^{230}Th - ^{234}U model ages of some uranium standard reference materials

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Summary. The “age” of a sample of uranium is an important aspect of a nuclear forensic investigation and of the attribution of the material to a source. The ^{230}Th - ^{234}U chronometer can be used to determine the production date of even very recently-produced material (^{234}U half life = $245\,250 \pm 490$ years; ^{230}Th half life = $75\,690 \pm 230$ years [1]), provided that the $^{230}\text{Th}/^{234}\text{U}$ at the time of formation is known, and that there has been no Th-U fractionation in the sample since production. For most samples of uranium, ages determined with this chronometer are “model ages”, because they are based on the assumptions of a) some initial amount of ^{230}Th in the sample, and b) closed-system behavior of the sample since production. The uranium standard reference materials originally prepared and distributed by the former US National Bureau of Standards and now distributed by New Brunswick Laboratory as certified reference materials (NBS SRM = NBL CRM) are good candidates for materials where these assumptions may be tested. The U isotopic standards have known purification and production dates and closed-system behavior in the solid form (U_3O_8) may be reliably assumed. In addition, these materials are widely available and can serve as informal round-robin inter-laboratory comparison samples.

We determined ^{230}Th - ^{234}U model ages for seven of these isotopic standards by isotope dilution mass spectrometry using a multi-collector ICP-MS. The standards dated for this study are U005-A, U010, U030-A, U100, U850, U900 and U970. Model ages obtained range from ~ 30 to ~ 52 years ago (reference date: 5-May-2009). The model age of U100 is the same as the purification date, within uncertainty. The other six standards analyzed all give model ages older than the purification dates of record. The magnitude of the discrepancy between model age and purification date does not correlate with the model age or the amount of ^{232}Th in the samples. This indicates that excess ^{230}Th in these six standards results from incomplete purification during production.

1. Introduction

Determining the age of a sample of illicitly obtained or transported uranium is an important aspect of a nuclear forensic investigation. The purification date of a uranium sample can be determined with the ^{230}Th - ^{234}U chronometer. This chronometer has been utilized by geochemists to

age-date corals and other natural samples with a very low Th/U ratio [2, 3]. Anthropogenic samples with abundant uranium allow the time limit and resolution of this method to be pushed to younger and more precise ages. For all samples, both natural and anthropogenic, the accuracy of dates determined with the ^{230}Th - ^{234}U chronometer relies upon several assumptions: 1) complete separation of Th from U during sample formation; 2) closed-system behavior of the sample after formation; 3) accurate ^{230}Th and ^{234}U measurements; and 4) an accurate value for the ^{234}U decay constant. Recent studies that determine ^{230}Th - ^{234}U age-dates for samples of nuclear-era depleted, natural and enriched uranium report precision ranging from 0.3% to 11% (corresponding to 48 d and 7 years), depending on the ^{235}U enrichment of the sample, the time of ^{230}Th in-growth (the age), the amount of sample analyzed, and the analytical methods used [4–6].

This method determines the time of complete separation of ^{234}U from its daughter, ^{230}Th , during formation of a sample, such as during purification of uranium for use as a nuclear material. The amount, if any, of excess ^{230}Th can be evaluated through the presence of significant natural Th (as ^{232}Th) in the sample. Excess ^{230}Th , resulting from incomplete separation or post-production contamination, will result in a model age older than the actual production age. For example, this is the case with NBL CRM 112-A (NBS SRM 960) uranium metal assay standard, which contains several ppm ^{232}Th , and the model-age of which predates the Manhattan Project [3]. In contrast to natural samples, however, excess ^{230}Th is not necessarily accompanied by ^{232}Th in anthropogenic uranium.

For the uranium isotopic certified reference materials distributed by New Brunswick Laboratory (NBL CRMs), retention of ^{230}Th in U_3O_8 (i.e., closed-system behavior) is a reliable assumption, so that any deviations of the model-age from the purification age can be ascribed either to variations in initial ^{230}Th , to the analytical uncertainty, or to uncertainty in the fundamental constants used in the calculation (i.e., the decay constants). We determined the model ages for seven different CRMs using isotope dilution mass spectrometry (IDMS) and compared these results with the purification ages of the samples [7].

