MULTI-COLLECTOR CONFIGURATION CONSIDERATIONS AND SUBSTRATE RELATIVE SENSITIVITY FACTOR EFFECTS FOR AGE-DATING MEASUREMENTS OF PARTICLES BY LARGE GEOMETRY SECONDARY ION MASS SPECTROMETRY

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ABSTRACT

Chronometry (a.k.a age-dating, AD) of materials by bulk mass spectrometric methods is a well-established technique based on analysis protocols that have been used in geological fields and by the non-proliferation communities for many years. Recently, it has been demonstrated it is possible to broaden the applicability of AD measurements to single uranium-containing particles using large geometry secondary ion mass spectrometry (LG-SIMS) showing that it is feasible to measure the ^{234}U – ^{230}Th mother-daughter chronometry pair in micrometer-sized particles. We present results building from that work focusing on two topics. The first topic will discuss the use of the multi-collector configuration — common in LG-SIMS instruments — to measure all isotopes needed for the AD measurement simultaneously. Our protocol developed for U-Th AD measurements uses the mono-collector configuration with the preponderance of the counting time of an analysis cycle being on the ^{230}Th. The multi-collector configuration allows the simultaneous counting of both ^{230}Th and ^{234}U, with the added advantage of allowing the collection of ^{231}Pa and ^{232}Th isotopes, too. Simultaneously counting all isotopes should improve the overall measurement precision, as well as eliminate transient artifacts during the analysis that could result in inaccurate data. We will also discuss results which show that different substrates can have a large effect on the relative sensitivity factor (RSF) of Th:U, which could result in inaccurate age estimates if this effect is ignored. We have previously reported a Th:U RSF of ~0.673 for measurements done on carbon planchettes under our specific analysis conditions. Carbon planchettes are not the only common substrate used by LG-SIMS labs. Others include silicon wafers, indium pucks, and stainless-steel disks. We have recently determined that the Th:U RSF measured on Si wafers is ~0.79, i.e. 17% higher than the RSF on carbon. This difference, as well as the RSF difference for other substrates, must be properly accounted for or AD results will be inaccurate.

INTRODUCTION

Both particle and bulk mass spectrometry measurements are widely used for precise isotopic measurements of uranium and trans-uranic materials.[1,2,3,4,5] Chronometry, or age-dating (AD), of uranium materials provides added value in addition to isotopic measurements, in that it reveals a processing timeline for materials. AD measurements are often constrained by low abundance of

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target radionuclide daughter products, which has made extending these measurements to individual particles challenging.[6] Due to this, while bulk AD measurements have been routine for some time where sufficient sample mass is readily available,[7,8] reliable techniques for individual particle-based methods have been slower to develop. Details describing a methodology for age dating individual uranium particles by large geometry secondary ion mass spectrometry (LG-SIMS) were discussed in a recent paper by Szakal *et al.*[9] This paper discusses using the ^{234}U – ^{230}Th parent-daughter chronometry pair for the age dating of U-containing particles, and specific statistical considerations which are key to interpreting the $^{230}Th/^{234}U$ ratio in the low ^{230}Th count regimes that are observed for many U-containing particles.

In this current work, we discuss our efforts to adopt the previously developed age-dating methodology onto the multi-collector detection configuration of the LG-SIMS. The previously published methodology used a mono-collector detection configuration and peak switching to perform the AD measurements. Many LG-SIMS instruments used worldwide are equipped with a multi-collector detection platform, and many labs use this configuration for routine U isotope measurements of particles. Multi-collector measurements generally improve measurement precision and detection limits due to simultaneous counting of all isotope signals, which is why SIMS analysts opt to use that configuration when possible. Determining a protocol for using the multi-collector configuration for AD measurements which can easily be integrated with commonly used mutli-collector protocols for isotopic measurements is anticipated to be a useful methodology for SIMS analysts performing these measurements of uranium containing particles.

This work will also discuss some differences in measured relative sensitivity factors (RSFs) for Th:U on different substrates. To perform particle analyses by SIMS, particles are first placed onto a sample planchette. Commonly used planchettes are carbon discs, Si wafers, In pucks, stainless steel discs, among others. When the analyzed U-containing particle is on the order of micrometers and because the sputtered/rastered area of the SIMS primary beam is on the order of 10s of micrometers for a particle analysis, a substantial amount of substrate material is co-sputtered by the SIMS primary beam during sample analysis. In some cases the bulk of the material being sputtered is from the substrate. In such cases the substrate chemistry has a major effect on the ion formation during the sputtering phase of SIMS analysis.[10] This can result in the SIMS sputtering altering the secondary ion formation of some elements relative to each other. For AD measurements, this is important to account for because the RSF between Th and U is used to correct the measured data during data processing. The difference between carbon and Si substrates will be discussed here.

