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# $^{230}\text{Th}$ - $^{234}\text{U}$ MODEL-AGES OF SOME URANIUM STANDARD REFERENCE MATERIALS

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## ABSTRACT

The “age” of a sample of uranium is an important aspect of a nuclear forensic investigation and of the attribution of the material to its source. To the extent that the sample obeys the standard rules of radiochronometry, then the production ages of even very recent material can be determined using the  $^{230}\text{Th}$ - $^{234}\text{U}$  chronometer. These standard rules may be summarized as (a) the daughter/parent ratio at time=zero must be known, and (b) there has been no daughter/parent fractionation since production. For most samples of uranium, the “ages” determined using this chronometer are semantically “model-ages” because (a) some assumption of the initial  $^{230}\text{Th}$  content in the sample is required and (b) closed-system behavior is assumed. 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 samples where both rules are met. The U isotopic standards have known purification and production dates, and closed-system behavior in the solid form ( $\text{U}_3\text{O}_8$ ) may be assumed with confidence. We present here  $^{230}\text{Th}$ - $^{234}\text{U}$  model-ages for several of these standards, determined by isotope dilution mass spectrometry using a multicollector ICP-MS, and compare these ages with their known production history.

## INTRODUCTION

The date that a sample of uranium was purified can be determined using the  $^{230}\text{Th}$ - $^{234}\text{U}$  chronometer, but the accuracy of this date compared to the true production date of the sample depends on several parameters, many of which are difficult to assess. These parameters are: (1) the completeness during purification of the separation of  $^{230}\text{Th}$  from its parent  $^{234}\text{U}$ ; (2) contamination of the sample with Th during production; (3) closed-system behavior after production; (4) the accuracy of the measurements; and (5) the accuracy of the decay constant for  $^{234}\text{U}$ . All of these parameters have been addressed by the geochemists who have been using this chronometer for decades to age-date corals and other natural samples where uranium is fractionated from thorium during formation [see for example 4,5,6].

The same analytical methodologies used to age-date natural samples by the  $^{230}\text{Th}$ - $^{234}\text{U}$  method may be applied to samples of anthropogenic uranium. The abundance of the U-parent in these samples, compared with the trace level of uranium in coral samples for example, allows the time limit and resolution of method to be pushed to younger and more precise ages. Recent studies [1,2,3] have shown that samples of depleted, natural, and enriched uranium may be dated. The precision reported in these studies on the ages of nuclear-era samples of uranium ranges from 0.3% to 11%

(corresponding to 48 days and 7 years), depending on the  $^{235}\text{U}$  enrichment of the sample, the time of in-growth (the age), the amount of sample analyzed, and the analytical methods used.

The amount of  $^{230}\text{Th}$  remaining with the uranium at the time of production or added later by contamination may be accessible through the presence of significant natural Th ( $^{232}\text{Th}$ ). Excess  $^{230}\text{Th}$  results in model-ages older than the actual production date. This is the case for NBL CRM 112-A (NBS SRM 960) uranium metal assay standard, which contains on the order of 0.1 wt %  $^{232}\text{Th}$ , and whose model-age predates the Manhattan Project [5]. In contrast to natural samples, however, excess  $^{230}\text{Th}$  is not necessarily accompanied by  $^{232}\text{Th}$  in man-made uranium.

For the uranium isotopic certified reference materials distributed by New Brunswick Laboratory (NBL CRMs), retention of  $^{230}\text{Th}$  in the  $\text{U}_3\text{O}_8$  (*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  $^{230}\text{Th}$ , 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].