2. Methods

The seven CRMs selected for this study, ranging from depleted to highly enriched uranium, are: U005-A, U010,

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U030-A, U100, U850, U900, and U970. Isotope dilution mass spectrometry (IDMS) analyses of ^{234}U and ^{230}Th are made using a ^{233}U spike calibrated with a natural uranium standard solution prepared from NBL CRM 112-A, and a ^{229}Th spike calibrated with the NIST SRM 4342A ^{230}Th radioactivity solution. All sample and spike sizes were determined by weight. All calculations involving activity to atom conversions, and the model-age calculations themselves, use half-lives for ^{230}Th and ^{234}U of $75\,690 \pm 230$ years and $245\,250 \pm 490$ years, respectively [1].

Duplicate primary sample solutions were made for each sample, for a total of 14 primary solutions. Variable-sized samples of the uranium oxides were added to 125 mL Teflon bottles and dissolved in three mL of concentrated HNO_3 , and then diluted to approximately 100 mL with 4 M HNO_3 . For each set of duplicate solutions, solution No2 contained a trace amount of HF (0.005 M HF), and solution No1 was left HF-free. Progressively less CRM U_3O_8 was dissolved for each sample from U005-A to U970, in order to crudely adjust the amount of ^{234}U (and hence ^{230}Th) in the primary solutions. Secondary dilutions of each of the 14 primary standards were made by weighing aliquots of these solutions and quantitatively diluting them in 250 mL polyethylene bottles with 1 M HNO_3 . The dilution factors for these secondary solutions were purposely varied from 1000 for U005-A to less than 200 for U970, to approximately equalize the amount of uranium in these solutions and to rationalize the sample-spike ratio for the IDMS analysis. Aliquots of the secondary standards were mixed with ^{233}U spike, equilibrated by heating in sealed Teflon vials, dried, and then re-dissolved in 2% HNO_3 for analysis by multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS). The concentrations of ^{234}U in the primary standard solutions were calculated from the results for the spiked secondary solutions.

For the ^{230}Th analyses, aliquots of the primary standard solutions were weighed, spiked with ^{229}Th , equilibrated, dried, re-dissolved in HCL and then dried again. Thorium was purified from these samples using standard anion exchange techniques: first, on a 2 mL AG1x8 resin bed in 9 M HCl in which U adsorbs and Th passes through; sec-

ond, adsorbing Th on a 1 mL AG1x8 resin bed in 8 M HNO_3 and then eluting it with 9 M HCl followed by 0.1 M HCl + 0.005 M HF; and third, by passing the Th through a final 0.3 mL AG1x8 resin bed in 9 M HCl. The purified Th fraction was dried, dissolved in a few drops of HNO_3 , dried again, and finally dissolved in 2% HNO_3 + 0.005 M HF for analysis by MC-ICPMS.

For most of the spiked uranium samples, IDMS measurements were made in replicate using both the IsoProbe and the NuPlasma HR MC-ICP mass spectrometers at LLNL. The results from these instruments agreed with each other within analytical uncertainty, and the measured uranium isotopic compositions for all the samples agreed with the certified values. For samples measured in replicate, an average of the results from the two instruments was used in the calculation of the ^{234}U content of the primary solutions. Instrumental mass bias and detector cross-calibration factors (*i.e.*, Faraday/pulse-counter gains) were made using NBL CRM 129A and U010. The spiked Th samples were measured on the NuPlasma HR, in simultaneous pulse-counting mode on two secondary electron multipliers. All signals were first corrected for detector baseline and for memory effects due to incomplete rinse-out of Th from the system. This instrumental memory is determined by making an analysis of the acid used to dissolve the samples immediately prior to the sample analysis, and is less than 1 part-per-thousand relative to the Th beams from the samples. The relative detector gain factors were determined by peak-jumping a beam from ^{229}Th on the two detectors, and the cross-over to the Faradays was determined using the ^{234}U beam in U010. The instrumental mass bias determined for the U010 standard was used to correct the $^{230}\text{Th}/^{229}\text{Th}$ ratio for mass bias.

