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Developing Radium-226 and Actinium-227 Age-Dating Techniques for Nuclear Forensics to Gain Insight From Concordant and Non-Concordant Radiochronometers

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radiochemistry, age-dating, radium, actinium, uranium, nuclear forensics

Abstract

The model age or 'date of purification' of a nuclear material is an important nuclear forensic signature. In this study, chemical separation and MC-ICP-MS measurement techniques were developed for radium-226 and actinium-227: grand-daughter nuclides in the uranium-238 and uranium-235 decay chains respectively. The ^{230}Th-^{234}U, ^{226}Ra-^{238}U, ^{231}Pa-^{235}U, and ^{227}Ac-^{235}U radiochronometers were used to calculate model ages for CRM-U100 standard reference material and two highly-enriched pieces of uranium metal from the International Technical Working Group Round Robin 3 Exercise. Results demonstrate the accuracy of the ^{226}Ra-^{238}U and ^{227}Ac-^{235}U chronometers and provide information about nuclide migration during uranium processing.

Introduction

Nuclear forensic science uses the analysis of nuclear or other radioactive material to reveal information that may provide evidence for nuclear attribution [1-2]. Because radioactive materials undergo the fundamental process of radioactive decay, paired parent-daughter decay nuclides provide radiochronometers that can be used to determine the model-ages or purification dates of nuclear materials [3-8]. The most commonly used radiochronometer for uranium material is the ^{230}Th-^{234}U chronometer because easily measured quantities of $^{230\mathrm{Th}}$ are produced by ^{234}U decay in a short time [7]. The application of radiochronometers relies on fundamental assumptions that: 1) all daughter nuclides are removed resulting in complete purification of the parent nuclide at the time when the material is produced, time = 0; and 2) the material remains a closed system after production where nuclides are neither added nor removed. While these conditions are often met, there have been multiple examples where daughter nuclides are not completely purified during production [6, 8] or where different chronometers, such as ^{230}Th-^{234}U and ^{231}Pa-^{235}U, yield different or 'non-concordant' ages [9, 10].

While non-concordant ages result in difficulty interpreting the model age of a nuclear material, it is important to note that non-concordant ages do not imply that age determination is incorrect. Assuming that analyses were made accurately, different ages from two chronometers may imply that the assumed conditions for determining an age were not met. For example, if thorium-230 was efficiently purified from a uranium material at the time of production, but protactinium-231 was not, the model age determined using the ^{231}Pa-^{235}U chronometer would be anomalously older than the ^{230}Th-^{234}U model age and the actual production age of the material. Such was the case for model ages of highly-enriched uranium (HEU) metal determined by one laboratory for the International Technical Working Group Round Robin 3 Exercise in 2010 [9].

Sturm et al. recently suggested that considering more than one plutonium radiochronometer allowed for additional information about plutonium material to be gained during forensic investigations and prevented erroneous conclusions from being drawn by using only chronometer [10]. In this work, we apply the same concept to uranium materials and suggest that the measurement of multiple chronometers guides more accurate model age interpretations and also adds to our knowledge of radionuclide migration during the production of uranium materials. For this purpose, we have developed methods to purify ^{226}Ra and ^{227}Ac from uranium matrices and measure concentrations by MC-ICP-MS using isotope dilution in order to combine the ^{226}Ra-^{238}U and ^{227}Ac-^{235}U chronometers with other existing radiochronometers. This study comprehensively uses chronometers in the ^{238}U decay chain (^{230}Th-^{234}U, ^{226}Ra-^{238}U) and ^{235}U decay chain (^{231}Pa-^{235}U, ^{227}Ac-^{235}U).

Experimental

Material investigated was carefully chosen to validate methods developed for ^{226}Ra and ^{227}Ac measurement by MC-ICP-MS and to investigate the behavior of grand-daughter nuclides in uranium metal with a known processing history. The uranium standard CRM-U100 was purified on January 8, 1959 [11], and certified for uranium isotopic composition in 1971 [12]. With a known purification date, CRM-U100 can be used to validate model ages calculated using ^{226}Ra-^{238}U and ^{227}Ac-^{235}U in nuclear era uranium materials. Concordant model-ages between the