## METHODS

The seven CRMs selected for this study range from depleted to highly enriched uranium and are U005-A, U010, U030-A, U100, U850, U900, and U970. IDMS analyses were made using a  $^{233}\text{U}$  spike calibrated with a natural uranium standard solution prepared from NBL CRM 112-A, and a  $^{229}\text{Th}$  spike calibrated with NIST SRM 4342A  $^{230}\text{Th}$  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 the half-lives for  $^{230}\text{Th}$  and  $^{234}\text{U}$  given in Cheng *et al.* [6]. Duplicate primary sample solutions (a total of 14) were made for each sample. Variable-sized samples of the uranium oxides were added to 125 mL Teflon bottles and dissolved in three mL of concentrated  $\text{HNO}_3$ , and then diluted to approximately 100 mL with 4 M  $\text{HNO}_3$ . Progressively less oxide was dissolved from U005-A to U970, in order to crudely adjust the amount of  $^{234}\text{U}$  (and hence  $^{230}\text{Th}$ ) 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 polybottles with 1 M  $\text{HNO}_3$ . 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 rationalize the sample/spike ratio for the IDMS analysis. Aliquots of the secondary standards were mixed with the  $^{233}\text{U}$  spike, equilibrated by heating in sealed Teflon vials, dried, and then re-dissolved in 2%  $\text{HNO}_3$  for analysis by multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS). The concentration of  $^{234}\text{U}$  in the primary standard solutions was calculated from the results for the spiked secondary solutions.

For the  $^{230}\text{Th}$  analysis, aliquots of the primary standard solutions were weighed, spiked with  $^{229}\text{Th}$ , equilibrated, dried and then dried again in concentrated HCl. Thorium was purified from these

samples using standard anion exchange techniques: first, by adsorbing U on a 2 mL AG1x8 resin bed in 9 M HCl where Th passes through; second, adsorbing Th on a 1 mL AG1x8 resin bed in 8 M HNO<sub>3</sub> 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, dried again with a few drops of HNO<sub>3</sub>, and dissolved in 2% HNO<sub>3</sub> + 0.005 M HF for analysis by MC-ICPMS.

The spiked uranium samples were measured on both an IsoProbe and a NuPlasma HR MC-ICPMS. 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. An average of the results from the two systems was used in the calculation of the <sup>234</sup>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 was 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 <sup>229</sup>Th on the two detectors, and the cross-over to the Faradays was determined using the <sup>234</sup>U beam in U010. The instrumental mass bias determined for the U010 standard was used to correct the <sup>230</sup>Th/<sup>229</sup>Th ratio for mass bias.

Model-ages were calculated from the measured <sup>230</sup>Th and <sup>234</sup>U contents of the primary standards using a computer program to iteratively solve the full “Bateman equations” from which t=time cannot be separated. This program also considers the <sup>238</sup>U content and can be used for samples of any age, but the simplified expressions for <sup>230</sup>Th-<sup>234</sup>U age dating [2-3] give essentially identical results ( $\pm 1$  day) for these relatively young samples.

## RESULTS

The model-ages calculated for the 14 samples are given in Table 1 along with the date when purification of the samples was completed [7]. The results are also shown in Figure 1 as the elapsed time between the reference date and the model-age (blue diamonds), and between the reference date and sample purification (red circles). The relative expanded uncertainties in Table 1 range between 0.4% to 0.6%, and range between 55 to 94 days. The size of the plot symbols for the model-age in Figure 1 is approximately  $\pm 80$  days. If the average model-age of each pair of duplicate samples is compared with the purification date for that standard, all samples, except U100, 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 days in this case, and the expanded uncertainty on the model-age (90 days) covers this gap.

Table. 1

Sample ID	Model Age (years before 5-May-09)	Expanded Uncertainty (k=2) (years)	Date Purification Finished [7]
U005-A-No1	29.703	0.151	July 1981
U005-A-No2	29.527	0.151	July 1981
U010-No1	51.040	0.258	5-Jun-58
U010-No2	51.444	0.239	5-Jun-58
U030-A-No1	29.709	0.169	July 1981
U030-A-No2	30.387	0.242	July 1981
U100-No1	50.215	0.242	8-Jan-59
U100-No2	50.167	0.249	8-Jan-59
U850-No1	51.943	0.211	31-Dec-57
U850-No2	52.306	0.217	31-Dec-57
U900-No1	51.854	0.205	24-Jan-58
U900-No2	51.639	0.210	24-Jan-58
U970-No1	44.349	0.209	March 1965
U970-No2	44.699	0.171	March 1965

