well understood problem for many forms of mass spectrometry. Due to the physical layout of LG-SIMS instruments, the effect is typically quite small, especially when using the mono-collector configuration which has a large, full  $90^\circ$  electrostatic analyzer (ESA) immediately before the detectors to further filter stray ions. However, because the signal is often very low for target daughter radionuclides of interest for age-dating ( $^{230}\text{Th}$  and  $^{231}\text{Pa}$ ), the abundance sensitivity needs to be quantified. In the case of AD measurements,  $^{235}\text{U}$  is considered the major nearby peak. Figure 1 shows the abundance sensitivity determined for our LG-SIMS for the mono- and multi-collector configurations.



**Figure 1.** Graph showing abundance sensitivity as deviation from major peak for the mono- and multi-collector configurations of the NIST LG-SIMS instrument. Error bars are  $1\sigma$ .

The values shown here for the mono-collector were previously reported<sup>9</sup> and both data sets are shown as deviations in amu from a major peak. The multi-collector abundance sensitivity was determined by aligning the EM detectors 1 amu apart and cycling the axial mass to measure a uranium isotope followed by a shift of 0.5 amu to measure regions in between peaks to determine background from a major peak scatter tail. For example an EM detector is positioned at mass 230.5 amu. The abundance sensitivity at whole amu peak positions was then calculated by interpolation between half mass peaks. For the data shown here, -5 amu corresponds to <sup>230</sup>Th and -4 amu corresponds to <sup>231</sup>Pa. Figure 1 shows the multi-collector has a larger background than the mono-collector due to scatter from the nearby major peak.

The half-life of <sup>234</sup>U is  $2.46 \times 10^5$  years which gives a decay constant for <sup>230</sup>Th ingrowth of  $2.82 \times 10^{-6} \text{ yr}^{-1}$ .<sup>15</sup> In terms of how the abundance sensitivity affects AD measurements of <sup>230</sup>Th, in the mono-collector configuration the <sup>235</sup>U tail creates a background for the <sup>230</sup>Th/<sup>234</sup>U ratio of  $\approx 1.0 \times 10^{-7}$ , and for the multi-collector configuration the tail creates a background in the same ratio of  $\approx 1.0 \times 10^{-6}$ . The numbers are indicated as approximate because the <sup>234</sup>U/<sup>235</sup>U ratio varies depending on U enrichment. For the mono-collector case, the abundance sensitivity background is equivalent to a few weeks of the model age, which is often within the measurement uncertainty and can be regarded as negligible.<sup>9</sup> In the multi-collector case, the abundance sensitivity background is more significant, equivalent to several months of model age and should be accounted for. The half-life of <sup>235</sup>U is  $7.038 \times 10^8$  years which gives a decay constant for <sup>231</sup>Pa formation of  $9.849 \times 10^{-10} \text{ yr}^{-1}$ .<sup>16</sup> In the case of the interference from the scatter tail on <sup>231</sup>Pa from <sup>235</sup>U, the interference is the abundance sensitivity reported in Figure 1 since the <sup>231</sup>Pa/<sup>235</sup>U ratio is the measured ratio of interest. In the mono-collector configuration the abundance sensitivity from the <sup>235</sup>U tail results in a background of  $4.0 \times 10^{-9}$  and for the multi-collector the background contribution is  $1.8 \times 10^{-8}$ . For the mono-collector case, this background is equivalent to 4 years, and for the multi-collector case the background is equivalent to 18 years. Both the mono- and multi-collector abundance sensitivity backgrounds are significant for <sup>231</sup>Pa AD measurements and need to be corrected for.