^{230}Th-^{234}U, ^{226}Ra-^{238}U, and ^{227}Ac-^{235}U chronometers are expected if the radiochronometry assumptions discussed above are met. A second material used for validation purposes is Table Mountain Latite (TML) - a Pliocene basalt from Sonora, California that has been distributed as a geologic rock standard for uranium-series analyses due to its high concentration of these elements (U ~ 10 ppm, Th ~ 30 ppm) [13-14]. This basalt is particularly useful because the Pliocene age of TML (> 2.6 million years old) ensures that secular equilibrium between ^{238}U-^{234}U ^{230}Th-^{226}Ra has been established. In secular equilibrium, $N_1\lambda_1= N_2\lambda_2$, where N_1 = number of atoms of the parent isotope and N_2 = number of atoms of the daughter isotope and λ_1 and λ_2 are the decay constants for the parent and daughter isotope. The presumption of secular equilibrium for TML enables a test of the accuracy of our ^{226}Ra concentration measurements. Four ores certified for ^{226}Ra activity by CANMET (Natural Resources Canada; DH-1a, BL4a, UTS-1, UTS-4) were analyzed as an additional accuracy test of ^{226}Ra measurements.

In addition to validation materials, uranium metals 'A' and "B' from the ITWG RR3 Exercise were analyzed, referred to here as samples ITWR-RR3-A and ITWG-RR3-B respectively. These metals were cast from two separate batches of HEU scrap material, at the same facility (Y-12 USA), under identical process conditions [9]. They were cuts from two hollow metal logs with slightly different uranium isotope compositions. Results from the round robin exercise showed non-condordant ages between the ^{230}Th-^{234}U and ^{231}Pa-^{235}U chronometers. The ^{230}Th-^{234}U model ages measured corresponded well to the metal casting ages while ^{231}Pa-^{235}U model ages were much older [9].

Enriched Spike Preparation for Isotope Dilution Analyses

An enriched-^{228}Ra spike was used for isotope dilution Ra concentration measurements. This spike was produced by milking Ra from a Th solution containing 3.25g of Th, prepared from Th-metal (Ames Laboratory). Complete separation of Ra from the Th-metal solution was accomplished through sorption of Th in 8 M HNO_3 to anion exchange columns (BioRad AG1-X8) with varying resin volumes (2-10ml). Radium was eluted (no sorption in 8 M HNO_3), and Th was then washed from the column with 0.1M HCl and stored. The process was repeated until the thorium concentration in the radium fraction was below ion-counting MC-ICP-MS detection limits (≤ 2 fg/mL in the test solution). The spike Ra concentration was calibrated by isotope dilution using the NIST SRM4967A ^{226}Ra standard.

The methods for isotope dilution measurement of ^{227}Ac developed here use a ^{229}Th standard to provide ^{225}Ac, which is used as the spike. Thorium-229 decays by alpha decay to ^{225}Ra ($t_{1/2}$ = 14.9 days) followed by beta decay to ^{225}Ac ($t_{1/2}$ = 10 days). If a solution of ^{229}Th is older than 3 months, secular equilibrium exists between the grand-daughter ^{225}Ac and parent ^{229}Th. The concentration of ^{225}Ac atoms in the solution can, therefore, be calculated using the half-lives of ^{229}Th and ^{225}Ac and the concentration of ^{229}Th. A ^{229}Th spike solution was prepared at a concentration appropriate for ^{225}Ac isotope dilution analyses, and calibrated by crossing with five aliquots of a Th standard prepared from Ames Th metal. This spike solution has a concentration of 4.542(14) x 10^{13} atoms ^{229}Th/g.

A ^{233}Pa spike was prepared for ^{231}Pa analyses following the methods of [8]. The spike was calibrated using multiple aliquot mixtures of ^{233}Pa spike and TML solution. Two separate chemical purification procedures [8 and 15] were used to purify and calibrate this spike, and the concentrations determined from the ^{233}Pa-TML mixtures using both methods were in agreement.

Sample Preparation and Purification

Sample solutions were prepared from powders or small metal pieces by acid dissolution. The uranium oxide (U_3O_8) standard, CRM-U100, was dissolved in 8M HNO_3 in quartz tubes on a hotplate at 125°C in two separate aliquots: U100A and U100B (ca. 0.1g and 0.07g of CRM-U100, respectively). Pieces of ITWG-RR3-A and ITWG-RR3-B were dissolved individually in concentrated HNO_3, directly in PFA vials. CRM-U100 aliquots were transferred to 30 mL PFA vials and all samples were diluted with Milli-Q H_2O to create 2M - 4M HNO_3 stock solutions. Concentrated HF was added to make the solutions 0.05M HF. Powdered TML and ores from CANMET were digested in a Milestone Ethos EZ microwave digestion unit using a 8:2 solution of concentrated HNO_3:HF. Fluorides created during digestion were decomposed with $HClO_4$ and H_3BO_3 hotplate evaporation steps, and a final stock sample solution was prepared with 2.5M HCl + 0.01M HF.

