In Revision (Round 3) for Rapid Communications in Mass Spectrometry
May 6 2025

Preliminary insights into the feasibility of determining the purification date of enriched uranium by direct measurement of the $^{230}Th/^{234}U$ ratio using an all-faraday detector configuration on the Neoma MC-ICP-MS

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Abstract

Rationale:

Mass spectrometric measurement of the $^{230}Th/^{234}U$ ratio to calculate the purification age of enriched uranium is typically conducted via a combination of ion counters and faraday detectors, thus requiring an inter-detector calibration scheme. Our aim is to understand whether the pursuit of a simplified measurement scheme involving only faraday detectors is feasible.

Methods:

We investigate the possibility of determining U-Th model ages for two enriched uranium standards (NBL U630 and U850) by direct measurement of the $^{230}Th/^{234}U$ ratio (without chromatographic separation or isotope dilution) on a ThermoFisher Scientific Neoma MC-ICP-MS utilizing both solution and laser ablation (LA) based sampling techniques and an all-faraday detector configuration.

Results:

For the solution mode analyses conducted on aliquots containing sub µg/mL total U, we produce composite average $^{230}Th/^{234}U$ model dates of May 19, 1988 (± 351 days) and March 26, 1961 (± 2.5 years) using the directly measured $^{230}Th/^{234}U$ ratios for the NBL U630 and U850 uranium standards, which have certified purification dates of June 6, 1988 (± 190 days) and December 31, 1957 (± 36.5

days), respectively. The ages produced by LA based sampling of dried residues of the same standards deposited onto cotton TexWipes are less accurate and of poorer precision (June 23 2004 ± 8.7 years for U630 and December 21 1965 ± 7.9 years for U850) but still yield meaningful information in regards to the purification date.

Conclusions:

We believe that further refinement of the all faraday detector measurement approach to include development of a more robust Th/U relative sensitivity factor determination, signal cutoff selection, and data processing protocols will allow for this approach to be confidently applied to enriched uranium materials with unknown purification histories. Potential advantages of the method include the reduced sample handling and infrastructure requirements as well as the ability to simultaneously generate a broad picture of the uranium isotopic composition in tandem with the U-Th age determination.

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Conflict of Interest Statement: The authors declare no conflict of interest

Introduction

Radiometric dating is a widely applied technique in the physical sciences whereby a material's 'age' can be determined by accurate determination of the ratio between a radioactive 'parent' nuclide and its radiogenic 'daughter' product (See review by Joshi et al. 2021). In the field of nuclear forensics, where the goal is to determine a material's history by integration of various physical, chemical, and isotopic properties (see review by Kristo and Tumey 2013), use of the ^{234}U - ^{230}Th decay series to obtain 'model' ages has continued to gain traction (see discussion by Kristo et al. 2018) since this chronometer was first published for use in highly enriched Uranium by Wallenius et al. (2002). This radiometric dating method is based on the principal that ^{234}U decays to ^{230}Th with a half-life of ~2.46×10^5 years (Wallenius et al. 2002). Therefore, a material's $^{230}Th/^{234}U$ ratio can be used to calculate an 'age' according to the derived (see NBL 2013) formula $t = \ln(((\lambda_{230Th} - \lambda_{234U})/ \lambda_{234U})x(^{230}Th/^{234}U))/(\lambda_{234U} - \lambda_{230Th})$ where λ_{230Th} and λ_{234U} are the decay constants for $^{230}Th = 9.193 \times 10^{-6} \cdot year^{-1}$ and $^{234}U = 2.823 \times 10^{-6} \cdot year^{-1}$ (λ values provided on the CRM U630 uranium isotopic and radiochronometric standard certificate of analysis; NBL 2013). If there was no ^{230}Th present in the material initially (e.g. the material was subject to a purification process to remove Th, which can take place during the nuclear fuel cycle), then the observed $^{230}Th/^{234}U$ 'age' can be used to determine the material's purification date, which in turn can be a valuable piece of information in the context of a nuclear material attribution study. The $^{230}Th/^{234}U$ chronometer has also been widely applied to various geological materials (Cheng et al. 2000; Hoffman et al. 2018; McCulloch and Mortimer 2008; Garnett et al. 2004), but the meaning of, and considerations relative to, the ages obtained for natural materials are somewhat different than for anthropogenically produced U-rich materials. Because of the relatively long half-life for the decay of ^{234}U to ^{230}Th (~2.46×10^5 years) in comparison to the length of time that the anthropogenic nuclear fuel cycle has been in existence (<100 years years), one of the major challenges associated with determining

accurate $^{230}Th/^{234}U$ ratios, which is a pre-requisite to obtaining meaningful $^{230}Th/^{234}U$ ages, is that there is often very little radiogenic ^{230}Th accumulated within the material under scrutiny. This is especially true if the material has low ^{234}U content, which can result in poorly constrained $^{230}Th/^{234}U$ ratios that translate into models ages with extremely high uncertainties. Despite this limitation, there are numerous studies presenting techniques for accurate determination of the $^{230}Th/^{234}U$ by mass spectrometry (see discussion by Kristo et al. 2018).

The majority of studies presenting $^{230}Th/^{234}U$ measurement techniques for anthropogenic nuclear materials rely on digestion of the material, chemical separation of U and Th, followed by isotope dilution (ID) – mass spectrometry (MS) to independently determine the number of atoms of ^{230}Th and ^{234}U in the original sample (Kristo et al. 2018, Lamont and Hall 2005; Wallenius et al. 2002; Harrison and Gaffney 2021; Wang et al. 2024; Knight et al. 2014). While this approach has been proven to produce accurate and precise $^{230}Th/^{234}U$ ratios, each step in the process has the potential to introduce uncertainty in the final isotope ratio while also being time consuming and requiring advanced laboratory expertise and infrastructure. The logical progression of this method is therefore a migration towards techniques that can accurately determine the $^{230}Th/^{234}U$ from a material by direct measurement, and there are indeed several studies demonstrating that such an approach is possible for enriched uranium samples. For example, Szakal et al. (2019) utilized secondary ion mass spectrometry (SIMS) to produce accurate $^{230}Th/^{234}U$ ages from micron sized uranium particles representing a variety of enrichment levels and with purification ages ranging from 10 to 60 years before the measurement session. More recently, Varga et al. (2024) and Humbert et al. (2024) utilize laser ablation (LA) – multi collector (MC) – inductively coupled plasma (ICP) – mass spectrometry (MS) to produce accurate $^{230}Th/^{234}U$ ages from pure highly enriched uranium. The use of laser LA sampling is also becoming more common in the geological applications of the $^{230}Th/^{234}U$ chronometer (Mertz-Kraus et al. 2010), but as stated earlier

there are different considerations for the application of this chronometer to geological materials as compared to nuclear materials.