The analyses were completed in three batches. In May 2009, solutions were prepared in duplicate and ^{230}Th and ^{234}U IDMS measurements were made for all samples. In October 2009, new ^{230}Th IDMS measurements were made on new aliquots of the original primary solutions for U030-A No1 and No2, and U970 No1 and No2. At this time, new secondary solutions were prepared and new IDMS measurements were completed for U970 No1 and No2. In November 2009, the primary solutions were adjusted to 0.05 M HF, agi-

Fig. 1. Model ages of uranium standard reference materials, relative to reference date of 5 May 2009. Also shown for comparison are purification dates of reference materials. Symbol size is larger than expanded uncertainty ($k = 2$) on model ages. See Table 2 for actual uncertainty for each analysis as well as the analysis date for each sample.

Table 1. ^{230}Th , ^{234}U and ^{232}Th concentrations of primary solutions.

Sample ID	^{230}Th atoms/g	^{234}U atoms/g	^{232}Th atoms/g
U005-A No1	$1.1699(50) \times 10^{+10}$	$1.3939(25) \times 10^{+14}$	$2.546(35) \times 10^{+10}$
U005-A No2	$9.444(41) \times 10^{+9}$	$1.1318(20) \times 10^{+14}$	$1.761(37) \times 10^{+10}$
U010 No1	$2.197(10) \times 10^{+10}$	$1.5231(13) \times 10^{+14}$	$3.516(48) \times 10^{+10}$
U010 No2	$1.3814(57) \times 10^{+10}$	$9.503(81) \times 10^{+13}$	$2.547(24) \times 10^{+10}$
U030-A No1	$1.0044(53) \times 10^{+10}$	$1.19630(84) \times 10^{+14}$	$1.1601(85) \times 10^{+11}$
U030-A No2	$6.956(53) \times 10^{+9}$	$8.1007(67) \times 10^{+13}$	$3.61(13) \times 10^{+10}$
U030-A No1 R1	$9.652(39) \times 10^{+9}$	$1.19630(84) \times 10^{+14}$	$2.132(17) \times 10^{+9}$
U030-A No2 R1	$6.531(26) \times 10^{+9}$	$8.1007(67) \times 10^{+13}$	$1.519(12) \times 10^{+9}$
U030-A No1 R2	$9.8666(49) \times 10^{+9}$	$1.19407(84) \times 10^{+14}$	$1.554(16) \times 10^{+9}$
U030-A No2 R2	$6.675(34) \times 10^{+9}$	$8.0856(67) \times 10^{+13}$	$3.415(34) \times 10^{+9}$
U100 No1	$3.190(14) \times 10^{+10}$	$2.2483(16) \times 10^{+14}$	$4.198(32) \times 10^{+10}$
U100 No2	$5.451(24) \times 10^{+10}$	$3.8451(32) \times 10^{+14}$	$2.971(20) \times 10^{+11}$
U850 No1	$1.3502(46) \times 10^{+11}$	$9.1987(88) \times 10^{+14}$	$9.424(78) \times 10^{+10}$
U850 No2	$3.933(14) \times 10^{+10}$	$2.6611(26) \times 10^{+14}$	$1.344(12) \times 10^{+10}$
U900 No1	$5.752(19) \times 10^{+10}$	$3.9255(33) \times 10^{+14}$	$3.692(34) \times 10^{+10}$
U900 No2	$1.1664(39) \times 10^{+11}$	$7.9934(86) \times 10^{+14}$	$5.589(57) \times 10^{+10}$
U970 No1	$2.745(11) \times 10^{+11}$	$2.1902(24) \times 10^{+15}$	$5.422(86) \times 10^{+10}$
U970 No2	$1.0739(34) \times 10^{+11}$	$8.5020(74) \times 10^{+14}$	$5.99(11) \times 10^{+10}$
U970 No1 R1	$2.690(11) \times 10^{+11}$	$2.183(10) \times 10^{+15}$	$1.1703(95) \times 10^{+10}$
U970 No2 R1	$1.0438(42) \times 10^{+11}$	$8.534(41) \times 10^{+14}$	$2.062(17) \times 10^{+10}$
U970 No1 R2	$2.769(14) \times 10^{+11}$	$2.1861(24) \times 10^{+15}$	$6.264(67) \times 10^{+10}$
U970 No2 R2	$1.0697(53) \times 10^{+11}$	$8.4862(74) \times 10^{+14}$	$6.29(65) \times 10^{+9}$