Five separate aliquots of all sample solutions (U100A, U100B, ITWG-RR3-A, ITWG-RR3-B, TML*, and CANMET ores*) were taken from the prepared stock solutions and spiked with appropriate amounts of ^{228}Ra, ^{229}Th (for ^{225}Ac), ^{229}Th (for ^{230}Th), ^{233}Pa and ^{233}U for isotope dilution analysis (*^{227}Ac not measured in TMl and ores).

Aliquots for ^{227}Ac measurement were spiked with 1.5mL of ^{229}Th spike providing approximately 100 femtograms of ^{225}Ac in secular equilibrium with ^{229}Th.

Radium was separated and purified from the bulk uranium and rock matrices by ion-exchange column chromatography developed and modified from methods used by previous studies [16-18]. The column purification procedures chosen were based on sample matrix and varied for nearly pure uranium oxide (CRM-U100), uranium metal (ITWG samples) and geologic matrices (TML and CANMET ores). Radium from U100 was separated from uranium and thorium using two Eichrom UTEVA resin beds (1.8ml followed by 0.6mL). Samples were loaded onto and eluted from the resin in 3M HNO_3. Radium was then purified from any Ba impurities using a 1ml resin bed of Eichrom Sr-Spec resin and 3M HNO_3. The purification of Ra from ITWG-RR3-A and B used the same UTEVA and Eichrom Sr-Spec resin steps described above but included an additional initial purification step on BioRad cation resin (AG50W-X8) to remove trace contaminants from the metal. The sample was loaded in 1M HCl and washed with progressively more concentrated HCl in 1M steps from 1M to 4M HCl to remove major cationic species (Ca, Na, Mg etc.). Radium remains on the column and is eluted in 6M HCl.

Separation of Ra from a rock matrix such as TML or ore material requires a more complex purification procedure than the Ra separation procedure from uranium materials. In this case, the sample is loaded onto a large 10mL BioRad AG50W-X8 cation resin bed. Following the washing procedure above, radium is eluted with the rare earth elements in 6M HCl. After this separation, the sample was dried, reconstituted in 1M HCl, and loaded onto a 1mL BioRad AG50W-X8 resin bed for a second purification of cationic species. The eluted fraction is dried and re-dissolved in 7M HNO_3 for separation from the rare earth elements using a 1mL Eichrom TRU resin bed. The sample was then dried again, and Ra was separated from Ba through a 1mL Sr-Spec column (same procedure used above for U100). Prior to analysis, all samples were purified again using a small 0.25mL BioRad AG50W-X8 cation resin clean-up column to remove ^{228}Th that is generated from ^{228}Ra by beta-decay ($t_{1/2} = 5.75$ years). This final purification is always conducted no more than 1 day prior to measurement of the sample by mass spectrometry.

Actinium is purified from a bulk uranium matrix through a three-stage column process. First, Th is separated from the matrix using a 2mL anion (BioRad AG-1-X8) resin bed. The sample is loaded in 8M HNO_3, Ac is eluted directly, and Th is left behind sorbed to the resin. The Ac fraction is dried, dried again in concentrated HCl, and then dissolved in 9M HCl. The sample is then loaded on a 9M HCl pre-conditioned stacked column arrangement with a 1mL anion (AG-1-X8) column stacked above a 1ml Eichrom DGA resin column. In this arrangement, U is sorbed to the upper column, Ac is sorbed to the lower DGA column, and a complete purification of ^{225}Ra is achieved through washing with 9M HCl. The upper anion column is removed, and Ac is eluted using 0.5M HCl. It is essential to note that the exact time when samples are loaded onto each column must be recorded during the purification of Ac. Both the parent ^{229}Th and intermediate nuclide ^{225}Ra affect the concentration of ^{225}Ac in the sample during purification. The timing of the separation of these nuclides is, therefore, required for decay corrections explained below for the calculation of ^{227}Ac concentration.

Uranium and thorium purification methods are described in [6]. Protactinium purification from bulk uranium followed procedures presented in [8]. Following purification samples are brought up in 2% HNO_3 for U and Ra analysis and 2% HNO_3 + 0.05M HF for Th, Pa, and Ac analysis by MC-ICP-MS.