While direct measurement of the $^{230}Th/^{234}U$ ratio (without any chromatographic separation of U and Th, and/or isotope dilution based approaches) by either SIMS (Szakal et al. 2019) or LA-MC-ICP-MS (Varga et al. 2024; Humbert et al. 2024) has been shown capable of producing accurate $^{230}Th/^{234}U$ ages reflecting the purification dates of the materials considered by the various studies, other studies that have attempted to produce U-Th ages from the directly measured $^{230}Th/^{234}U$ have been unsuccessful. For example, Wallenius et al. (2007) attempted to calculate $^{230}Th/^{234}U$ ages directly from the measured $^{230}Th/^{234}U$ ratio by solution ICP-MS on a Nu Plasma instrument for various enriched uranium standards but found the result to be highly inaccurate (ranging from -21.5% to 35.6% lower than the expected value), which they attributed to possible differences in the ionization potential of U and Th and/or spectral interferences. Another potential pitfall of these techniques is that the ^{230}Th is signal is measured by ion counting whereas the ^{234}U is measured by faraday detector (Varga et al. 2024; Humbert et al. 2024). The use of two different detector types is regarded as necessary because of the low intensity of the ^{230}Th signal, which would be below the usable range of faraday detectors equipped with 10^{11} resistors in their amplifier feedback loops whereas the ^{234}U signal is likely to be far above the saturation limit of an ion counter during the analysis of enriched uranium. However, the use of different detector types creates the need for the development of a calibration scheme to account for the different response rates and signal conversion efficiencies of the faraday and ion counter type detectors (see discussion by Varga et al. 2024). While such calibrations have become commonplace in the nuclear analytical chemistry community, as well as other analytical science disciplines where there is a need to simultaneously detect small and large ion beams (see discussion by Richter et al. 2009, 2016; Davis 2020), recent advances in faraday detector technology involving the addition of 10^{13} ohm resistors in their amplifier feedback loops have pushed the signal intensity cutoff for faraday detectors towards

lower values (Vollstaedt et al. 2017; Bouman et al. 2015). There are now studies demonstrating that it is sometimes possible to achieve improved accuracy and precision for an isotope ratio where one isotope has a weak ion beam while the other is considerably stronger when measured on two faraday detectors equipped with 10^{11} and 10^{13} Ω resistors compared to the more traditional faraday detector and ion counter combination (See discussion by Zirakparvar et al. 2023 and Reinhard et al. 2024).

The aim of the present study is to determine whether use of an all-faraday cup detector scheme involving a combination of 10^{11} and 10^{13} Ω resistance amplifiers is worth pursuing for the determination of $^{230}Th/^{234}U$ model ages in enriched uranium. The justification for the pursuit of such a method is that eliminating the need for the application of an inter-detector calibration scheme, and other issues related to use of ion counting type detectors (e.g. signal dead time corrections, degradation in counting efficiency over time, detector signal overload, etc), would further simplify the determination of $^{230}Th/^{234}U$ ages thus eliminating possible barriers to producing accurate and precise $^{230}Th/^{234}U$ ages in nuclear materials. At a minimum, its possible that direct measurement of the $^{230}Th/^{234}U$ could be used as a screening tool to guide more in-depth analytical work for a suite of materials under study. We investigate the behavior of the $^{230}Th/^{234}U$ ratio in CRM 650 and CRM850, both of which have known purification dates and an enriched ^{234}U concentration that is amenable to the detection of ^{230}Th produced by ingrowth from the decay of ^{234}U on the ThermoFisher Scientific Neoma MC-ICP-MS in both solution mode and by laser ablation (LA) based sampling of the dried CRM on a cotton TexWipe. While our results are not meant to be construed as a fully developed and tested method, we do show that meaningful $^{230}Th/^{234}U$ ages can be obtained directly from the observed $^{230}Th/^{234}U$ ratio when there is enough ^{230}Th to produce a response on the faraday detector. While there are several complexities apparent in our preliminary dataset, our results indicate that further methodological development should be focused on the determination of $^{230}Th/^{234}U$ ages by direct measurement of this ratio on the various MC-ICP-MS platforms using all faraday detection.

Methods, Materials, and Data Processing

Both modes of isotopic data collection (solution and laser ablation based sampling) reported in this study were collected on a ThermoScientific Neoma MC-ICP-MS (without the MS/MS option) using the following faraday cup configuration: ^{230}Th on cup L3 coupled to a $10^{13}\Omega$ resistor, ^{231}Pa on cup L2 coupled to a $10^{13}\Omega$ resistor, ^{232}Th on cup L1 coupled to a $10^{13}\Omega$ resistor, ^{234}U on the center cup coupled to a $10^{11}\Omega$ resistor, ^{235}U on cup H1 coupled to a $10^{11}\Omega$ resistor, ^{236}U on cup H2 coupled to a $10^{11}\Omega$ resistor, ^{238}U on cup H3 coupled to a $10^{11}\Omega$ resistor, and $^{238}U^{1}H$ on cup H4 coupled to a $10^{11}\Omega$ resistor. A detector gain and baseline calibration was performed using the instrument control software prior to the measurement session. For the solution analyses, nine dilutions each of the NBL U630 and U850 standards were prepared at concentrations ranging from 2.5 ppm down to 0.02 ppm (in a 2% HNO_3 carrier). Individual analyses consisted of 20 cycles of data collection, each with a 4 second integration time. Prior to each analysis, a blank solution consisting of only 2% HNO_3 was analyzed. Washouts between each analysis were achieved by aspirating 5% HNO_3 for approx. 5 minutes. For the solution analyses, a glass spray chamber was utilized and the sample gas flow on the Neoma was ~1.01 L/min (Ar). These conditions, as well as other details, can be found summarized in table 1.

