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Inter-comparison of the Radio-chronometric Ages of Plutonium Certified Reference Materials with Distinct Isotopic Compositions

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ABSTRACT: An inter-comparison of the radio-chronometric ages of four distinct plutonium certified reference materials varying in chemical form, isotopic composition, and period of production are presented. The cross-comparison of the different $^{234}U/^{238}Pu$, $^{235}U/^{239}Pu$, $^{236}U/^{240}Pu$, and $^{241}Am/^{241}Pu$ model purification ages obtained at four independent analytical facilities covering a range of laboratory environments from bulk sample processing to clean facilities dedicated to nuclear forensic investigation of environmental samples enables a true assessment of the state-of-practice in 'age dating capabilities' for nuclear materials. The analytical techniques evaluated used modern mass spectrometer instrumentation including thermal ionization mass spectrometers and inductively coupled plasma mass spectrometers for isotopic abundance measurements. Both multi-collector and single collector instruments were utilized to generate the data presented here. Consensus values established in this study makes it possible to use these isotopic standards as quality control standards for radio-chronometry applications. Results highlight the need for plutonium isotopic standards that are certified for $^{234}U/^{238}Pu$, $^{235}U/^{239}Pu$, $^{236}U/^{240}Pu$, $^{241}Am/^{241}Pu$ model purification ages as well as other multi-generational radio-chronometers such as $^{237}Np/^{241}Pu$. Due to the capabilities of modern analytical instrumentation, analytical laboratories that focus on trace level analyses can obtain model ages with marginally larger uncertainties than laboratories that handle bulk samples. When isotope ratio measurement techniques like thermal ionization mass spectrometry and inductively coupled plasma mass spectrometry with comparable precision are utilized, model purification ages with similar uncertainties are obtained.

Currently at: [a]ESH-RSO, ESH Repository Science operations & [b]Strategic Development Office

1. Introduction

The chronometric ages of nuclear materials provide critical information relevant to the fields of nuclear forensics, safeguards, and non-proliferation[1-6]. Traditional forensics utilizes evidence such as fingerprints, fibers, and other residues to identify linkages between suspects and criminal activities. The goal of nuclear forensics, on the other hand, is to identify the origin and history of the nuclear material by the measurement of the major analyte isotopic and elemental (impurity) composition together with macroscopic, microscopic, and morphological characteristics[7-12]. The forensic data constrain the production process and the intended use of the material which can then be compared against information databases[13, 14]. Plutonium (Pu) is produced from uranium (U) materials in nuclear reactors through neutron capture reactions and radioactive decay. Consequently, isotopic distribution of Pu offers an opportunity to evaluate the irradiation history (reactor type, irradiation condition, and U enrichment) of the material providing information that may be useful for material attribution. The ^{240}Pu isotopic abundance directly determines the "grade" of the Pu material and provides information on the intended use of the material. Weapons (low-burn-up) materials have ^{240}Pu abundances of <7% whereas fuel (high-burn-up) materials have ^{240}Pu abundances of up to >18%. Another key parameter in forensic applications is the 'age' of the nuclear material. Here, the 'age' of nuclear material refers to the time elapsed between the production (which is also assumed to be the time when Pu material was purified/separated from the U and Am radioactive daughter nuclides) of the material and the reference date of the analysis. Model purification ages are calculated utilizing the abundances of in-grown progeny from the radioactive decay of parent nuclides and represent the time since last material processing/purification[2, 3, 6]. For example, in Pu materials with no U present the ^{236}U/^{240}Pu ratio is solely governed by radioactive decay of ^{240}Pu to ^{236}U since Pu was last purified (assumption is made that the purification step associated with the material production step removed U completely). As the number of facilities with declared production capabilities for plutonium is limited and the timelines for which these facilities operated are known, the material can be associated with the production facilities with a relatively high degree of confidence, thus their production can be verified [6].

Nuclear materials that are of interest for chronometric characterization in forensics, safeguards, and nonproliferation efforts can include a wide variety of material types. Forensic materials may arrive in a variety of forms and quantities and may have been produced by different processes during distinct periods of the nuclear era[7, 15-20]. These processes can lead to a large range of isotope compositions and distinctive patterns in elemental impurities. Significant progress has been made recently to characterize more readily handled material types, such as U ore concentrates[15, 21, 22] and collection media, such as on cotton swipe samples [19]. In contrast, few investigations have focused on the rare or difficult to handle materials, such as Pu, Np or Am[23, 24] that frequently require specialized facilities for production and processing.