^{230}Th concentrations are for a reference date of 5 May 2009. The tabulated ^{230}Th , ^{234}U and ^{232}Th concentrations include contributions from reagent and processing blanks, which vary among individual analyses. However, the magnitude of the potential contributions to ^{230}Th and ^{234}U from the blank are trivial relative to the measured ^{230}Th and ^{234}U signals. The measured ^{232}Th concentrations do not correlate with the apparent excess ^{230}Th , *i.e.*, with the difference between the measured ages and the purification ages. Expanded uncertainties ($k = 2$) are given in parentheses.

Table 2. Model ages of uranium standard reference materials.

Sample ID	Analysis date	Model age (years before 5-May-09)	Expanded uncertainty ($k = 2$)	Model date	Date purification finished [7]
U005-A No1	May 09	29.70	0.15	23 Aug 79	Jul-81
U005-A No2	May 09	29.53	0.15	26 Oct 79	Jul-81
U010 No1	May 09	51.04	0.26	22 Apr 58	5-Jun-58
U010 No2	May 09	51.44	0.24	26 Nov 57	5-Jun-58
U030-A No1	May 09	29.71	0.17	20 Aug 79	Jul-81
U030-A No2	May 09	30.39	0.24	15 Dec 78	Jul-81
U030-A No1 R1	Oct 09	28.55	0.13	16 Oct 80	Jul-81
U030-A No2 R1	Oct 09	28.53	0.13	23 Oct 80	Jul-81
U030-A No1 R2	Nov 09	29.24	0.16	07 Feb 80	Jul-81
U030-A No2 R2	Nov 09	29.21	0.16	18 Feb 80	Jul-81
U100 No1	May 09	50.21	0.24	16 Feb 59	8-Jan-59
U100 No2	May 09	50.17	0.25	06 Mar 59	8-Jan-59
U850 No1	May 09	51.94	0.21	26 May 57	31-Dec-57
U850 No2	May 09	52.31	0.22	13 Jan 57	31-Dec-57
U900 No1	May 09	51.85	0.21	27 Jun 57	24-Jan-58
U900 No2	May 09	51.64	0.21	14 Sep 57	24-Jan-58
U970 No1	May 09	44.35	0.21	29 Dec 64	Mar-65
U970 No2	May 09	44.70	0.17	23 Aug 64	Mar-65
U970 No1 R1	Oct 09	43.61	0.28	25 Sep 65	Mar-65
U970 No2 R1	Oct 09	43.28	0.28	21 Jan 66	Mar-65
U970 No1 R2	Nov 09	44.82	0.25	08 Jul 64	Mar-65
U970 No2 R2	Nov 09	44.61	0.24	26 Sep 64	Mar-65

tated, and new aliquots were taken and IDMS measurements were completed for ^{230}Th concentrations for U030-A No1 and No2, and U970 No1 and No2.

Model-ages were calculated from the measured ^{230}Th and ^{234}U contents of the primary standards (Table 1) using

a computer program to iteratively solve the full Bateman [8] equations from which $t = \text{time}$ cannot be separated. This program also considers the ^{238}U content and can be used for samples of any age, but the simplified expressions for ^{230}Th - ^{234}U age dating [5, 6] give essentially identical results

Table 3. Representative uncertainty budget.

U100-No2 Model Age 50.17 ± 0.25 years	Contribution to combined uncertainty (%)
²³⁰ Th in U100-No2	
²²⁹ Th spike	
²³⁰ Th NIST standard	14.61
²²⁹ Th spike calibration	9.34
²³⁰ Th/ ²²⁹ Th analysis	
Weighing spike	1.73
Weighing sample	0.08
Mass bias correction	0.11
Ratio measurement	55.19
²³⁴ U in U100-No2	
²³³ U spike	
Primary U standard	0.03
²³³ U spike calibration	1.64
²³⁴ U/ ²³³ U analysis	
Weighing spike	0.12
Sample weighings and dilutions	0.06
Mass bias correction	< 0.01
Ratio measurement	0.94
²³⁰ Th half-life	≪ 0.01
²³⁴ U half life	16.15
Total	100.00

(within 1 h) for these relatively young samples (Table 2; Fig. 1).