For the laser ablation measurements, the NBL U630 and U850 standards were deposited onto a ~3.2 mm diameter cutout of a TexWipe 304 cotton cloth affixed to a TedPella SpectroTab carbon sticky tab and then dried in a HEPA filtered laminar flow hood at room temperature. We took the approach of repeatedly doping (and drying) 10 µl aliquots of the 2.5 ppm solution on the cloth such that each cloth received a total dose of 0.25 µg of total U. Laser ablation was performed using an Elemental Scientific NWR193 laser ablation system being operated at a repetition rate of 100Hz and tuned to deliver ~5.952 J/cm^2 at the sample surface. Analyses were conducted by setting up a grid consisting of multiple 50 µm

diameter spots (each with a 10 second ablation time chosen at random on the TexWipe surface) and then augmented by targeted sampling of areas yielding a high U signal. The Neoma was set up to collect 1,000 cycles of data (each with a 1 second integration time) over the course of the laser ablation sampling on each of the NBL doped TexWipes. The ablated material was transported into the plasma using approximately 500 mL/min of He carrier gas, while the Neoma Ar sample gas flow was set to approximately 0.9 L/min. These conditions, along with additional details, can be found summarized in table 1.

For data processing of both the solution mode and laser ablation based analyses, raw data (in the form of the average voltage observed during each cycle of data collection during any given analysis) was exported from the instrument control software and processed in Microsoft Excel. This raw data is provided in the electronic appendix. For the solution mode analyses, the voltages observed on the blank solution immediately preceding each analysis were used to apply a blank subtraction to each cycle of data collected for various dilutions of the two NBL standards (2.5 ppm down to 0.02 ppm), These blank corrected intensities were then utilized to calculate the various isotope ratios of interest ($^{230}Th/^{234}U$, $^{231}Pa/^{235}U$, $^{234}U/^{238}U$, $^{235}U/^{238}U$, $^{236}U/^{238}U$, and $^{238}U^{1}H/^{238}U$) at each cycle of data. These were then averaged together over the course of each analysis, and a within-run uncertainty was calculated by computing the standard error of the mean. These are the ratios and uncertainties reported in supplementary table 1. Calculation of the model ages reported on supplementary table 1 will be discussed in the subsequent section. For the laser ablation data, a similar approach to the solution data was taken except that only ratios from cycles with >0.1V of ^{234}U were utilized to compute the ratios and uncertainties reported in supplementary table 1. No blank subtraction was applied as there was no discernible U, Th, or Pa signal observed when the laser was not being fired, nor when the laser was fired onto an undoped TexWipe or the carbon sticky tab substrate underpinning the cotton TexWipe material

Results and Discussion

Overview of analytical results

Prior to consideration of the $^{230}Th/^{234}U$ isotope ratio data in the context of the age calculations, it is first necessary to consider the overall quality of the MC-ICP-MS data. This can be achieved by consideration of the behavior of the raw isotope ratios (i.e. uncorrected for mass fractionation or instrumental drift) comprised of the more abundant isotopes present in the U630 and U850 standards (^{234}U, ^{235}U, ^{236}U, and ^{238}U), which are depicted graphically in figure 1. The nine replicates of the NBL CRM U630 standard analyzed in solution mode at varying dilution levels (2.5 ppm down to 0.02 ppm) produced average $^{234}U/^{238}U = 0.0172565 \pm 0.0000073$, $^{235}U/^{238}U = 1.77614 \pm 0.00056$, and $^{236}U/^{238}U = 0.027177 \pm 0.000010$ (uncertainties shown are the 1σ standard deviation of the 9 replicate analyses). These values are < 1% lower than the $^{234}U/^{238}U = 0.017353207$, $^{235}U/^{238}U = 1.783827356$, and 236U/238U = 0.0272109 calculated from the isotope amount fractions of ^{234}U (0.61894), ^{235}U (63.353), ^{236}U (0.96230), and ^{238}U (35.066) provided on the NBL CRM U630 Certificate of Analysis (NBL 2013). Eight replicates of the NBL CRM U850 standard analyzed in solution mode at varying dilution levels (2.5 ppm down to 0.02 ppm) produced average $^{234}U/^{238}U = 0.045467 \pm 0.000016$, $^{235}U/^{238}U = 6.0450 \pm 0.0020$, and $^{236}U/^{238}U = 0.026599 \pm 0.000010$ (uncertainties shown are the 1σ standard deviation of the eight replicate analyses; note that nine analyses were conducted but one was rejected from consideration in the above calculation due to the ^{235}U signal being >100V, which is the limit of the faraday detector). These values are also <1% lower than the $^{234}U/^{238}U = 0.046483247$, $^{235}U/^{238}U = 6.147963605$, and $^{236}U/^{238}U = 0.0267475$ calculated from the isotope amount fractions of ^{234}U (0.6437), ^{235}U (85.137), ^{236}U (0.3704), and ^{238}U (13.848) provided on the NBL CRM U850 Certificate of Analysis (NBL 2020). Another consideration is that the standard 1σ s.d. values for the average isotope ratios are all ≤ 0.04%, which compare favorably to the isotope amount fraction uncertainties reported on certificate of analysis for CRM U630 and U850 which range from as low as 0.019% (the ^{235}U content of U850) to as high as 0.217%

(the ^{234}U content of U850). As expected, the within-run uncertainties for the individually measured isotope ratios made in solution mode vary according to the signal intensity of the specific ratio's minor isotope, which in turn is a function of the dilution level and isotopic composition. All of these values can be found in the supplementary table 1.

For the analyses conducted by LA-MC-ICP-MS on the dried CRM U630 and U850 deposited on the cotton TexWipe material, which utilized the same collector and amplifier configuration as the solution mode analyses (described in the preceding paragraph), U630 yielded average $^{234}U/^{238}U$ = 0.01687 ± 0.000065, $^{235}U/^{238}U$ = 1.730 ± 0.013, and $^{236}U/^{238}U$ = 0.02631 ± 0.00011 and CRM U850 yielded average $^{234}U/^{238}U$ = 0.04325 ± 0.00055, $^{235}U/^{238}U$ = 5.70 ± 0.10, and $^{236}U/^{238}U$ = 0.02488 ± 0.00031 (ratios calculated for individual cycles displaying > 0.1V of ^{234}U signal; reported uncertainty is the 1σ standard error of all the cycles used to compute the average ratio; refer to supplementary table 1 for additional details). Similarly to the solution mode analyses, the isotope ratios determined by LA sampling of the dried CRM U630 and U850 are lower than the isotope ratios calculated from the isotope amount fractions specified on the certificate of analysis for these two CRMS (these are provided in the preceding paragraph). The within-run standard error values for the LA data are higher compared to the population standard deviations computed from the individual analyses conducted in solution mode, but this is to be expected given the highly unstable signal produced during LA analysis.