In this work, we present a detailed chronometric evaluation of four distinct Pu certified reference material (CRM) standards (CRM 136, 137, 138 and 126-A). Note that literature data on model purification ages of Pu isotopic standards, especially for CRM 136 - formerly known as standard reference material (SRM) 946 - vary significantly[21, 22, 25].

The primary goal of the present study is to date these widely used isotopic standards by expert laboratories so that consensus values for model purification ages of these traceable standards may be established. This will make it possible to use them as quality control (QC) standards in chronometric applications in support of nuclear safeguards and nuclear forensics. Comparison of the different model purification ages resulting from different daughter/parent isotope combinations will help identify any systematic biases that may exist for specific daughter/parent chronometers. A comparison of the analytical processes of the expert laboratories can lead to the development of best practices for chronometric applications and identify factors that might influence the result significantly. Until traceable isotopic standards certified for model production dates are available from reference material producers like Joint Research

Centre, Geel (JRC-Geel, formerly known as Institute for Reference Materials and Measurements, IRMM) or New Brunswick Laboratory (NBL, US), user facilities will need to develop strategies for the production and characterization of working reference materials (WRMs) that can be used as QC materials for analytical activities related to safeguards. Recognizing the need for standards across multiple disciplines that nuclear safeguards interact with, the International Atomic Energy Agency (IAEA) has taken a leadership role in establishing standardized criteria for production and characterization of WRMs. Meanwhile, analytical laboratories are pursuing strategies at developing standards for the various tasks that support nuclear forensics.[26]

Among the plutonium/uranium chronometers, the $^{236}U/^{240}Pu$ ratio is considered the most reliable for the age determination of Pu materials[4] (high-fidelity chronometer). The reasons for this are twofold. First, in most Pu materials, the ^{240}Pu is present in sufficient abundances that it is one of the major isotopes (the other being ^{239}Pu). Second, the ^{236}U daughter is occurring in natural materials at $< 3 \times 10^{-9}$ abundances[27, 28] and is less likely to be added as an external contaminant during the processing of the sample if no irradiated U is processed in the facility. Therefore, in general all the ^{236}U measured in the sample would have originated from the decay of ^{240}Pu. Other radio-chronometers that utilize U daughter and Pu parent nuclides are: the $^{234}U/^{238}Pu$ clock, the $^{235}U/^{239}Pu$ clock, and the $^{238}U/^{242}Pu$ clock[2, 12, 16, 21, 22, 25]. Among these, the $^{235}U/^{239}Pu$ chronometer is considered another high-fidelity chronometer. The $^{238}U/^{242}Pu$ clock is, generally, not preferred due to the long half-life of the parent nuclide ^{242}Pu ($T_{1/2} = 3.73 \times 10^5$ years) and predominance of ^{238}U in laboratory blanks. The small amounts of the ^{238}U produced from this decay are susceptible to contamination from natural background[16]. The $^{241}Am/^{241}Pu$ clock is the most commonly used chronometer for plutonium materials. The preferred methods for dating with this clock in bulk samples are gamma spectrometry[16-19, 21, 22], alpha spectrometry, or TIMS and ICP-MS[15-18, 21, 22, 29 - 31].

The measurement techniques used for dating bulk Pu samples via the Pu/U clocks are TIMS[3, 20, 21] and ICP-MS[29, 30]. For age determination measurements of Pu particles secondary ion mass spectrometry (SIMS) can also be used, preferably on the $^{236}U/^{240}Pu$ clock [17]. Considering more than one clock for the age determination of Pu is recommended because this improves the reliability of the results and enables additional information about the material, as using only one clock might lead to erroneous conclusions[4, 31, 32]. Discordance between different clocks can indicate that the sample consists of a mixture of two or more different materials of different ages[3, 7] or the model assumptions (i.e. complete purification of parent and no addition or loss of daughter) are incorrect. Both incomplete removal of the decay products from the parent nuclides at time zero and any addition of daughter isotopes during the time between the initial separation and the age dating measurement will result in older ages. For the considered daughter/parent systems, the possibility of a contamination of a Pu sample – for instance, in the facility where it was processed – with natural or non-natural U should be kept in mind as well. Inconsistent U/Pu ages from different chronometers, however, give additional information relevant to the history of the sample.

2. Summary Information on the Pu Standards

Three of the four Pu isotopic reference materials discussed in this report were originally named by National Bureau of Standards (NBS – US certifying body and predecessor to National Institute of Standard and Technology, NIST) as SRMs 946, 947, and 948[33-35]. These SRMs were re-named CRMs 136, 137, and 138 in the 1980s when NBS formally transferred the production, certification, maintenance of adequate supply, storage, and distribution of nuclear reference materials responsibilities to NBL. The fourth isotopic standard, CRM 126-A [36], was produced in July 2003 at Los Alamos National Laboratory (LANL). A brief summary of the history of each of these primary Pu isotopic standards is included in the following paragraphs.