MATERIALS AND EQUIPMENT

Particle samples were produced by dispersing Certified Reference Material (CRM) uranium oxide materials onto either 25 mm carbon planchettes or Si wafers. The density of the dispersions was kept low to allow for sufficient space between particles so that single particle measurements could be made. Three different U-series materials, whose distribution is now controlled by New Brunswick Laboratories Program Office, were used for these studies: U200, U630, and U900.[11] Additionally, uraninite from Topsham, Maine was also used.

The LG-SIMS instrument used for this work is a CAMECA IMS-1270E7/1280 (Cameca Instruments INC., 5470 Nobel Dr, Fitchburg, WI, USA).[12] This instrument was originally acquired as an IMS 1270, and has been 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.

MULTI-COLLECTOR CONFIGURATION FOR AGE-DATING MEASUREMENTS

The specific instrument operating parameters, with a focus on AD measurements, have been previously described in detail.[9] To be consistent with the prior published methodology, this work has not deviated from the published instrument configuration when using the mono-collector configuration. For the multi-collector configuration, attempts were made to deviate as little as possible from instrument configuration settings used for the mono-collector. The main difference is that, because the XY beam shaping mode produces a beam image on the detector plane which is long compared to the physical size of the multi-collector electron multiplier (EM) detectors (which are physically smaller than the mono-collector EM), circular (CIRC) beam shaping mode needed to be used since it produces a smaller beam image – in the y direction – at the detector. Key instrument parameters are summarized in Table 1.

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 μm	125 μm
Contrast Aperture (CA)	400 μm	400 μm
Field Aperture (FA)	6000 μm	6000 μm
Energy Slit bandpass	50 eV	50 eV
Max Field of view (MA)	50 μm x 50 μm	50 μm x 50 μm
Beam Shaping Mode	XY	CIRC
EM Threshold	75 mV	75 mV
Exit Slit	250 μm	250 μm(S2)

The IMS1280 LG-SIMS multi-collector system has five electron multiplier (EM) detectors, allowing for five simultaneous isotopic measurements. The standard configuration for U-isotopic analysis is to align the detectors to measure ^{234}U, ^{235}U, ^{236}U, ^{238}U, and ^{238}U-^{1}H (which serves as a hydride correction) simultaneously. This is a standard protocol used by many SIMS analysts.[13] A favorable multi-collector configuration for ^{230}Th/^{234}U age dating measurement would take advantage of the detectors placed as they are for U isotopic measurements, so that the trolleys holding each detector would not need to move. The most straightforward approach to accomplish this is to adjust the magnet mass setting down by 4 a.m.u (i.e. 4u) from the U isotope setting. This scheme is advantageous because, by shifting the masses down 4 a.m.u from the isotopic configuration, one captures both ^{230}Th and ^{232}Th masses as well as the ^{231}Pa-^{235}U chronometer pair, which may be useful to monitor in some unknown samples.[14,15] ^{232}Th is also worthwhile to measure as it may indicate the presence of natural/mineral contamination in the sample or incomplete purification of isotopically natural uranium. Such contaminants could lead to abnormally high ^{230}Th/^{234}U ratios, implying that the source material is not from a closed system. This scheme is illustrated below:

U Isotope Configuration		^{230}Th/^{234}U age dating Configuration
L2 – ^{234}U		L2 – ^{230}Th
L1 – ^{235}U		L1 – ^{231}Pa
C – ^{236}U	4 a.m.u. shift down $\rightarrow$	C – ^{232}Th
H1 – ^{238}U		H1 – ^{234}U
H2 – ^{238}U-^{1}H		H2 – ^{235}U