In total, basic observations regarding the behavior of $^{234}U/^{238}U$, $^{235}U/^{238}U$, and $^{236}U/^{238}U$ ratios produced in both solution mode and during LA based sampling of the CRM U630 and U850 indicate that the Neoma is capable of producing precise and accurate (to within <1% without any mass bias correction) uranium isotope ratio data across a range of signal intensities and sampling modalities. They also indicate that the instrument remained stable across the analytical sessions conducted in this study, which is an important consideration as the discussion shifts towards examining the behavior of the $^{230}Th/^{234}U$ ratio in the context of the model age determination for these two standards. Given the

expectedly low signal intensity of ^{230}Th, it is important to be able to rule out substantial instrumental drift, and/or other variables, prior to interpretation of the $^{230}Th/^{234}U$ data. The behavior of the isotope ratios comprised of the more abundant isotopes, which are summarized in the preceding two paragraphs as well as on figures 1, suggest that the major instrumental issues can be ruled out when interpreting the $^{230}Th/^{234}U$ data. For example, if the ion beams had migrated towards the peak shoulders during the measurement sessions, we would expect to see substantial shifts in the major isotope ratios over the course of the session. We would also expect elevated session standard deviation values exceeding the uncertainty values on the certificates for these standards, which is not observed. Lastly, another important consideration is there is potentially a different ionization efficiency between U and Th, which could potentially skew the raw $^{230}Th/^{234}U$ ratios beyond what would be expected for simple mass bias. We did collect some data in solution mode focused on this issue, but this will be discussed in subsequent sections after presentation of the $^{230}Th/^{234}U$ ages.

Lastly, an important note is that the laser ablation measurements on the cotton TexWipe materials doped with the NBL U630 and U850 standards often resulted in total penetration of the TexWipe such that the carbon sticky tab became visible at the bottom of the ablation crater. Previous work (Zirakparvar et al. 2023) focused on laser ablation measurement of uranium isotopes for reference material solutions deposited and dried onto the same batch of TedPella SpectroTabs (that were also utilized to affix the cotton TexWipe in the present study) indicates that the carbon sticky tab does not impart any systematic shifts in the observed isotopic composition relative to a solution-mode measurement. While we did not observe at U or Th signal when the laser was fired onto the blank carbon sticky tab (or cotton TexWipe material) at the start of the session, it is possible that the transition from cotton TexWipe into carbon sticky tab during the individual ablation cycles could have imparted some sort of matrix effect on the observed isotope ratios. At the end of the laser ablation session, powdery white material (presumably ablated TexWipe material that did not get swept up into

the carrier gas and transported to the plasma) was observed in the vicinity of the ablation craters. For radiological safety reasons, the entire mount containing the doped TexWipes were immediately discarded into the radiological materials waste stream. Therefore, no photomicrographs or other images of the ablation spots are available. This highlights the importance of the need for additional methodological development focused on optimal ablation conditions specific to this type of measurement.

Calculation of the 'model ages' and comparison with the known purification dates

The model ages and dates reported in supplementary table 1 were calculated by using the $^{230}Th/^{234}U$ ratios observed on the analysis dates (March 6th and 8th, 2024 for the LA and solution mode analyses, respectively) to determine an age in years relative to the analysis date using the formula $t = \ln(((\lambda_{230Th} - \lambda_{234U})/ \lambda_{234U})x(^{230}Th/^{234}U))/(\lambda_{234U} - \lambda_{230Th})$; Where λ_{230Th} and λ_{234U} are the decay constants for ^{230}Th ($9.193 \times 10^{-6} \cdot year^{-1}$) and ^{234}U ($2.823 \times 10^{-6} \cdot year^{-1}$). These are the same age equations and decay constants provided on the NBL U630 certificate of analysis (NBL 2013) and which were used in determining the certified purification date of the material. The 'DATE' function in Microsoft Excel, which allows for the calculation of a specific calendar date in relation to an input date (e.g. the date of the $^{230}Th/^{234}U$ measurements conducted in this study) and numerical value in years (e.g. the 'age' calculated according to the aforementioned age equation), was then utilized to determine the model date relative to the actual analysis dates for the solution and laser ablation analytical sessions. On figure 2, the observed (on March 8, 2024) $^{230}Th/^{234}U$ ratios from the solution mode analyses are shown against the $^{230}Th/^{234}U$ ratio of the U630 and U850 (red lines) standards which were back-calculated for the March 8, 2024 solution mode analysis date. These back-calculations are based on the June 6, 1989 (± 190 days) purification date for CRM U630 indicated on this standard's certificate of analysis (NBL 2013), and Dec 31, 1957 (± 73 days) for CRM U850 which is the date purification was finished according to Williams and Gaffney (2011) and references therein. Note that the uncertainty of ± 73 days for U850 is based on the

303 expanded uncertain of ~0.2 years for the model date of U850 determined by Williams and Gaffney
304 (2011). It is also worth noting that the U850 standard does not have a 'certified' purification date and
305 that there may be some uncertainty in the purification history of this material. For example, Denton et
306 al. (2020) state that purification of U850 took place over an interval from December 3, 1957 to
307 December 31 1957 but also indicate that scant information about the actual purification process is
308 available. On figure 2, the 'average model dates' computed using only the $^{230}Th/^{234}U$ ratios from
309 analyses that had >0.1V ^{234}U result in a model dates of May 19, 1988 (± 351 days) for U630 and March
310 26, 1961 (± 2.5 years) for U850. Note that these uncertainties are the standard deviations associated
311 with the average dates reported at the 1σ level.