The processing steps for SRMs 946, 947, and 948 were similar, as the present chemical form of these

isotopic standards are plutonium sulfate tetrahydrate. The Pu starting materials for SRMs 946 and 947 originated from commercial power reactor spent fuel. In an effort to produce two fuel grade (high burn-up) Pu isotopic standards, these materials were processed, purified, and certified at the same facility. SRM 948 pre-dates SRMs 946 and 947 by approximately 5 years. SRM 948 material originated from reactors that were used to produce weapons grade (low burn-up) Pu.

The Pu starting material for SRM 946 was reprocessed fuel at the Yankee Atomic Electric Company (Rowe, Massachusetts). The spent fuel was reprocessed at the Nuclear Fuel Service (NFS) West Valley, New York in the late 1960s, utilizing the Plutonium Uranium Redox Extraction (PUREX) process [37]. The material was purified via ion exchange chemistry between March and April 1970 (to remove americium and impurities), and converted to plutonium sulfate tetrahydrate [38]. For both SRMs 946 and 947, this two-month period can be considered a conservative uncertainty associated with the production date of the material.

The Pu starting material for SRM 947 was reprocessed fuel at the Commonwealth Edison Dresden reactor #1 located near Morris, Illinois. The spent fuel reprocessing likely took place at the NFS West Valley plant sometime in the late 1960's, utilizing the PUREX process. The solution was transferred to Richland, Washington. The material was dissolved, purified via ion exchange chemistry in September 1970, and converted to plutonium sulfate tetrahydrate. For both SRMs (946 and 947), the officially adopted NBS Certificate of Analysis (dated August 18, 1982) used the provisional certificate values obtained in 1971. The values in the provisional certificate were decayed to January 1, 1982, using the half-lives listed on the 1982 Certificate of Analysis [33, 34].

The Pu starting material for SRM 948 came from an unknown source. The exact timing of production of this Pu standard is not known. The Pu material for SRM 948 material was either a Hanford or Savannah River reactor. Both sites were producing weapons grade Pu from 1944 (Hanford) and 1955 (Savannah River). The SRM material was likely produced by converting a high-purity metal to the sulfate tetrahydrate sometime in 1963, and the bottling was completed in early 1964. The original certification measurements for isotopic abundances did not include ^{238}Pu. The average values for the material were decay corrected to June 1, 1964. The uncertainty associated with the production date of this material, SRM 948, is likely larger than the two months stated earlier for SRMs 946 and 947.

CRM 126-A is a plutonium metal assay and isotopic standard [36] with nominally weapons grade isotope composition. The source material for CRM 126-A was a double electro-refined metal that was cast into rods prior to being extruded into a wire, cut into 1-gram pieces, and packaged into an inert atmosphere in quartz ampoules for storage and shipment. Per on-site documents, the most recent material purification for CRM 126-A appears to have occurred at LANL in early July 2001.

Table 1 lists the certified isotope ratios of the Pu isotopic standards included in the present study and the dates of the initial certification. The standards included in this study represent a wide range of isotopic compositions from nominally weapons grade plutonium to fuel grade plutonium. Updated certificates for SRMs 946, 947, and 948, did not involve additional measurements or processing of the materials. For discussions that follow, SRMs 946, 947, and 948 will be referenced using their modern names CRMs 136, 137, and 138.

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3. Experimental Techniques

The analytical techniques used for dissolution, aliquoting, and separation of the analytes of interest from other interferences varied from facility to facility. Bulk samples were dissolved at the Chemistry Division, Actinide Analytical Chemistry Group (C-AAC) of Los Alamos National Laboratory (LANL). C-AAC also prepared the shipments received by Joint Research Centre, Karlsruhe (JRC-Karlsruhe, formerly known as Institute for Transuranium Elements, ITU) and Lawrence Livermore National Lab (LLNL). The Chemistry Division, Nuclear and Radiochemistry Group (C-NR) of Los Alamos National Laboratory (LANL) purchased CRMs 136, 137, 138, and CRM 126-A

separately and conducted an independent bulk dissolution of the CRMs. Separate CRM units were analyzed by the different facilities. Therefore, the present cross-comparison study also enable an assessment of the unit-to-unit heterogeneity of these Pu isotopic standards.