A representative uncertainty budget for the age-dating analyses is given for sample U100-No2 in Table 3. The largest part of the uncertainty in these analyses comes from the ²³⁰Th measurement, of which the uncertainty on the primary NIST SRM used to calibrate the ²²⁹Th spike is a significant contributor. Improvement in the uncertainty could be obtained by increasing the sample size, thereby increasing the ²³⁰Th ion beam intensity and the precision on the measurement of the ²³⁰Th/²²⁹Th ratio. The uncertainty of the instrumental mass bias correction factors is minor, whereas the absolute uncertainty on the value used for the decay constant of ²³⁴U contributes 16% to the combined standard uncertainty for this sample.

3. Results

The model-ages calculated for the 14 samples and the corresponding purification dates are given in Table 2 and Fig. 1. The relative expanded uncertainties in Table 2 range from 0.4% to 1.1%, corresponding to 55 to 175 d. In all cases, the duplicate solutions for each standard analyzed at the same time yield identical ages, confirming that the CRM U₃O₈ oxide powders are homogeneous at the milligram-scale. The reanalyses of samples U030-A and U970 completed in October 2009 yield model ages that are younger than the respective ages determined from the May 2009 analyses by amounts ranging from 0.74 to 1.86 years. Following these analyses, additional hydrofluoric acid was added to the standard solutions to achieve a final composition of 4 M HNO₃ + 0.05 M HF. Subsequent analyses of these solutions

in November 2009 agree within analytical uncertainty with the May 2009 results. We attribute these collective results to the precipitation of Th from the primary solutions between May and October, most likely by sorption of Th on the bottle walls as hydrolyzed species. Loss of Th resulted in younger model ages for the October analyses. The addition of HF to the primary solutions in November quantitatively brought Th back into solution, as indicated by model ages that are in agreement with those determined from the May analyses.

Comparing the average model age for each pair of duplicate samples with the purification date for that standard, all samples, except U100 (and the U970 October replicate analysis), have model ages that are older than the purification ages by amounts that exceed the expanded uncertainty. The average model-age for U100 is younger than the purification age by 0.3%, or 48 d in this case, and the expanded uncertainty on the model-age (90 d) covers this gap. The average model-ages for U005-A and U030-A are significantly older (by 1.8 and 2.2 years for the May 2009 analyses) than the purification dates. These differences are likely the result of excess initial ²³⁰Th. The ²³²Th content of these two samples is not systematically higher than the other samples, so that contamination by common Th cannot be called upon to explain the results. Instead, it is more likely that the production process for these two standards, prepared in 1981, was not as effective at eliminating ²³⁰Th as the methods used earlier. It should be noted that the purification dates in Table 2 are not necessarily the dates of final oxide production (*i.e.*, system closure). The results presented here indicate that for most samples, if a pure uranium end-member (*i.e.*, one without ²³⁰Th) ever existed, then it pre-dates the purification.

In a nuclear forensic investigation, the straightforward interpretation of the ²³⁰Th-²³⁴U age of sample of uranium as the “production date” is unwarranted. This study shows that even highly purified uranium oxides may retain some initial ²³⁰Th. However, the model-age of the sample will represent the maximum possible time since production, which is an important constraint on its origin.

4. Conclusions

We have determined the ²³⁰Th-²³⁴U model-ages for seven of the NBL uranium isotopic standards and find that six of the seven give ages older than the purification dates of record. We find the age for U100 to be identical within analytical uncertainty to the purification date. The magnitudes of the age discrepancies do not correlate with apparent age or with the ²³²Th content of the samples, which, for these standards, indicates that the excess ²³⁰Th results from incomplete initial purification during production. Therefore, while ²³⁰Th-²³⁴U model ages may not necessarily faithfully record the time of U₃O₈ production, they nonetheless can provide constraints on the maximum possible ages, which is important information for a nuclear forensic investigation.

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