Multi-Collector Inductively Coupled Plasma Mass Spectrometry

Purified U, Th, Pa, Ra, and Ac fractions were analyzed using a Nu Plasma HR MC-ICP-MS at LLNL. Samples were introduced in 2% HNO_3 or 2% HNO_3 + HF solutions accordingly. U, Th, and Pa measurements were made according to methods described by [6] and [8]. Static multi-collection routines were written to measure ^{226}Ra and ^{228}Ra simultaneously for Ra and ^{225}Ac and ^{227}Ac simultaneously for Ac on two ion counters (IC0 and IC1). Corrections to the ^{226}Ra/^{228}Ra and ^{225}Ac/^{227}Ac ratios were made using mass bias and relative ion counter efficiency factors calculated from U analyses of the NBL uranium standard U010, which assumes that the instrumental mass bias correction derived from uranium is appropriate for Ra and Ac measurements. NBL uranium standard U005A was analyzed as an unknown for quality control of the uranium mass bias corrections and the cross-calibration of the ion counters. For both Ra and Ac, data for each sample were collected in one 40-cycle block with a 15 second on-peak integration time for each cycle. All sample signals were corrected for detector baselines measured before analysis at ± half-mass.

Model Age Determination

Model ages reported here were calculated from the measured ^{226}Ra and ^{227}Ac sample concentrations. Full solutions of the Bateman (U-series decay) equations [19-20] were used in a computer program to model ^{226}Ra as well as ^{227}Ac ingrowth from initial ^{238}U, ^{234}U, and ^{235}U concentrations measured directly from the U fractions of samples (following similar procedures as [6]). This method requires the assumption that at the time of purification, purification was complete and no daughter nuclides of Th, Ra, Pa, or Ac from the decay of uranium were present. The modeled time of ingrowth necessary to produce the measured ^{226}Ra and ^{227}Ac concentrations in the sample is the "model age" of the sample and corresponds to the time that passed between purification of uranium and the time of ^{226}Ra or ^{227}Ac separation and measurement. We report model dates, which correspond to a reference date minus the model age of the sample and, therefore, define the date on which the uranium-bearing sample was originally purified of uranium daughter nuclides, provided that the assumptions of complete purification and subsequent closed-system behavior of the material are met.

Reference dates are determined differently for each chronometer. Because the enriched ^{228}Ra spike is continuously decaying (^{228}Ra $t_{1/2}$ = 5.75 years), measured ^{226}Ra/^{228}Ra ratios are decay-corrected from the measurement date back to the date of calibration of the ^{228}Ra spike using the following equation:

$$\frac{\mathrm{Ra}^{226}}{\mathrm{Ra}^{228}}_{decay\ corrected} = \frac{\mathrm{Ra}^{226}}{\mathrm{Ra}^{228}}_{measured} \left(\frac{e^{-\lambda^{226Ra}t}}{e^{-\lambda^{228Ra}t}}\right) \tag{1}$$

where t = time between measurement and calibration date. Therefore, model age calculations for Ra use the ^{228}Ra spike calibration date (for this study 26-Apr-13) as the reference date.

Concentrations of ^{227}Ac are determined from a known concentration of ^{225}Ac atoms added to the sample from the ^{229}Th spike with ^{225}Ac in secular equilibrium and the measured ^{225}Ac/^{227}Ac ratio of the sample. However, ^{225}Ac is not the direct daughter of ^{229}Th. As described above, ^{229}Th decays first to ^{225}Ra ($t_{1/2}$ = 14.5 days), and then ^{225}Ra decays to ^{225}Ac ($t_{1/2}$ = 10 days). This results in complex behavior of ^{225}Ac during chemical purification of Ac from a U matrix (shown by curve in **Figure 1**). Initially, ^{225}Ac atoms represent the concentration predicted from secular equilibrium with ^{229}Th. After the first column purification, ^{229}Th is removed, and ^{225}Ac begins to decay but remains partially supported by decay from ^{225}Ra remaining in the sample:

$$\mathrm{Ac}^{225}_{column\ 2} = \frac{\lambda^{225Ra}}{(\lambda^{225Ac} - \lambda^{225Ra})} \times \mathrm{Ra}^{225}_{\sec eq}\left(e^{-\lambda^{225Ra}t_1} - e^{-\lambda^{225Ac}t_1}\right) + \mathrm{Ac}^{225}_{\sec eq}\left(e^{-\lambda^{225Ac}t_1}\right) \tag{2}$$

where t_1 = hours between column 1 (Th purification) and column 2 (Ra purification). In the second column purification, ^{225}Ra is removed from the sample solution leaving ^{225}Ac unsupported. The ^{225}Ac in the sample then decays following simple decay until the time of measurement:

$$\mathrm{Ac}^{225}_{measurement} = \mathrm{Ac}^{225}_{column\ 2}\left(e^{-\lambda^{225Ac}t_2}\right) \tag{3}$$

where t_2 = hours between column 2 (Ra purification) and the time of measurement. Using these decay relationships and the timing of purification, the ^{225}Ac atoms at the time of measurement can be calculated. Model age calculations for Ac, are calculated using a reference date that corresponds to the time of measurement. Model ages for the ^{230}Th-^{234}U and ^{231}Pa-^{235}U chronometers were calculated according to [6] and [8] respectively.