The sample dissolution and preparation methodologies are explained in **Table 2a** (C-AAC, LANL), **Table 2b** (C-NR, LANL), **Table 2c** (JRC-Karlsruhe), and **Table 2d** (LLNL). Details on the instrumentation used for the isotopic abundance measurements and assay measurements are also detailed in these tables. Additionally, the tables also provide relevant information on the standards used for instrument calibration as well as standards used for QC. Tables 2a, 2b, 2c, and 2d also list the instruments used, quantities of analytes used for each analysis, which corrections are applied to the data, and the magnitude of the analytical blanks. Tables 2a - 2d show that not only different analytical instruments were used for the isotopic abundance measurements but diverse methods were also used for dissolution of the samples and for purification of the analytes before analyses. Extraction chromatography and ion exchange were used for separations while TIMS, ICP-MS, and gamma spectrometry were used for isotope abundance determination.

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Table 2c goes here as a two column insert

Table 2d goes here as a two column insert

4. Chronometric Calculations

Specific considerations for chronometry of Pu materials were discussed in detail elsewhere [2-12, 16]. All chronometric calculations were performed using the generic Bateman equations [44], assuming that no progeny nuclei were present at $t = 0$. For each daughter/parent nuclide combination, the model purification ages (time elapsed since the daughter nuclide was separated from the parent nuclide, i.e., model purification ages) is calculated using **equation (1)**,

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where λ_P is the decay constant (in years^{-1}) of the parent nuclide (^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu)) λ_D is the decay constant (in years^{-1}) of the daughter nuclide (^{234}U, ^{235}U, ^{236}U, and ^{241}Am. $N_{D(t)}/N_{P(t)}$ is the ratio of the daughter nuclide to the parent nuclide amount at time t (in years). t represents the time elapsed since the daughter nuclide was separated from the parent nuclide (age).

For accurate model purification ages from radiochronometry, the following basic conditions must be met: (i) the daughter nuclides should be completely removed from their respective parent nuclides at time zero ($t = 0$, corresponding to the time when the parent/daughter separation was made); (ii) the material remains a closed system (i.e., no parent or daughter nuclide was added or removed during the time interval under consideration) [3, 6, 21, 22, 25].

Figure 1 shows a schematic of the decay schemes utilized in the present study. All daughter/parent nuclides used for the estimation of the model purification ages are shown. For simplification, only few multi-generational chronometers are shown.

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5. Results and Discussion: Model Purification Ages

Model Purification ages calculated using JRC, C-AAC, C-NR, and LLNL data are given in **Tables 3, 4, 5,** and **6**, respectively. The model purification dates and uncertainties listed in the Tables represent the values reported by each facility. These values in some cases are averages of multiple measurements and in other instances result of a single determination. The uncertainty estimations followed different uncertainty evaluation strategies (additional details are provided in a later section).

Table 3 goes here as a two column insert

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Figure 2 shows a comparison of the model purification ages obtained for CRM 136. Analytical results along with the uncertainties reported by the different facilities are given (uncertainties shown are expanded uncertainties at the 95% confidence levels using a coverage factor of $k = 2$). The reference value for the production date of this CRM based on information available from NBL is also shown.