312 On figure 2, there are also a series of 'x' symbols juxtaposed against the black and gray circles
313 denoting the solution-mode $^{230}Th/^{234}U$ ratios. These 'x' symbols portray the $^{230}Th/^{234}U$ ratios (as
314 observed on March 8, 2024) adjusted based on a Th/U 'relative sensitivity factor' (RSF) designed to
315 account for the different ionization efficiency of Th and U. This RSF value was determined by analysis of
316 a series of solutions containing varying proportions of natural Th (presumably all ^{232}Th) and U (a mixture
317 of ^{234}U, ^{235}U, ^{236}U, and ^{238}U) produced by High Purity Standards, and then computing an average RSF.
318 The resulting Th/U RSF of 0.904 is broadly consistent with the RSF values documented in previous
319 studies utilizing other analytical methodologies. For exampleSzakal et al. document a long term average
320 Th/U RSF value of 0.673 for the SIMS technique, and Varga et al. 2024 documented Th/U RSF values
321 ranging from 0.7 to 1.3 for the LA-MC-ICP-MS technique. Application of the Th/U RSF of 0.904results in a
322 shift towards higher RSF corrected $^{230}Th/^{234}U$ compared to the as-measured values. In turn, these higher
323 $^{230}Th/^{234}U$ ratios result in older average model dates of August 5, 1984 (± 364 days) for U630 and July 28,
324 1954 (± 2.7 years) for U850. It is also worth noting that the uncertainty (represented here by the 1σ
325 standard deviation) associated with the older RSF corrected average model ages also increases
326 compared to the younger ages calculated without application of the U/Th RSF factor. The U and Th data

used to calculate the RSF factor for the solution mode analyses are provided in supplementary table 1 along with the $^{230}Th/^{234}U$ ratios and associated data. An important note is that future work will need to focus on the best approach to constrain the U/Th RSF factor. Ideally, a gravimetrically prepared solution that is independently calibrated for U and Th concentration and isotopic composition will be utilized for the RSF determination in contrast to the volumetric approach tested in this study.

For the LA analyses, the individual cycle's $^{230}Th/^{234}U$ (observed on March 6, 2024, which is the date when the LA session was conducted) is shown against that cycle's ^{234}U voltage for both the U630 and U850 standards in figure 3a – b. Similarly to the solution mode results in figure 2, the red-lines on figure 3 depict the $^{230}Th/^{234}U$ ratio of the U630 and U850 back-calculated to March 6, 2024 based on the purification dates provided on the certificate of analyses for these two standards. The average model dates depicted on figure 3a-b for the LA are only computed for analyses with greater than 0.1V of ^{234}U. The average model dates adjusted for the Th/U RSF factor determined during the solution mode analyses are also provided. For the U630 analyzed by LA, theaverage model dates of June 23, 2004 (± 8.7 years) and May 24, 2002 (± 9.6 years), with and without application of the U/Th RSF factor respectively, were obtained for the cycles exhibiting > 0.1V ^{234}U. For the U850 analyzed by LA, the average model dates of December 21, 1965 (± 7.9 years) and October 25, 1959 (± 8.7 years), with and without application of the U/Th RSF factor respectively, were obtained for the cycles exhibiting > 0.1V ^{234}U. The appropriateness of using an RSF value determined for solution mode analyses to correct LA based data will be discussed in the following section along with other issues affecting the data quality.

Issues affecting data quality and avenues for future investigation

While the observed $^{230}Th/^{234}U$ ratios from the NBL U630 and U850 produce model ages that are broadly coincidental with the certified purification dates of these standards, there are clearly some

limitations with regard the approach of using the direct observed $^{230}Th/^{234}U$ ratio to calculate a U-Th age. The first limitation is signal related and is evidenced by the trend towards increasing within-run uncertainty and degraded accuracy as the ^{230}Th and ^{234}U voltage decreases (Fig. 2-3) for both solution and LA-based sampling modalities. In the case of our study, we chose to exclude from consideration datapoints for which the ^{234}U was below 0.1V, but selecting this cutoff value was only made possible by the fact that we were able to compare the observed $^{230}Th/^{234}U$ with the calculated $^{230}Th/^{234}U$ of the standards on the analysis date as a function of the ^{234}U voltage. For a situation where an unknown material was being analyzed, it would be necessary to have some external constraints bearing on the appropriate low signal cutoff levels. These considerations would need to be session specific and tailored to the materials under scrutiny. For example, a uranium material with extreme ^{234}U enrichment but that underwent purification immediately prior to analysis (e.g. separation of U and Th) could have far less radiogenic ^{230}Th compared to an older material with lower ^{234}U enrichment. Therefore, the issue of how to select signal cutoff levels when dealing with materials of unknown provenance will need to be explored further in subsequent studies.

For the two standards analyzed in this study, it can be seen in figure 4a that there are two clearly distinguishable linear trends between the observed ^{234}U and ^{230}Th voltage for the various dilutions analyzed in solution mode (2.5 ppm down to 0.02 ppm). However, at lower concentrations it can be seen that the linear trends eventually merge, which could be used to pinpoint a signal level below which a meaningful $^{230}Th/^{234}U$ ratio would no longer be expected. However, such an approach would likely be instrument and detector specific and will require further assessment to determine its potential validity and/or usefulness. Examination of figure 4b, which depicts the within-run uncertainty (e.g. 'internal precision) on the $^{230}Th/^{234}U$ ratio versus the ^{234}U signal intensity for the solution mode measurements, reveals that there is a ^{234}U signal level below which the uncertainty dramatically increases. The relationship between the internal precision and signal level observable on figure 4b is

expected, and could theoretically also be utilized to determine a signal cutoff level below-which a ratio becomes un-usable. However, this would also require instrument (and likely session) specific considerations if the goal was to interpret the observed $^{230}Th/^{234}U$ from an unknown material.

Another major unknown is how to develop a raw data correction scheme to account for the different ionization efficiency of Th and U in both the solution- and LA-based sampling modes. This has been successfully achieved in other studies presenting U-Th model ages obtained by direct measurement of the $^{230}Th/^{234}U$ ratio (Szakal et al. 2019; Varga et al. 2024), and in theory, the development of this correction factor should be simpler in the case of an all faraday detector method because there is no longer the need to account for an inter-detector calibration. Our preliminary RSF value, which was obtained by analysis of a series of solutions containing known amounts of natural U and Th from High Purity Standards, results in ~9% shift in the $^{230}Th/^{234}U$ ratios towards more elevated values. For both the solution and LA analyses, the result of applying this RSF value is a shift towards older model ages. For the U850 standard, this pushes the observed ages closer to the known purification date whereas for the U630 standard, the resultant ages become erroneously old. Clearly more work is necessary to develop an appropriate RSF determination scheme in both the solution- and LA-based sampling scenarios. For example, it may be more productive to calculate a Th/U RSF value using a standard with a certified Th/U ratio rather than the approach taken in this study of assuming 'natural' U and Th isotopic abundances and relying on the correctness of the U and Th concentration in the High Purity Standards solutions used for the RSF determination. Ideally this RSF factor would be monitored regularly throughout an analytical session to account for changes in plasma conditions, mass bias regimes, and other factors that could cause drift in the ion beams.