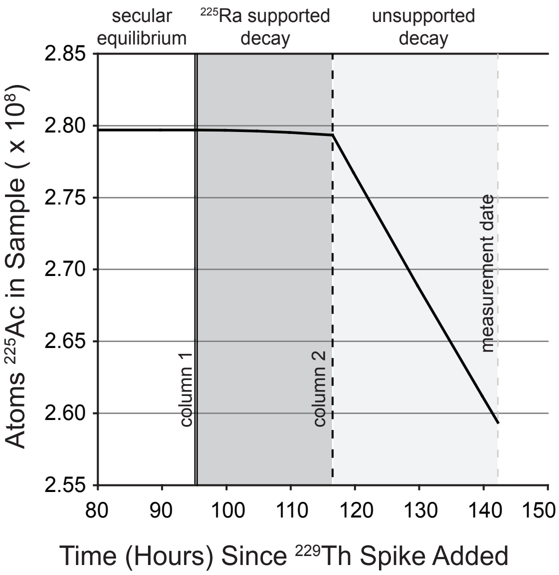

Figure 1. ^{225}Ac decay from secular equilibrium during chemical purification. At the time of column 1 (black vertical line), ^{229}Th is purified and ^{225}Ac and ^{225}Ra concentrations start to decrease. ^{225}Ac is supported by ^{225}Ra decay until column 2 (black dashed line). At this time, ^{225}Ra is purified and ^{225}Ac decays unsupported until the time of measurement (grey vertical dashed line).

Results and Discussion

Concentrations of all measured actinides (^{238}U, ^{235}U, ^{234}U, ^{230}Th, ^{231}Pa, ^{226}Ra, and ^{227}Ac) for samples U100A, U100B, ITWG-RR3-A, ITWG-RR3-B as well as a laboratory blank are reported in **Table 1**. Uncertainties reported represent a coverage factor of 2, (k-2) and propagate all known influence factors with the measurement with the exception of the errors associated with the decay constants of ^{226}Ra, ^{228}Ra, ^{225}Ac, and ^{227}Ac. Uncertainty derived from these decay constants represents less than 0.01% of the total uncertainty. Verification ^{226}Ra concentrations for TML and CANMET ores are provided as Supplemental Information. TML ^{226}Ra concentrations agree with those predicted by secular equilibrium, and measured ^{226}Ra concentrations for CANMET ores agree with certified ^{226}Ra activities.

Concentrations from **Table 1** are used calculate model ages for all of the sample materials shown in **Table 2**. Calculated model ages are subtracted from the appropriate reference dates for each chronometer to provide a model

Table 1 Actinide Concentrations of CRM-U100, ITWG-RR3-A and ITWG RR3-B Primary Solutions

Sample	U100-1	U100-2	ITWG-RR3-A	ITWG-RR3-B	Blank
^{238}U	7.578(16) x 10^{18}	6.551(14) x 10^{18}	9.394(16) x 10^{18}	5.947(25) x 10^{18}	1.71(88) x 10^{8}
^{235}U	8.609(21) x 10^{17}	7.440(18) x 10^{17}	1.2081(29) x 10^{20}	9.811(35) x 10^{19}	4.54(15) x 10^{9}
^{234}U	5.725(21) x 10^{15}	4.942(18) x 10^{15}	1.2905(33) x 10^{18}	1.0584(40) x 10^{18}	2.024(39) x 10^{11}
^{230}Th	9.182(46) x 10^{11}	7.942(40) x 10^{11}	3.444(17) x 10^{13}	3.928(19) x 10^{13}	6.65(75) x 10^{8}
^{231}Pa	4.69(11) x 10^{10}	4.043(94) x 10^{10}	3.631(82) x 10^{12}	4.75(11) x 10^{12}	7.2(57) x 10^{6}
^{226}Ra	2.214(66) x 10^{8}	1.905(58) x 10^{8}	1.872(41) x 10^{9}	2.031(44) x 10^{9}	8.7(99) x 10^{6}
^{227}Ac	1.619(40) x 10^{7}	1.410(38) x 10^{7}	6.08(10) x 10^{8}	7.60(12) x 10^{8}	ND*

* not detectable, ^{a} uncertainties represent expanded uncertainty (k=2), ^{b} concentrations reported in atoms per gram of primary solution.

date for the purification of each sample. These model dates as well as the known dates of purification, or the "paper age" of the samples are summarized in **Table 2**.