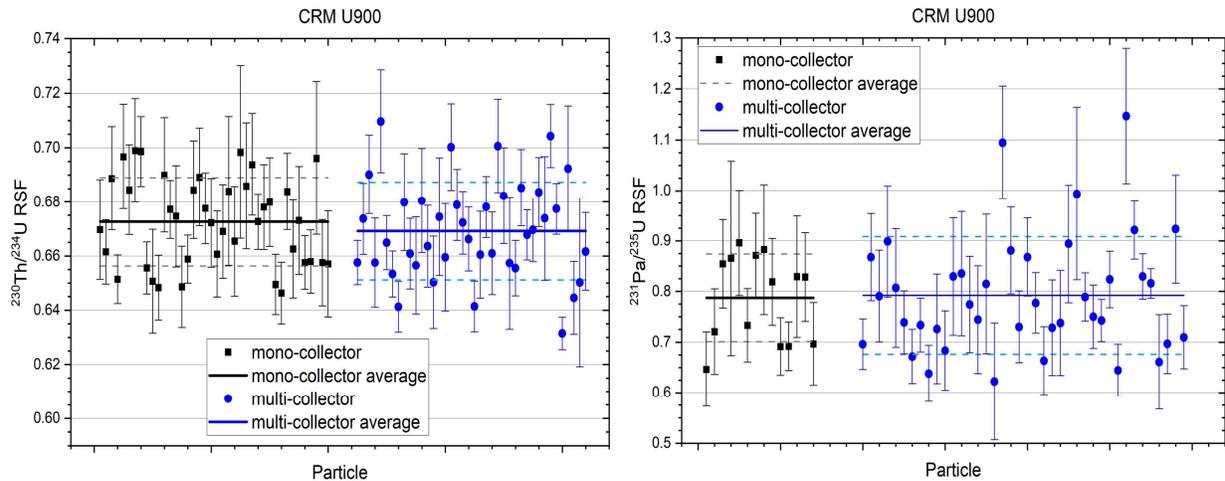
We note that the abundance sensitivities reported here, shown in Figure 1, are specific to our LG-SIMS instrument. However, it is likely that all LG-SIMS instruments will have some measurable abundance sensitivity which is larger for the multi-collector configuration — especially for <sup>231</sup>Pa — due to the physical design constraints of the multi-collector systems. These systems are typically designed with movable EM detectors with smaller than 90° ESAs before the EM detectors, which likely do not have as large a background rejection as the mono-collector configuration.

## 5. DUAL CHRONOMETER MEASUREMENT COMPARISONS

SIMS is a mature and widely used mass spectrometry technique for measuring isotopic ratios of solid materials over a large dynamic range. As-measured data by themselves are not absolute and biases introduced by instrumental effects and sample/substrate chemistry affect intra- and inter-elemental measurements. Calibration against known standards is required for accurate and meaningful measurements. In the case of AD measurements, the key calibration value needed is the relative sensitivity factor (RSF) between U and Th or Pa. The RSF arises because of

differences in the rate and efficiency of sputtering and ionization of different elements by the primary ion beam used during a SIMS analysis to create secondary ions. The RSF is determined by comparing as-measured ratios to expected ratios in a known standard. Since RSF determination is an important requirement for AD measurements by SIMS, it has been chosen as the figure of merit in this work to compare results between the mono- and multi-collector configurations.