Additional areas to focus future investigation include how to recognize and mitigate the possibility of isobaric interferences on the observed $^{230}Th/^{234}U$ ratios, which is an issue raised by previous studies seeking to produce $^{230}Th/^{234}U$ ages by direct measurement of enriched uranium

materials (Szakal et al. 2019; Varga et al. 2024). While the age determinations presented in this study are unlikely to be effected by isobaric interferences due to the fact that pure U CRM materials were utilized, previous studies on the Neoma MC-ICP-MS involving the analysis of U reference materials doped with varying metallic elements (Scott et al. 2024; Zirakparvar et al. 2024) have shown that major and unpredictable perturbations to the observed U isotopic compositions can sometimes occur. The preliminary results presented in this study will also need to be verified in a broader suite of uranium materials with varying enrichment levels and purification ages to establish the bounding conditions over which a direct measurement of the $^{230}Th/^{234}U$ ratio can yield meaningful results. Lastly, the preliminary laser ablation dataset collected in this study highlights the need for further investigation of the optimal conditions for laser sampling and data acquisition. This is especially true considering that the laser conditions utilized in this study often resulted in complete penetration of the cotton TexWipe and the generation of visible residue that was not carried into the mass spectrometer. Other areas of consideration pertain to the amplifier configuration. It is our opinion that a 10^{11} Ω amplifiers will not afford adequate sensitivity for the ^{230}Th detection whereas the expected signal for the ^{234}U, ^{235}U, ^{236}U, and ^{238}U in enriched uranium will typically be above the 0.5V maximum signal cutoff level for the 10^{13} Ω amplifiers. However, differences in the response time between the 10^{11} Ω and 10^{13} Ω amplifiers (Craig et al. 2019) may become an issue during laser ablation sampling due to the transient nature of the signal. This is especially true if spatially resolved analytical data is desired. While the laser ablation technique has been shown capable of producing accurate model ages for solid CRM materials in other studies (e.g.Varga et al. 2024), the ablation of cotton TexWipe material appears to pose an additional set of challenges that will require additional methodological development in order to improve the efficiency of direct analyses.

Conclusions

Direct measurement of the $^{230}Th/^{234}U$ ratio in the NBL U630 and U850 enriched uranium isotopic standards on the Neoma MC-ICP-MS in solution and by LA using an all-faraday detector configuration on the ThermoFisher Scientific Neoma MC-ICP-MS indicate the following:

1) Assuming an adequate signal intensity (in the case of this study, a cutoff value of 0.1V of ^{234}U is utilized), meaningful U-Th model dates can be calculated directly from the observed $^{230}Th/^{234}U$ ratio. The results from the solution mode analyses are more precise and accurate compared to the LA measurements, but the LA measurements still produce ages that could be used to differentiate between materials with old (e.g. >40 years) vs young (<10 years) purification dates.
2) An all-faraday detector configuration utilizing 10^{13} Ω amplifiers for the low abundance isotopes and 10^{11} Ω amplifiers for the more abundant isotopes appears to have both the sensitivity and dynamic range to obtain both the $^{230}Th/^{234}U$ age and the $^{234}U/^{238}U$, $^{235}U/^{238}U$, and $^{236}U/^{238}U$ isotope ratios during a single measurement.
3) Use of an all-faraday detector configuration circumvents the need for separate analysis of the U and Th fractions by isotope dilution, while also removing the need to perform an inter-detector calibration in situations where the U and Th are measured simultaneously (e.g. between ion counter and faraday type detectors).
4) While further work is necessary to evaluate the potential applicability of an all-faraday method, our initial results indicate that this method could certainly be useful as an initial screening tool and possibly as a means of obtaining robust $^{230}Th/^{234}U$ ages.

Supplementary Information

The raw data and processed MC-ICP-MS data collected as part of this study are contained in a Microsoft Excell workbook provided as an electronic supplement. The workbook contains four individual worksheets. The worksheet entitled 'SupplementaryTable1' provides a summary of the processed analytical data, whereas the remaining three worksheets contain the raw analytical data and calculations specific to each of the three analytical sessions described in the text.

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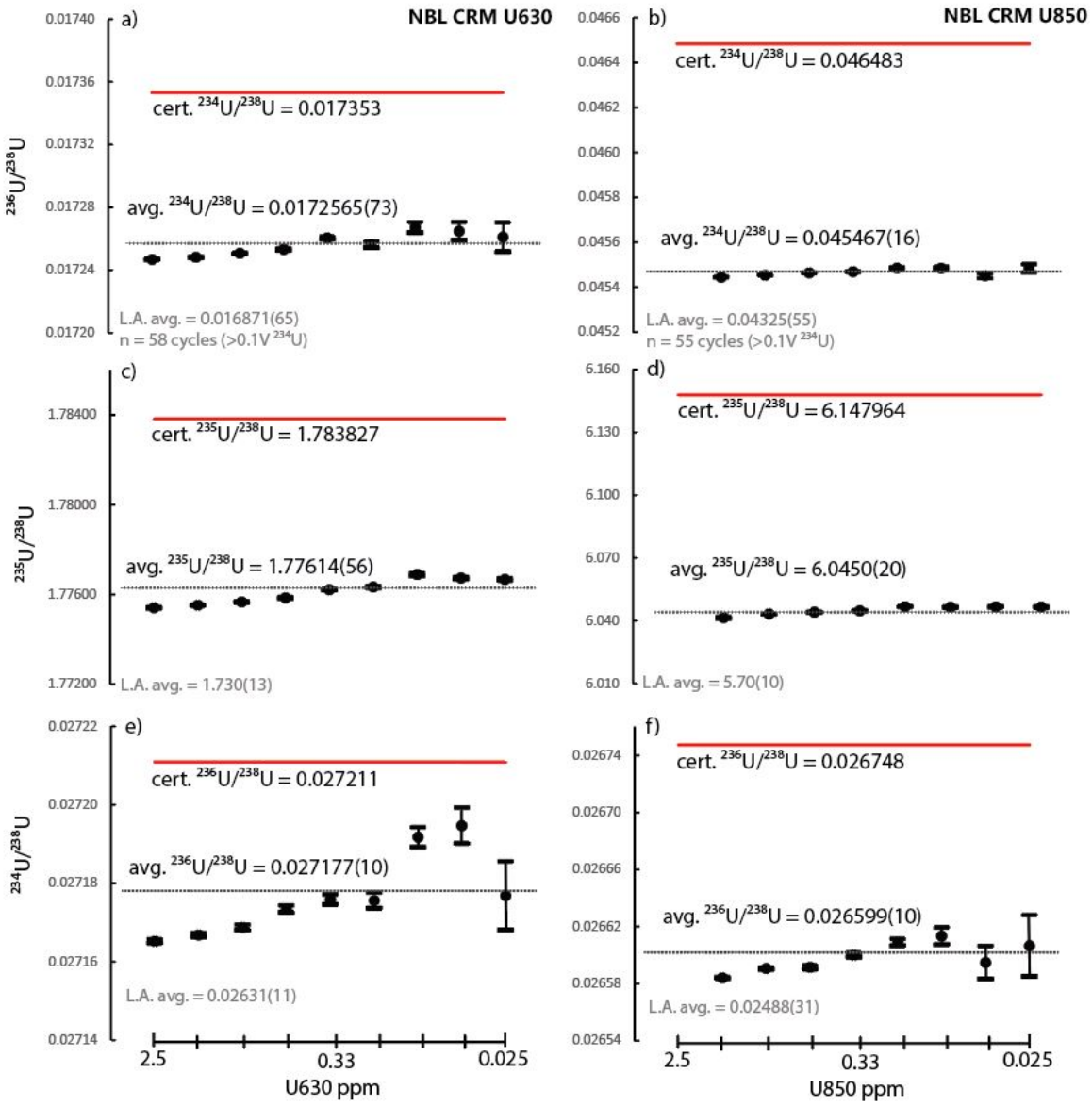
Figures and Captions:



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550 **Figure 1.** Plots of the $^{234}U/^{238}U$ (a-b), $^{235}U/^{238}U$ (c-d), and $^{236}U/^{238}U$ (e-f) for the solution mode analyses
551 conducted on the various dilutions (2.5 ppm down to 0.02 ppm) of the NBL U630 (left-hand panels) and
552 U850 (right-hand panels) standards. The individual analyses and population averages, which are
553 denoted with their within-run 1σ standard errors and standard deviations respectively, are shown
554 relative to the 'certified' isotope ratios that were calculated from the atom percentages for the various
555 isotopes reported on the certificate of analyses for the U630 and U850 standards. At the bottom of
556 each panel the results obtained by laser ablation (LA) sampling, depicted as the average isotope ratio for
557 cycles where the ^{234}U voltage exceeded 0.1V, are provided for comparison with the solution values.

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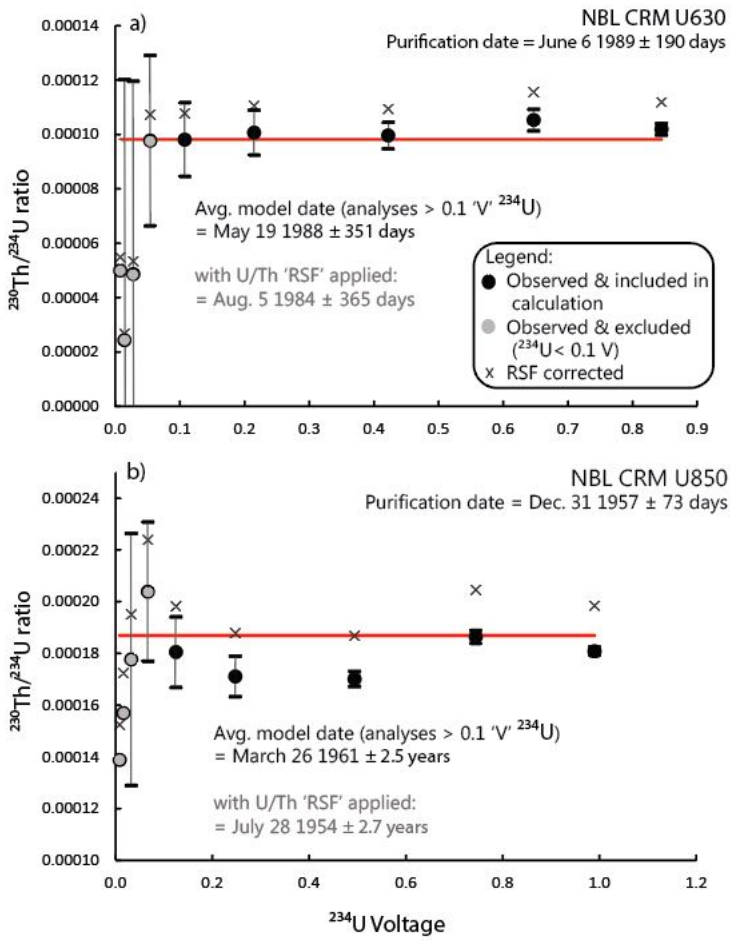

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560 **Figure 2.** Plots of the $^{230}Th/^{234}U$ ratio versus each analyses average ^{234}U voltage for the NBL U630 (figure
561 2a) and U850 (figure 2b) standards measured in solution mode on the Neoma MC-ICP-MS. The error
562 bars correspond to the within-run standard error of the mean (shown at the 1σ level) for each analysis
563 (not provided for the 'RSF' corrected values which are denoted using the 'x' symbols). For the analyses
564 at the lower end of the range of ^{234}U voltages, the error bars are not always shown due to the extremely
565 high within-run uncertainty. It is also important to note that the gray dots (at low ^{234}U voltages) were
566 not included with computing the average model date and uncertainty (1σ standard deviation) provided
567 on the figure. The red line corresponds to the certified purification date of the NBL U630 standard (NBL
568 2013) on figure 2a and the reported purification date for the U850 standard (Williams et al. 2011) on
569 figure 2b. Note that the $^{230}Th/^{234}U$ ratios shown on the y-axis are as measured on March 8 2024 (the
570 'true' values of the NBL U630 and U850 are also calculated for this date).