When the trolleys holding each detector (EM) are aligned for one configuration and the mass analyzer (magnet) is set accordingly, adjusting the magnet to align the detectors for the other measurement (i.e., switching from U isotopics to ^{230}Th/^{234}U AD) – the 4 a.m.u. shift – will cause the detectors to be misaligned in this new configuration. This is because even the short magnet jump is significant enough to alter the dispersion of the isotopic signals exiting the mass analyzer and affect the physical spacing, in real space, of the distance between mass peaks separated by 1 a.m.u. There are two conventional remedies for this misalignment following a magnet shift. 1) Shift the trolleys in real space to account for the altered dispersion & 2) Alter the dispersion of the isotopic signals exiting the magnet such that the mass peaks are aligned with the detectors in their current physical location. This is accomplished by altering the voltage applied to the horizontal axis stigmation component of the octupole which is located just after the exit of the magnetic sector mass analyzer in the ion flight path (referred to as DSP2 S1). Typically, a large value needs to be set on this stigmation component (DSP2 S1) to increase the magnet dispersion to aide in aligning the trolleys holding the multi-collector EMs for U isotope measurements. So, there is leeway to reduce this value following a magnet shift. This correction is an electronic correction and therefore more repeatable than physically shifting the trolleys, which could be affected by motor hysteresis. For simplicity and to minimize having to move the trolleys physically between configurations, a scheme using primarily electronic corrections was developed.

Table 2 shows the instrument parameters which need to be adjusted to shift from a U isotopic measurement configuration to a ^{230}Th/^{234}U AD measurement configuration for a multi-collector configuration. These settings were optimized to make it possible to switch back and forth between configurations with no other tuning or trolley adjustments, and this has been verified. It should also be noted that the instrument parameters described here were worked out for the NIST instrument and exact instrument values may not be directly transferrable to other instruments. However, the general scheme is adaptable and should apply for any LG-SIMS instrument.

Table 2. Instrument parameter changes needed to switch from U isotopic to ^{230}Th/^{234}U AD measurements

Setting	U Isotopic Measurement Configuration	^{230}Th/^{234}U AD measurement configuration
Magnet Setting (axial m/z value)	^{238}U (238.05)	^{234}U (234.04)
DSP2 S1 (dispersion)	1500 (-218 V)	1296 (-188 V)
HC1 Stig (peak shape correction)	-64 (-24V)	-54 (-21 V)
H2 EM Trolley Shift	0	+100 DAC units (µm)

Aside from the 4 a.m.u magnet shift, two electronic corrections were needed. The first is the previously described adjustment to the dispersion (DSP2 S1), which needed to be reduced from a DAC value of 1500(-218 V) to 1296 (-188 V). The second electronic value that needed to be adjusted is for a beam shaping hexapole called HC1 stig. This setting is often used to correct distortions in peak/beam shape that arise from altering the dispersion setting, so expectedly an adjustment is needed. The DAC value on this setting was increased from -64 (-24 V) to -54 (-21

V). Additionally, despite best efforts, it was not possible to develop a scheme that wholly eliminated the need for a physical trolley shift. However, with this scheme the only trolley that needs to be shifted is the H2 trolley by +100 dac units (which is also physically in µm). This is the highest mass trolley ($^{238}U^1H$ or ^{235}U depending on measurement configuration). Because this scheme involves only the movement of one exterior trolley, this compromise was judged to not be overly burdensome.