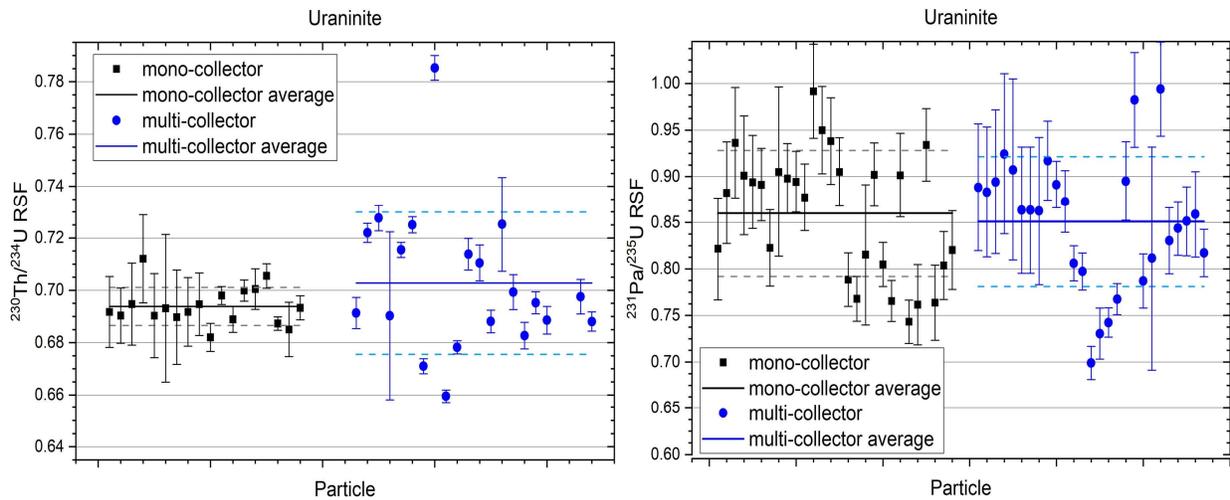
CRM U900 has a known production date (January 24, 1958).<sup>15</sup> It is therefore straightforward to calculate the expected  $^{230}\text{Th}/^{234}\text{U}$  and  $^{231}\text{Pa}/^{235}\text{U}$  ratios which should be present from radioactive decay. It is assumed that both the  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  were completely purified from the U900 material upon production,<sup>17,18</sup> and all  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  present in CRM U900 is from radioactive decay from parent U isotopes. Figure 2(left) shows the  $^{230}\text{Th}/^{234}\text{U}$  RSF for measurements made by the mono- and multi-collector configurations from CRM U900. The mono-collector configuration had an average RSF of  $0.673 \pm 0.016$  ( $1\sigma$ ) and the multi-collector configuration had an average RSF of  $0.669 \pm 0.018$  ( $1\sigma$ ). These  $^{230}\text{Th}/^{234}\text{U}$  RSF values are consistent with each other, within uncertainty. Figure 2(right) shows the  $^{231}\text{Pa}/^{235}\text{U}$  RSF for measurements made by the mono- and multi-collector configurations from CRM U900. The mono-collector configuration had an average RSF of  $0.789 \pm 0.085$  ( $1\sigma$ ) and the multi-collector configuration had an average RSF of  $0.792 \pm 0.116$  ( $1\sigma$ ). These  $^{231}\text{Pa}/^{235}\text{U}$  RSF values are consistent with each other, within uncertainty.



**Figure 2.** (left) Graph showing  $^{230}\text{Th}/^{234}\text{U}$  RSF determined from CRM U900 for datasets obtained from mono- (N=40) and multi-collector (N=40) configurations. (Right) Graph showing  $^{231}\text{Pa}/^{235}\text{U}$  RSF determined from CRM U900 for datasets obtained from mono- (N=14) and multi-collector (N=40) configurations. Error bars in both graphs are  $1\sigma$ .

Both multi-collector data sets and the  $^{231}\text{Pa}$  mono-collector data were corrected for abundance sensitivity. There was some scatter in both mono- and multi-collector datasets for the Th/U RSF data, but neither appears to be more significant. The scatter in the Pa/U RSF data does appear to be more significant for the multi-collector dataset, however we note that this is a substantially larger dataset (N=14 vs N=40).

The uraninite used in this study is from Topsham, Maine USA and is a natural mineral which has been shown to be more than 100 million years old.<sup>19</sup> As such, the expected  $^{230}\text{Th}/^{234}\text{U}$  and  $^{231}\text{Pa}/^{235}\text{U}$  ratios are assumed to be at their secular equilibrium values which can be determined by the ratio of the decay constants for both parent and daughter isotopes. The secular equilibrium value for  $^{230}\text{Th}/^{234}\text{U}$  is 0.306 and the value for  $^{231}\text{Pa}/^{235}\text{U}$  is  $4.65 \times 10^{-5}$ .<sup>15,16, 20,21</sup> Figure 3(left) shows the  $^{230}\text{Th}/^{234}\text{U}$  RSF for measurements made by the mono- and multi-collector configurations from uraninite. The mono-collector configuration had an average RSF of  $0.694 \pm 0.007$  ( $1\sigma$ ) and the multi-collector configuration had an average RSF of  $0.703 \pm 0.027$  ( $1\sigma$ ). These  $^{230}\text{Th}/^{234}\text{U}$  RSF values are consistent with each other, within uncertainty. Note the  $^{230}\text{Th}/^{234}\text{U}$  RSF values for uraninite appear larger than those obtained for CRM U900, although they slightly overlap within  $1\sigma$  uncertainty. This is consistent with prior observations,<sup>9</sup> and may be attributed to differences in the chemical composition of the natural mineral, uraninite, and the synthetically produced CRM U900. Figure 3(right) shows the  $^{231}\text{Pa}/^{235}\text{U}$  RSF for measurements made by the mono- and multi-collector configurations from uraninite. The mono-collector configuration had an average RSF of  $0.860 \pm 0.068$  ( $1\sigma$ ) and the multi-collector configuration had an average RSF of  $0.851 \pm 0.070$  ( $1\sigma$ ). These  $^{231}\text{Pa}/^{235}\text{U}$  RSF values are consistent with each other, within uncertainty. As was the case with the  $^{230}\text{Th}/^{234}\text{U}$  RSF, the  $^{231}\text{Pa}/^{235}\text{U}$  RSF values for uraninite were larger than those of CRM U900, likely for the same reason.