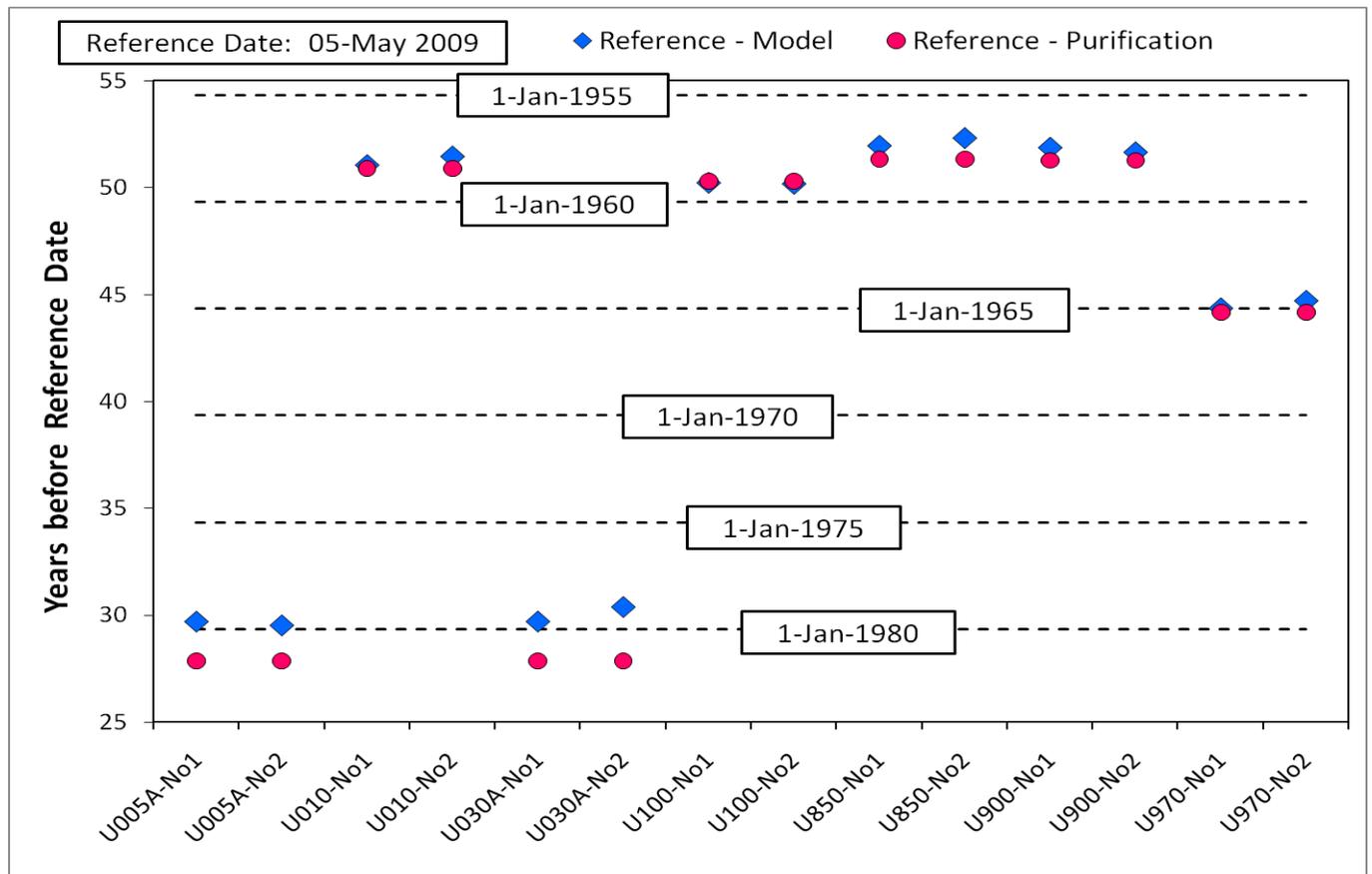


Figure 1. Model-ages (blue diamonds) compared with the purification ages (red circles)

The average model-ages for U005-A and U030-A are significantly older (by 1.8 and 2.2 years) than the purification dates, which is probably the result of excess initial  $^{230}\text{Th}$ . The  $^{232}\text{Th}$  content of these two samples is not systematically higher than the other samples (Table 3), 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  $^{230}\text{Th}$  as the methods used earlier.

It should be noted that the purification dates in Table 1 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  $^{230}\text{Th}$ , ever existed, then it pre-dates the purification.