The paper by Szakal *et al.* describes, in detail, considerations about mass resolution required to eliminate mass interferences from, primarily, Pb-based polyatomic species.[9] For reasons outlined in that paper, an exit slit of 250 µm was used to achieve a mass resolution ~ 3400 m/Δm. Figure 1 shows that a mass resolution of ~3400 m/Δm can also be achieved using the multi-collector configuration, 250 µm exit slits, and CIRC mode tuning. Note that the 'flat-top' region of the top of the CIRC mode tuned peaks is somewhat narrow, which could adversely affect measurement precision.
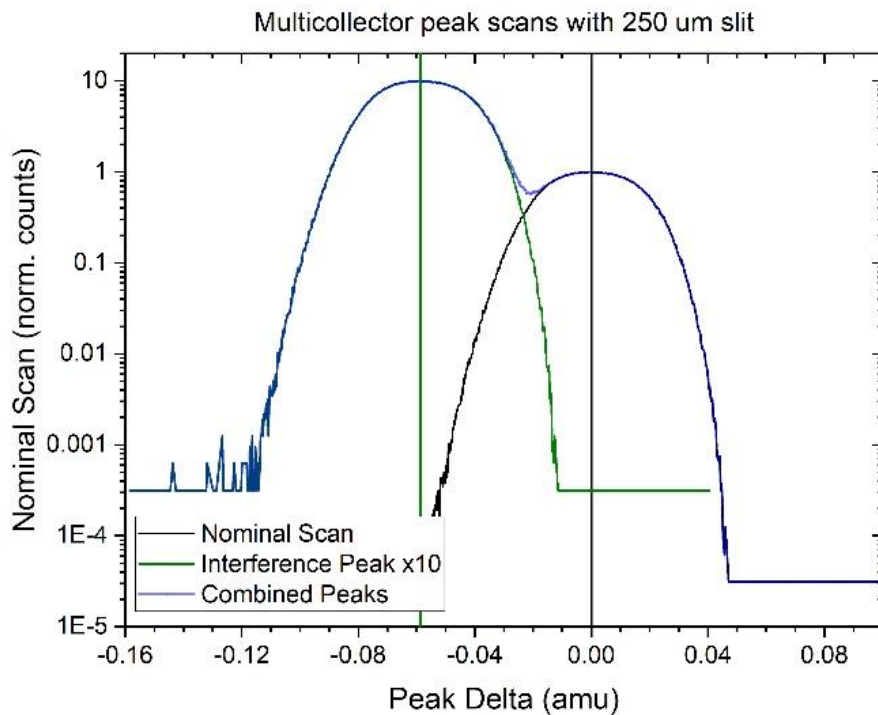

Figure 1: Mass scan of ^{230}Th with a simulated $^{206}Pb^{12}C$ interference peak. The peak shape shown is obtained using the multi-collector configuration from Table 1, with a 250 µm exit slit. The simulated interference peak is shifted -0.587 a.m.u. from the nominal mass and multiplied by 10. It can be seen that there is sufficient separation of the high mass peak tail to eliminate interference in ^{230}Th measurements.

COMPARISON OF MONO- AND MULTI-COLLECTOR AGE-DATING PROTOCOLS

The mono-collector protocol uses a total count time (actual dwell and wait times) of 28 seconds per cycle.[9] Since the multi-collector does not need to vary magnet positions, a count time of 28 seconds per cycle was chosen to reduce bias in comparing the two methods. A typical particle analysis is 20 cycles. Because a large amount of data is available on CRM U900 measured by the mono-collector protocol and good statistics about the performance exist, this material was chosen to investigate the

performance of the multi-collector method. Additionally, because the abundance of [230]Th in this material is reasonably high, data processing is straightforward and conventional Gaussian statistics can be used for both mono- and multi-collector data. The figure of merit that was chosen for comparison is the derived RSF as measured on an individual particle. Because CRM U900 has a known production date (Jan. 24, 1958), it is straightforward to calculate the expected [230]Th/[234]U which should be present from radioactive decay. The ratio of the measured value to the expected value is the RSF value. This is defined by the following equation:

$$RSF_{Th:U} = \frac{230_{Th}/234_U \; (meas.)}{230_{Th}/234_U \; (expected)}$$

Figure 2 shows a comparison of a collection of particles (N=20) of CRM U900 that were measured by the multi-collector protocol to the previously published value of the $RSF_{(Th:U)}$, 0.673 ± 0.024 (1σ), which was measured on several hundred particles by the mono-collector protocol.[9] The average value determined from this set for the multi-collector measurement was 0.687 ± 0.030 (1σ). While slightly divergent in the average values, the two values overlap in uncertainty(1σ). It can also be observed in Figure 2 that all of the individual particle data for the multi-collector measurement overlap within uncertainty(1σ) of the mono-collector measurement value.
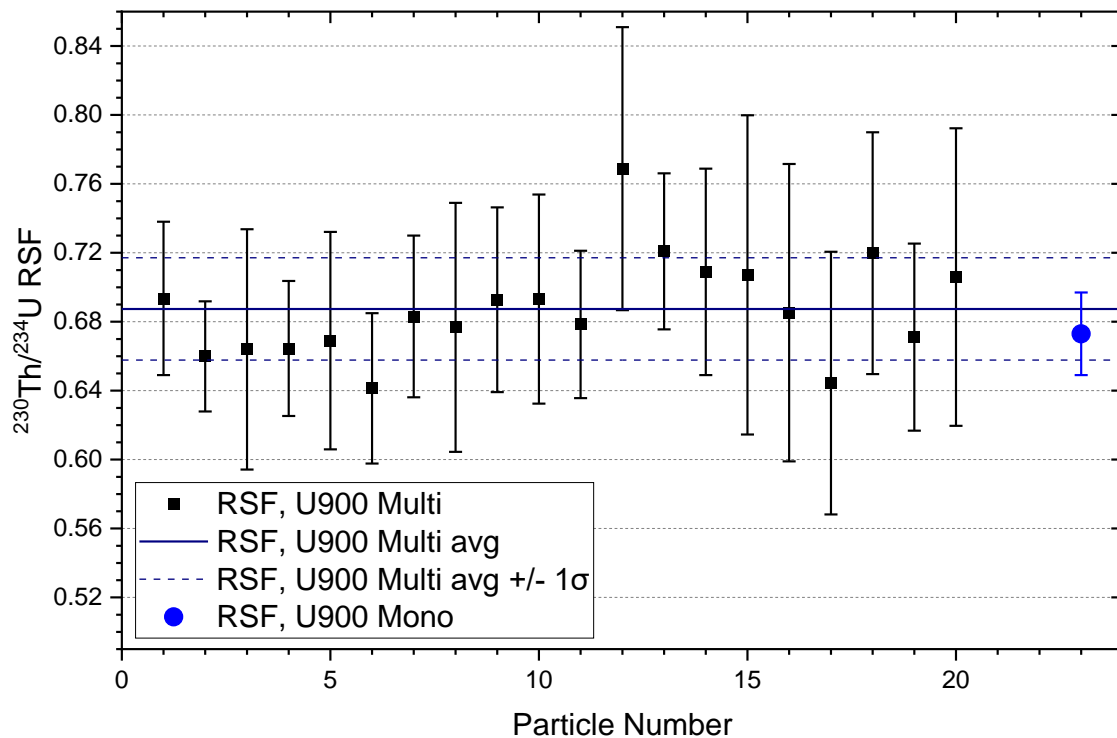

Figure 2. Graph comparing RSF values from CRM U900 as measured by the multi-collector protocol compared to the previously published RSF value determined from CRM U900 and measured by the mono-collector protocol. Error bars shown for individual data points are 1σ.

A second comparison of the multi- and mono-collector protocols was done using uraninite material. This material was chosen as a test material because as a naturally occurring mineral, there are

substantial amounts of potential interferences from Pb-based polyatomic species, which form ions with m/z values close to ^{230}Th. Therefore, a material like uraninite serves as a good indicator that the multi-collector measurement protocol is not easily negatively impacted by commonly found levels of interfering species. Additionally, as with CRM U900, the abundance of ^{230}Th and ^{234}U are large enough such that normal Gaussian statistics can be used to evaluate the data. Figure 3 shows the comparison of two sets of data obtained on uraninite for the multi-collector measurement (N=12) and for the mono-collector measurement (N=10). The data in Figure 3 are plotted as the derived RSF values. This source of uraninite is from Topsham, Maine and the ^{230}Th and ^{234}U are in secular equilibrium, and ^{230}Th/^{234}U = 0.306. For uraninite, the RSF is the ratio of the measured value to the secular equilibrium value.
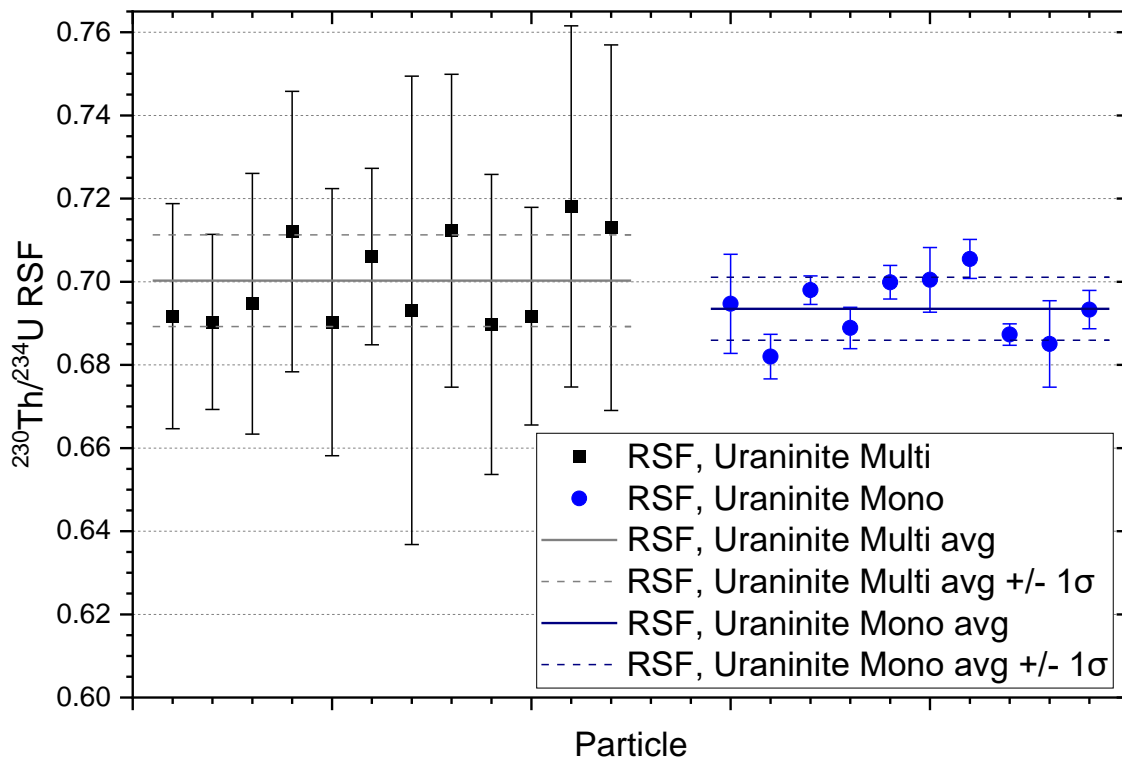