**Figure 3.** (left) Graph showing  $^{230}\text{Th}/^{234}\text{U}$  RSF determined from uraninite for datasets obtained from mono- ( $N=18$ ) and multi-collector ( $N=20$ ) configurations. (Right) Graph showing  $^{231}\text{Pa}/^{235}\text{U}$  RSF determined from uraninite for datasets obtained from mono- ( $N=28$ ) and multi-collector ( $N=27$ ) configurations. Error bars in both graphs are  $1\sigma$ .

Both the mono- and multi-collector data sets for the  $^{231}\text{Pa}$  data have been corrected for abundance sensitivity, although this is a small correction in both cases (less than 1 part per thousand). There is more scatter in the multi-collector datasets for the Th/U RSF data, compared to the mono-collector data set. This is clear in Figure 3(left) and in the larger uncertainty ( $1\sigma$ )  $\pm 0.007$  vs  $\pm 0.027$ . This was unexpected, especially given the Th/U RSF results for CRM U900 shown in Figure 2. This will need to be investigated further to determine if the scatter is an artifact of this relatively limited ( $N=14$ ) dataset or something more systematic. For the Pa/U RSF data, there is some scatter in both mono- and multi-collector datasets, but neither appears to more significant.

An important observation from this study is the larger uncertainty of the Pa/U RSF compared to the Th/U RSF. This is true for both the relative and absolute values. Large RSF uncertainty will limit overall measurement uncertainty which could be obtained for measurements of the  $^{231}\text{Pa}/^{235}\text{U}$  chronometer in uranium-containing particles. In the case of  $^{230}\text{Th}$ , there are a few CRMs certified for  $^{230}\text{Th}$  age at the bulk level and the half-life of the parent isotope ( $^{234}\text{U}$ ) is much shorter. Previous results have shown that, within the uncertainty of SIMS, the  $^{230}\text{Th}$  age is consistent with the bulk value at the particle level,<sup>9</sup> and there is a sufficient amount of  $^{230}\text{Th}$  in some CRMs to determine the Th/U RSF within a reasonable level of uncertainty. Trying to use the same CRMs for  $^{231}\text{Pa}$  for particle measurements has limitations because the parent isotope ( $^{235}\text{U}$ ) has a substantially longer half-life, limiting the amount of  $^{231}\text{Pa}$  present in particles, which limits the precision of measurements of the Pa/U RSF from standards. The materials which have been investigated here do contain relatively significant amounts of  $^{231}\text{Pa}$ , and are some of the best available for the purpose of Pa/U RSF determination from uranium-containing particles. However, the  $^{231}\text{Pa}$  amounts are a small quantity at the particle level to use as a reference standard, which results in lower than ideal measurement precision and yields a RSF with a large uncertainty. For CRM U900, which was 65 years old on January 24, 2023 the expected ratio for  $^{231}\text{Pa}/^{235}\text{U}$  is  $6.40 \times 10^{-8}$ , which is  $\approx 22$  times less  $^{231}\text{Pa}$  than  $^{230}\text{Th}$ . For the uraninite, the  $^{231}\text{Pa}/^{235}\text{U}$  ratio is the secular equilibrium value of  $4.65 \times 10^{-5}$ , which is a small but measureable ratio and is equivalent to  $\approx 18$  times less  $^{231}\text{Pa}$  than  $^{230}\text{Th}$ . However, it should be noted that the  $^{235}\text{U}$  is only in natural abundance (0.72%) in uraninite, so the total amount of  $^{231}\text{Pa}$  is quite small. To improve the efficacy of using the  $^{231}\text{Pa}/^{235}\text{U}$  chronometer in uranium-containing particles, it is likely that uranium particle standards doped with  $^{231}\text{Pa}$  will need to be produced.

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