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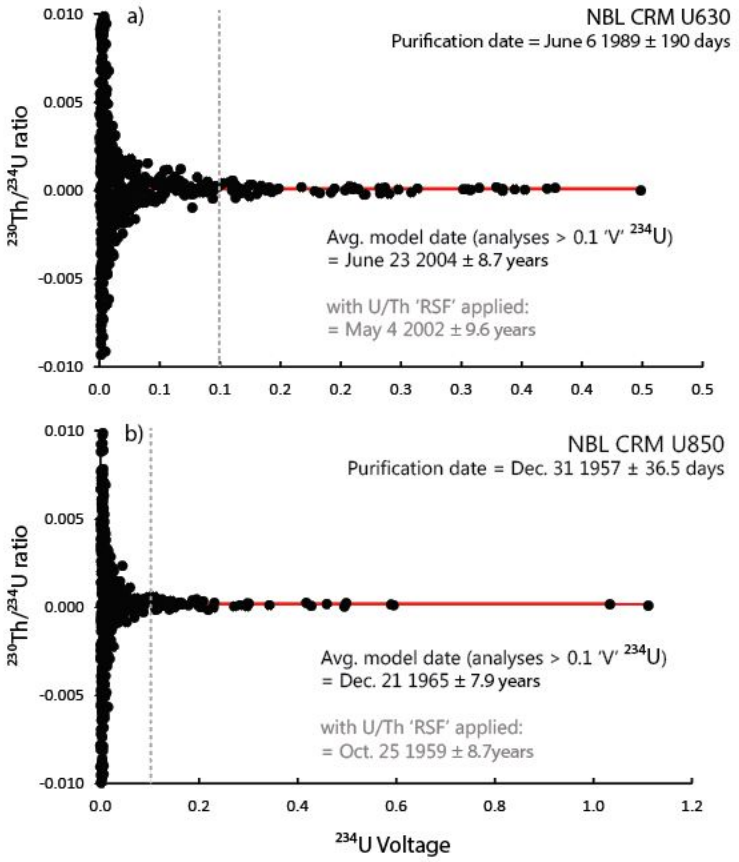
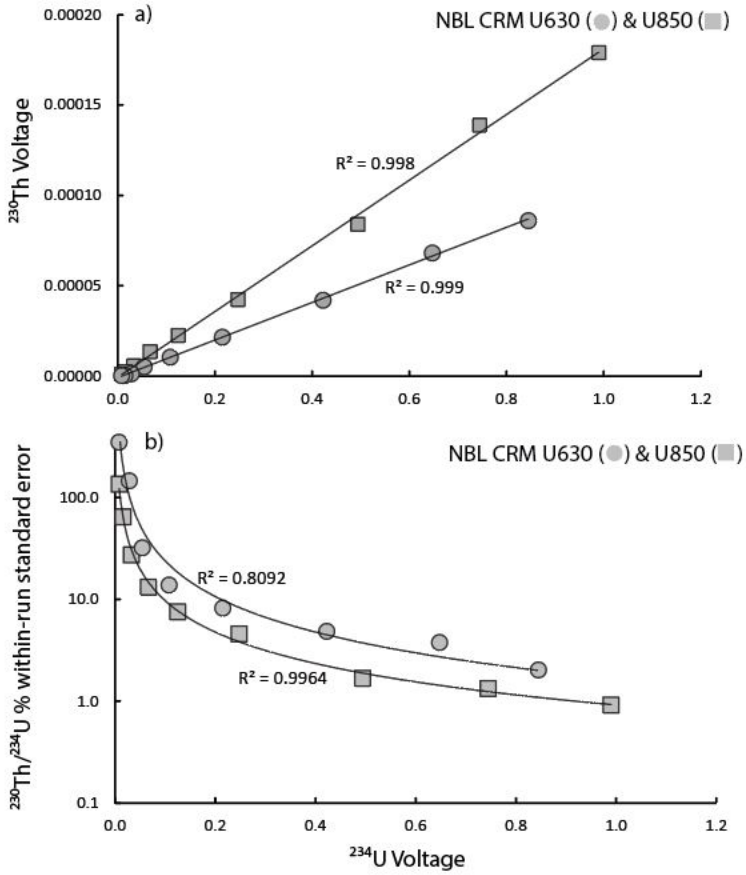


Figure 3. Plots of the observed (on March 6 2024) $^{230}Th/^{234}U$ ratio versus the ^{234}U voltage for each cycle of data collected by laser ablation based sampling of the TexWipe material doped with the NBL U630 (figure 3a) and U850 (figure 3b standards). The average model dates shown on the figures were computed by averaging the $^{230}Th/^{234}U$ for data points with greater than 0.1V of ^{234}U (the signal cutoff level determined by examination of the solution dataset).



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586 **Figure 4.** Plots of the observed ^{230}Th voltage (4a) and within-run standard error of the mean on the
587 ^{230}Th/^{234}U ratio expressed in percent and shown at the 1σ level (4b) for each analysis versus that
588 analyse's average ^{234}U voltage for the solution measurements conducted on the Neoma MC-ICP-MS for
589 the NBL U630 and U850 standards. Note that different symbols are utilized for the analyses conducted
590 on the two different NBL standards.

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Cup Configuration (Solution and Laser Ablation Sampling):	
L3 ($10^{13}\Omega$) = ^{230}Th; L2 ($10^{13}\Omega$) = ^{231}Pa; L1 ($10^{13}\Omega$)= ^{232}Th; Center Cup ($10^{11}\Omega$) = ^{234}U; H1 ($10^{11}\Omega$) = ^{235}U; H2 ($10^{11}\Omega$) = ^{236}U; H3 ($10^{11}\Omega$) = ^{238}U; H4 ($10^{11}\Omega$) = $^{238}U^{1}H$	
Solution Measurement Session:	
Materials analyzed	NBL U630 and U850; HPS natural U and Th
Neoma MC-ICP-MS conditions (Standard Introduction System)	
Nebulizer gas (Ar):	1.01 L/min
Cooling gas (Ar):	13 L/min
Auxiliary gas (Ar):	0.76 L/min
Plasma power:	1199 W
Data Acquisition Parameters:	
Integration time	4 second/cycle
Cycles per analysis	20
Laser Ablation Session:	
Materials Analyzed:	NBL U630 and U850 doped on TexWipe 304
Neoma MC-ICP-MS conditions (standard introduction system)	
Nebulizer gas (Ar):	0.9 L/min
Cooling gas (Ar):	13 L/min
Auxiliary gas (Ar):	0.76 L/min
Plasma power:	1199 W
Elemental Scientific NWR 193 laser ablation system:	
Carrier gas flow (He):	0.5 L/min
Spot size and rep rate:	50 µm @ 100 Hz
Laser Power:	5.952 J/cm^2 @ surface
Data Acquisition Parameters:	
Integration time	1 second/cycle
Total cycles	1,000 on each doped cloth

Table 1. Summary of analytical conditions utilized for the solution and laser-ablation based sampling on the Neoma MC-ICP-MS. Additional details are provided in the analytical methods section of the main text.