Table 2 Calculated Model Ages of CRM-U100 [11], ITWG-RR3-A and ITWG RR3-B [9]

Sample	Chronometer	Reference Date	Model Age (Years)	Uncertainty (Years, k=2)	Model Date	Uncertainty (Days, k=2)	Paper Age [9,11]
U100-1	^{230}Th-^{234}U	20-Feb-15	56.76	0.37	18-May-58	135	8-Jan-59
U100-2	^{230}Th-^{234}U	20-Feb-15	56.87	0.37	10-Apr-58	135	8-Jan-59
U100-1	^{226}Ra-^{238}U	26-Apr-13	54.89	0.81	5-Jun-58	296	8-Jan-59
U100-2	^{226}Ra-^{238}U	26-Apr-13	54.79	0.84	11-Jul-58	307	8-Jan-59
U100-1	^{231}Pa-^{235}U	3-Oct-14	55.3	1.3	11-Jun-59	469	8-Jan-59
U100-2	^{231}Pa-^{235}U	3-Oct-14	55.2	1.3	17-Jul-59	472	8-Jan-59
U100-1	^{227}Ac-^{235}U	8-Jan-15	54.64	0.85	12-Jul-60	310	8-Jan-59
U100-2	^{227}Ac-^{235}U	8-Jan-15	54.90	0.94	8-Apr-60	343	8-Jan-59
ITWG-RR3-A	^{230}Th-^{234}U	20-Feb-15	11.51	0.07	17-Aug-03	26	22-May-03
ITWG-RR3-B	^{230}Th-^{234}U	20-Feb-15	10.77	0.07	14-May-04	24	14-Jan-04
ITWG-RR3-A	^{226}Ra-^{238}U	26-Apr-13	11.70	0.13	13-Aug-01	47	22-May-03
ITWG-RR3-B	^{226}Ra-^{238}U	26-Apr-13	11.04	0.12	11-Apr-02	44	14-Jan-04
ITWG-RR3-A	^{231}Pa-^{235}U	27-Mar-15	37.59	0.85	21-Aug-77	312	22-May-03
ITWG-RR3-B	^{231}Pa-^{235}U	27-Mar-15	39.91	0.92	27-Apr-75	335	14-Jan-04
ITWG-RR3-A	^{227}Ac-^{235}U	8-Jan-15	28.00	0.28	8-Jan-87	95	22-May-03
ITWG-RR3-B	^{227}Ac-^{235}U	8-Jan-15	28.23	0.27	15-Oct-86	99	14-Jan-04
ITWG-RR3-A	^{227}Ac-^{235}U$_{corr}$*	8-Jan-15	11.16	0.19	10-Nov-03	69	22-May-03
ITWG-RR3-B	^{227}Ac-^{235}U$_{corr}$	8-Jan-15	10.37	0.17	25-Aug-04	62	14-Jan-04

*the ^{227}Ac-^{235}U$_{corr}$ chronometer provides a corrected model age calculated assuming an initial ^{231}Pa excess of 2.360 x 10^{12} and 3.182 x 10^{12} for samples ITWG-RR3-A and ITWG-RR3-B respectively. This excess represents the initial ^{231}Pa necessary to result in a ^{231}Pa-^{235}U model age that matches the paper age for the materials.

U100: Validation of Methods

The model dates calculated for two separate aliquots of U100A and U100B are nearly concordant within uncertainty for all chronometers used in this study: ^{230}Th-^{234}U, ^{226}Ra-^{238}U, ^{231}Pa-^{235}U, and ^{227}Ac-^{235}U (**Table 2**, **Figure 2**) (minor discordance between ^{230}Th-^{234}U and ^{227}Ac-^{235}U). However the model dates vary slightly between chronometers. The calculated purification dates from the ^{230}Th-^{234}U chronometer of May 18, 1958 for U100A and April 10, 1958 for U100B are approximately 9 months older than the paper age of the material [11] (**Figure 2**). This new model-date is

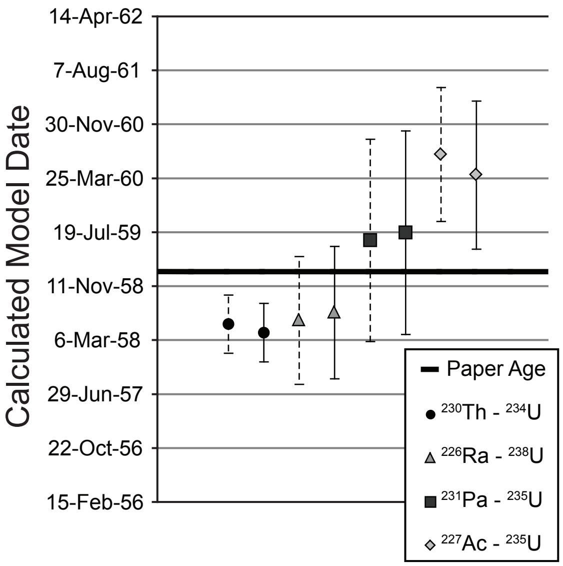

Figure 2. Calculated model ages for U100A (symbols with dashed error bars) and U100B (symbols with solid error bars. Model ages show relative concordance between chronometers – with only minor discordance between ^{230}Th-^{234}U and ^{227}Ac-^{235}U. Chronometers results in ages that agree will with the paper production ages of CRM-U100 [11].