The quantities of uranium used in the IDMS analyses of  $^{234}\text{U}$  and  $^{230}\text{Th}$  are given in Table 2 and the uranium and the  $^{232}\text{Th}$  concentrations of the primary standard solutions are given in Table 3.

Sample ID	234U	230Th	atoms 230Th in analytical fraction
U005-A-No1	3.170	9025	6.51E+10
U005-A-No2	2.706	9008	6.46E+10
U010-No1	1.925	6320	1.24E+11
U010-No2	1.144	5530	1.10E+11
U030-A-No1	0.373	1155	6.83E+10
U030-A-No2	0.257	1031	6.24E+10
U100-No1	0.187	441	1.07E+11
U100-No2	0.310	500	1.22E+11
U850-No1	0.084	48	1.17E+11
U850-No2	0.025	45	1.10E+11
U900-No1	0.035	39	1.14E+11
U900-No2	0.072	53	1.53E+11
U970-No1	0.034	61	3.39E+11
U970-No2	0.087	25	1.28E+11

Sample ID	microgram U/g	nanogram 232Th/g	Th/U (g/g)
U005-A-No1	1622	0.006	3.5E-09
U005-A-No2	1317	0.003	2.6E-09
U010-No1	1116	0.010	8.6E-09
U010-No2	696	0.007	1.0E-08
U030-A-No1	170	0.041	2.4E-07
U030-A-No2	115	0.011	9.9E-08
U100-No1	131	0.009	7.2E-08
U100-No2	224	0.104	4.7E-07
U850-No1	56	0.010	1.8E-07

U850-No2	16	-0.003	-1.8E-07
U900-No1	20	0.003	1.4E-07
U900-No2	40	0.004	1.1E-07
U970-No1	51	0.003	5.0E-08
U970-No2	20	0.004	2.0E-07
232Th concentrations are blank subtracted. The measured reagent and processing blank of 5.88E+10 atoms 232Th was subtracted from each sample.			

A representative uncertainty budget for the age-dating analyses is given for sample U100-No2 in Table 4. The largest part of the uncertainty in these analyses comes from the <sup>230</sup>Th measurement, of which the uncertainty on the primary NIST SRM used to calibrate the <sup>229</sup>Th spike is a significant contributor. Improvement in the uncertainty could be obtained by increasing the sample size, thereby increasing the <sup>230</sup>Th ion beam intensity and the precision on the measurement of the <sup>230</sup>Th/<sup>229</sup>Th ratio. The uncertainty of the instrumental mass bias correction factors is of trivial concern, whereas the absolute uncertainty on the value used for the decay constant of <sup>234</sup>U contributes 16% to the combined standard uncertainty for this sample.

Table 4.

<b>U100-No2 Model Age (50.167 ± 0.249) years</b>	<b>Uncertainty Budget (%)</b>
<b>230Th in U100-No2</b>	
<b>229Th Spike</b>	
230Th NIST Standard	14.61
229Th Spike Calibration	9.34
<b>230Th/229Th analysis</b>	
Weighing Spike	1.73
Mass Bias Correction	0.11
Ratio Measurement	55.19
Weighing Sample	0.08
<b>234U in U100-No2</b>	
<b>233U Spike</b>	
Primary U-Std	0.03
233U Spike Calibration	1.64
<b>234U/233U Analysis</b>	
Weighing Spike	0.12
Mass Bias Correction	< 0.01
Ratio Measurement	0.94
Weighings & Dilutions	0.06
<b>230Th Half-life</b>	<< 0.01
<b>234U Half-life</b>	16.15
	100

## CONCLUSIONS

We have determined the  $^{230}\text{Th}$ - $^{234}\text{U}$  model-ages for seven of the NBL uranium isotopic standards and find that six of the seven give older ages 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  $^{232}\text{Th}$  content of the samples, which, for these standards, indicates that the excess  $^{230}\text{Th}$  is from incomplete initial purification during production.

While the  $^{230}\text{Th}$ - $^{234}\text{U}$  date of a sample of illicitly obtained or transported uranium is an important part of a nuclear forensic investigation into the origin of the sample, this study of high purity uranium oxides elucidates some limitations of its literal application.

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