$^{230}$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 ± 490 years; $^{230}$Th half life = 75 690 ± 230 years [1]), provided that the $^{230}$Th-$^{234}$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 ($^{232}$UO$_3$) 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$_2$O$_5$ (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,
U030-A, U100, U850, U900, and U970. Isotope dilution mass spectrometry (IDMS) analyses of 234U and 230Th are made using a 233U spike calibrated with a natural uranium standard solution prepared from NBL CRM 112-A, and a 229Th spike calibrated with the NIST SRM 4342A 230Th 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 230Th and 234U of 75690 ± 230 years and 245250 ± 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 HNO3, and then diluted to approximately 100 mL with 4 M HNO3. For each set of duplicate solutions, solution No1 was left HF-free. Progressively less CRM U3O8 was dissolved for each sample from U005-A to U970, in order to crudely adjust the amount of 234U (and hence 230Th) 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 HNO3. 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 233U spike, equilibrated by heating in sealed Teflon vials, dried, and then re-dissolved in 2% HNO3 for analysis by multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS). The concentrations of 234U in the primary standard solutions were calculated from the results for the spiked secondary solutions.

For the 230Th analyses, aliquots of the primary standard solutions were weighed, spiked with 229Th, 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; second, adsorbing Th on a 1 mL AG1x8 resin bed in 8 M HNO3, 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 HNO3, dried again, and finally dissolved in 2% HNO3 + 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 234U 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 229Th on the two detectors, and the cross-over to the Faradays was determined using the 234U beam in U010. The instrumental mass bias determined for the U010 standard was used to correct the 230Th/229Th ratio for mass bias.

The analyses were completed in three batches. In May 2009, solutions were prepared in duplicate and 230Th and 234U IDMS measurements were made for all samples. In October 2009, new 230Th IDMS measurements were made on new aliquots of the original primary solutions for U030A 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-

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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.
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 and $^{234}$U from the blank are trivial relative to the measured $^{230}$Th and $^{234}$U signals. The measured $^{230}$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 |
Table 3. Representative uncertainty budget.

| U100-No2 Model Age     | Contribution to combined uncertainty (%) |
|------------------------|--------------------------------------------|
| 50.17 ± 0.25 years     |                                            |

$^{230}$Th in U100-No2

- $^{229}$Th spike
  - $^{230}$Th NIST standard 14.61
  - $^{230}$Th spike calibration 9.34
- $^{230}$Th/$^{238}$Th analysis
  - Weighing spike 1.73
  - Weighing sample 0.08
  - Mass bias correction 0.11
  - Ratio measurement 55.19

$^{234}$U in U100-No2

- $^{235}$U spike
  - Primary U standard 0.03
  - $^{235}$U spike calibration 1.64
- $^{234}$U/$^{238}$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 $^{230}$Th measurement, of which the uncertainty on the primary NIST SRM used to calibrate the $^{229}$Th spike is a significant contributor. Improvement in the uncertainty could be obtained by increasing the sample size, thereby increasing the $^{230}$Th ion beam intensity and the precision on the measurement of the $^{230}$Th/$^{238}$Th 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 $^{234}$U 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 U$_3$O$_8$ 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 HNO$_3$ + 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 $^{230}$Th. The $^{230}$Th 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 $^{230}$Th 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 $^{230}$Th) ever existed, then it pre-dates the purification.

In a nuclear forensic investigation, the straightforward interpretation of the $^{230}$Th-$^{234}$U age of sample of uranium as the “production date” is unwarranted. This study shows that even highly purified uranium oxides may retain some initial $^{230}$Th. 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 $^{230}$Th-$^{234}$U 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 maximum possible age, which is important information for a nuclear forensic investigation.

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