earlier than the date published for U100 in [6]. This could suggest that uranium purification in January of 1959 was not complete, and that a small amount of ^{230}Th remained in U100 at the time of purification. Model ages for U100A and B calculated from the ^{226}Ra-^{238}U and ^{227}Ac-^{235}U chronometers agree within uncertainty of the paper age of January 8, 1959 (**Figure 2**). These results demonstrate the accuracy (approximately 10 months for a material from 1959) and precision of the ^{226}Ra-^{238}U chronometer developed here for the age-dating of nuclear materials. The ^{227}Ac-^{235}U system provides model dates for U100A and B of July 12, 1960 and April 8, 1960 respectively, which are 15-18 months younger than the known purification date of CRM-U100, though these ages are within uncertainty of ages from the ^{226}Ra-^{238}U and ^{231}Pa-^{235}U chronometers (**Figure 2**). A systematic bias between the ^{238}U and ^{235}U decay-series chronometers is suggested, but there are too few results at the present time to be certain of this. Model ages from ^{227}Ac-^{235}U, despite being slightly younger than the paper age, are relatively accurate given the small quantity of material available for measurement (femtograms of ^{227}Ac). Used together, these model ages represent maximum and minimum ages of purification for CRM-U100 that bracket the age of the material from early 1958 to late 1960 and demonstrate the power of multiple chronometers for determining the age of nuclear material.

ITWG Round Robin 3 Exercise Uranium Metal Model Ages

Model ages for the ITWG Round Robin 3 uranium metals from the ^{230}Th-^{234}U, ^{226}Ra-^{238}U, ^{231}Pa-^{235}U, and ^{227}Ac-^{235}U chronometers are significantly discordant and differ by as much as 29 years (^{231}Pa-^{235}U model age 39.9 years relative to ^{230}Th-^{234}U model age of 10.7 years for ITWG-RR3-B) (**Table 2, Figure 3**). The ^{230}Th-^{234}U chronometer model dates of August 17, 2003 and May 14, 2004 are 3-5 months younger than the known metal-casting dates of May 22, 2003, and January 14, 2004 for ITWG-RR3 A and B respectively. These ages are outside the uncertainty assigned to the analyses, and while they demonstrate that Th was efficiently segregated from uranium metal during the metal casting at Y-12, these "too young" ages may indicate some post-casting fractionation of Th from U. If not an analytical error, this may be a case where the closed-system assumption of the model age has been violated; perhaps ^{230}Th was removed from the metal pieces during cutting for sample preparation. Alternatively, the slightly younger ages reported here may reflect aging of the LLNL sample solution from 2010 to 2015 and loss of Th to PFA vial walls in which the sample solutions were stored. ^{226}Ra-^{238}U model dates of August 13, 2001 and April 11, 2002 for ITWG-RR3-A and B respectively, are 20-21 months older than the known casting dates of the metals. These older ages suggest that Ra may not be as efficiently purified as Th during metal casting and minor amounts of excess ^{226}Ra may exist in the uranium metal at the time of casting.