Figure 3. Graph comparing RSF values from uraninite as measured by the multi-collector protocol and the mono-collector protocol. Error bars shown for individual data points are 1σ.

The average values for the mono- and multi-collector measurements were 0.693 ± 0.008 (1σ) and 0.700 ± 0.011 (1σ), respectively. These values are in good agreement with each other, within uncertainty(1σ). From Figure 3, its clear that individual particle measurements made by the multi-collector protocol had higher individual uncertainty, and slightly larger scatter in the average values than the mono-collector measured particles. Counting statistics would predict that the multi-collector data should have smaller individual particle uncertainty values, since the counting times for both ^{230}Th and ^{234}U are longer per cycle. The higher than expected uncertainty may be due to the instrument tuning and setup not being completely optimal in the multi-collector configuration, which indicates further optimization of the measurement protocol may be needed.

SUBSTRATE EFFECTS ON Th:U RSF

As mentioned previously, the substrate chemistry can have a large effect on the RSF$_{(Th:U)}$. In addition to carbon planchettes, Si wafers are another commonly used SIMS substrate. The rationale for using Si is that often, due to the high quality Si wafers produced for the semiconductor industry, very pure, extremely flat, high quality material is available. Also, the use of Si wafers as substrates has been shown to reduce hydride formation when compared to carbon planchettes, which helps improve the detection limits of some species with large hydride interference, like ^{236}U.[16] For these advantages in using Si wafers as substrates, it's important to understand how substrate effects may influence the RSF$_{(Th:U)}$. Three CRM U-series materials were chosen to investigate the role of Si on RSF$_{(Th:U)}$: U200, U630, and U900. These represent a range of enrichments and production dates. The production dates are Nov 4, 1957, Jun 6, 1989, and Jan 24, 1958 for U200, U630, and U900, respectively. For each CRM U-series material, 10 particles were measured for each and compared to the previously published value for the RSF$_{(Th:U)}$, as determined for U900 on carbon planchettes (0.673 ± 0.024). A comparison on the values is shown in Figure 4.