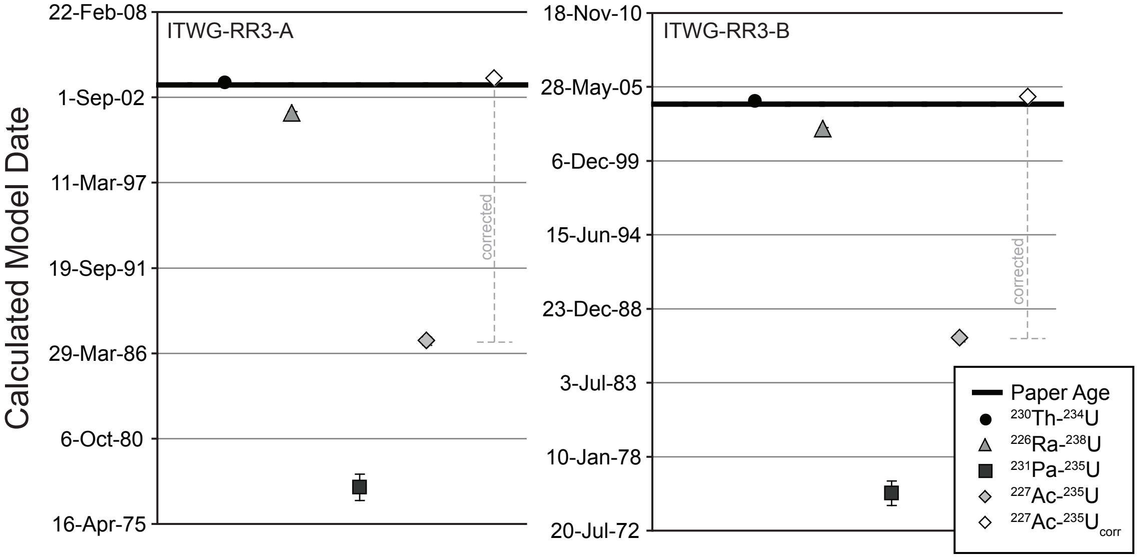

Figure 3. Model ages for ITWG-RR3-A (left) and ITWG-RR3-B (right) uranium metals. Model ages calculated from the ^{230}Th-^{234}U (black circles) and ^{231}Pa-^{235}U (black squares) chronometers differ significantly for both metals. The older age from the ^{231}Pa-^{235}U chronometer provides evidence for excess ^{231}Pa in the uranium metals at the time of metal casting. If this excess 231Pa is accounted for, new ^{227}Ac-^{235}U corrected model ages can be calculated (white diamonds) – change between uncorrected ^{227}Ac-^{235}U model ages (grey diamonds) and corrected values is shown by the grey dashed line. These corrected model ages agree well with the known casting dates of the metal.

Model ages from the ^{231}Pa-^{235}U chronometer, which suggest purification of the uranium metals in 1977 and 1975, are 26-29 years older than the known casting dates of these metals (**Table 2, Figure 3**). These much older ages demonstrate that excess ^{231}Pa must have existed during uranium metal casting. Similarly, the ^{227}Ac-^{235}U model ages for ITWG-RR3A and B are January 8, 1987 and October 15, 1986, which again, significantly deviate from the known purification dates (**Table 2, Figure 3**). However, because we observe deviation between the ^{230}Th-^{234}U and ^{231}Pa-^{235}U chronometers and relative concordance between ^{230}Th-^{234}U and ^{226}Ra-^{238}U, we can calculate the amount of ^{231}Pa excess that would need to exist at the time of purification in order for the model age of the ^{231}Pa-^{235}U chronometer to agree with the metal casting date [9]. The ^{231}Pa excess required is 2.49 x 10^{12} per gram primary solution of metal A and 3.42 x 10^{12} atoms per gram primary solution of metal B. Using these calculated amounts of excess ^{231}Pa at the initial time of casting and re-calculating the ^{227}Ac-^{235}U model ages, the corrected model ages for this system are within 6 months of the known casting date (**Figure 3**). These model ages are labeled ^{227}Ac-^{235}U$_{corr}$ in **Table 1** and **Figure 3** accordingly. These results suggest that the apparent ^{227}Ac excess has been supported by ^{231}Pa excess since the time of metal casting, and that ^{227}Ac was segregated as efficiently as ^{230}Th from U at this time.

Conclusions

We have developed chemical separation and MC-ICP-MS methods to use the grand-daughter chronometers in the decay chains of ^{238}U and ^{235}U age-date materials for nuclear forensic investigations: ^{226}Ra-^{238}U and ^{227}Ac-^{235}U. These methods have been validated by the measurement of model ages calculated for the CRM-U100 reference material where the ^{230}Th-^{234}U, ^{226}Ra-^{238}U, ^{231}Pa-^{235}U, and ^{227}Ac-^{235}U chronometers that agree well with the known purification date of this material. Investigation of uranium metals from the ITWG Round Robin 3 Exercise using these new chronometers demonstrates that during metal casting, ^{230}Th, ^{226}Ra, and ^{227}Ac are efficiently purified from uranium metal, though ^{226}Ra is purified to a lesser extent than ^{230}Th. Protactinium-231 was not completely separated from uranium metal during casting, and this ^{231}Pa excess must be taken into account. None of these model ages are necessarily “incorrect. Instead, taken together they supply information on relative elemental segregation during U casting, which can be used in the interpretation of unknown samples in a nuclear forensic investigation. Continued use of all four chronometers for nuclear material age-dating has the potential to increase our understanding of radionuclide migration and behavior during uranium processing.

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