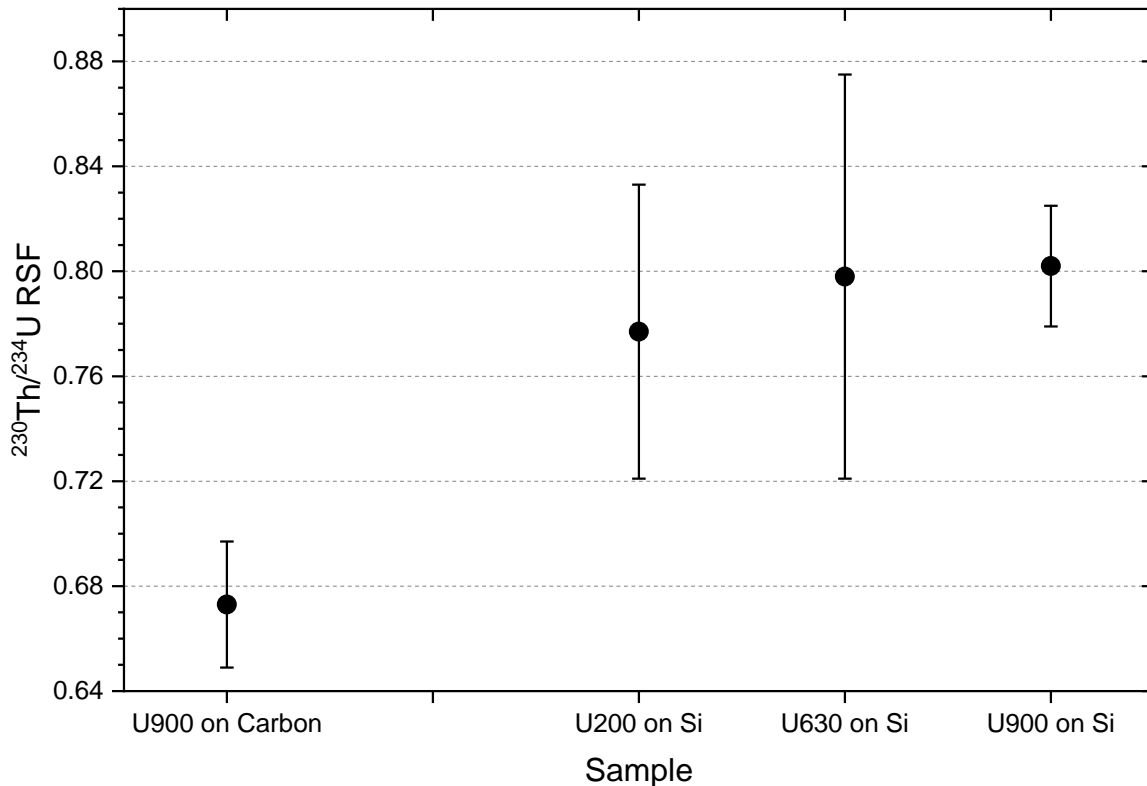**Figure 4.** Graph comparing RSF(Th:U) of CRM U-series materials on carbon planchettes and Si wafers. Error bars shown for individual data points are 1σ.

The following RSF$_{(Th:U)}$ values were obtained: U200 = 0.777 ± 0.056, U630 = 0.798 ± 0.77, and U900 = 0.802 ± 0.023. The larger uncertainties obtained for the U200 and U630 values compared to the U900 value is not unexpected. U200 and U630 are much lower in ^{230}Th abundance, due to enrichment level for U200 and younger age for U630. From Figure 4, it's clear that the RSF$_{(Th:U)}$ value for materials on Si wafer are shifted compared to carbon planchettes. Note that previously it

has been demonstrated that for CRM U-series materials on carbon planchettes, the $RSF_{(Th:U)}$ value is consistent across the various materials in the series, which is expected since they share the same chemistry (U_3O_8).[11] While this result showing a systematically different value for $RSF_{(Th:U)}$ on Si wafers is not surprising, it is important to be aware of when setting up SIMS analyses so that standards and unknowns are measured using the same substrates to avoid eliminating potential data processing errors.

CONCLUSION

A methodology for using the multi-collector configuration common to LG-SIMS instruments has been developed for age dating U-containing particles based on the ^{234}U – ^{230}Th parent-daughter chronometry pair. This method is premised on taking advantage of a common configuration used for uranium isotopic measurements with the goal of allowing simple and straightforward switching between uranium isotopic and uranium age-dating measurements. Evaluation of the methodology by comparison to previously established age-dating protocols developed for the mono-collector configuration was done and showed the multi-collector methodology produces results consistent with the mono-collector method. It was noted that uncertainty in individual particle measurements was higher than should be expected, indicating improvements in instrument setup are likely needed.

The difference in $RSF_{(Th:U)}$ values caused by particles being mounted on different substrates was also demonstrated. The two substrate chemistries studied were carbon planchettes and silicon wafers, and a clear difference in $RSF_{(Th:U)}$ values was observed. While not a surprising result, this effect is important to be aware of when performing uranium age dating measurements.

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