Figure 2 goes here as a two column insert

For CRM 136, an average model purification date of July 9, 1970 (± 199 days) is obtained using the $^{234}U/^{238}Pu$ chronometer (here, and in the discussion that follows in this section, the uncertainty shown for the average model purification date using the different daughter/parent chronometry systems represent the standard deviation of the model purification dates from the different laboratories. Uncertainty on each chronometry age reported by the facilities are shown in Tables 3, 4, 5, and 6. These uncertainties can be larger or smaller than standard deviation shown above for the average model production date, depending on the analytical method that was utilized). This average model purification date is younger than the known production age of this CRM (from NBL records) by 102 days. Uncertainties on the $^{234}U/^{238}Pu$ model ages reported by the facilities ranged from 44 days (C-AAC) to 438 days (JRC). The $^{234}U/^{238}Pu$ model age from C-NR was younger by 303 (± 398) days and the LLNL age was older by 157 (± 216) days (within their respective uncertainties, all $^{234}U/^{238}Pu$ model ages overlapped the archived production date from NBL). The $^{235}U/^{239}Pu$ chronometer yielded an average model purification date of June 20, 1970 (± 84 days). This model purification date is younger than the known production date of this CRM by 83 days. Uncertainties on the $^{235}U/^{239}Pu$ model ages reported by the facilities ranged from 44 days (C-AAC) to 168 days (JRC & C-NR). The $^{235}U/^{239}Pu$ model age from JRC was younger by 141 (± 168) days and the LLNL age was older by 39 (± 135) days (apart from C-AAC data, all $^{235}U/^{238}Pu$ model ages, within the uncertainties reported, overlapped the archived production date from NBL). The model age from C-AAC was younger by 135 ± 44 days. The $^{236}U/^{240}Pu$ chronometer yielded an average model purification date of June 26, 1970 (± 173 days) for CRM 136. This model purification date is younger than the known production date of this CRM (from NBL records) by 88 days. Uncertainties on the $^{236}U/^{240}Pu$ model ages reported by the facilities ranged from 47 days (C-AAC) to 219 days (JRC). Whereas the $^{236}U/^{240}Pu$ model ages from JRC and C-AAC are younger than the archived production dates from NBL by (320 ± 220 days and 117 ± 47 days) those from C-NR and LLNL matched the archived production date. The $^{241}Am/^{241}Pu$ chronometer yielded an average model purification date of May 11, 1970 (± 154 days) for CRM 136. This model purification date is younger than the known production date of this CRM (archived NBL records) by 43 days. Uncertainties on the $^{241}Am/^{241}Pu$ model ages reported by the facilities ranged from 77 days (C-AAC, TIMS data) to 237 days (JRC). Within the uncertainties reported, the model ages from C-AAC (TIMS data), JRC, C-NR, and LLNL overlap the production date of this CRM. Only the γ-counting model purification date from C-AAC (indicated by 2* in Figure 2) yielded older (by 456 days) age than the archived NBL production date (this older age is not included in the average purification date shown above for the $^{241}Am/^{241}Pu$ chronometer). Within the large uncertainty of 354 days, the $^{238}U/^{242}Pu$ chronometric date of February 14, 1970 from C-AAC is consistent with the ages from other chronometry systems.

Figure 3 shows a comparison of the model purification ages obtained for CRM 137. Analytical results along with the uncertainties reported by the different facilities are shown. The production date of this CRM based on information available from NBL is also shown.

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For CRM 137, an average model purification date of July 8, 1971 (± 250 days) is obtained using the $^{234}U/^{238}Pu$ chronometer. This average model purification date is younger than the known production date of this CRM (from NBL records) by 296 days. Uncertainties on the $^{234}U/^{238}Pu$ model ages reported by the facilities ranged from 135 days (C-AAC) to 913 days (JRC). The $^{234}U/^{238}Pu$ model age from C-AAC was younger by 72 (± 135) days and the JRC age was younger by 615 (± 913) days. All reported model purification dates reported by

the facilities, even though younger than the archived production date from the manufacturer, overlap the reference value for the production date of this Pu isotopic standard. The $^{235}U/^{239}Pu$ chronometer yielded an average model purification date of January 9, 1971 (± 36 days) for CRM 137. This model purification date is younger than the known production date of this CRM by 117 days. Uncertainties on the $^{235}U/^{239}Pu$ model ages reported by the facilities ranged from 40 days (JRC & C-AAC) to 135 days (C-NR & LLNL). The $^{235}U/^{239}Pu$ model age from C-NR was younger by 151 (± 133) days and the LLNL age was younger by 66 (± 135) days. Within the uncertainties reported (40 days) the $^{235}U/^{239}Pu$ model ages from JRC and C-AAC are younger than the archived production date by ~125 days. All model ages using both $^{234}U/^{238}Pu$ and $^{235}U/^{239}Pu$ chronometers yielded younger ages than the production date from the CRM manufacturer. The $^{236}U/^{240}Pu$ chronometer yielded an average model purification date of November 1, 1970 (± 49 days) for CRM 137. This model purification date is younger than the known production date of this CRM by 48 days. Uncertainties on the $^{236}U/^{240}Pu$ model ages reported by the facilities ranged from 44 days (C-AAC) to 177 days (C-NR). Whereas C-NR reported model purification dates that is older than the production date by 11 (± 177) days JRC & LLNL ages overlap the producer's value. The model purification date from C-AAC was younger by 109 (± 44) days. Excluding the γ-counting data from C-AAC (indicated by 2* in Figure 3), the $^{241}Am/^{241}Pu$ chronometer yielded an average model purification date of November 2, 1970 (± 98 days) for CRM 137. This model purification date is younger than the known production date of this CRM by 48 days. Uncertainties on the $^{241}Am/^{241}Pu$ model ages reported by the facilities ranged from 102 days (C-AAC, TIMS data) to 223 days (C-AAC, γ-counting data). Whereas LLNL reported a model purification date that is older than the production date by 76 (± 142) days JRC reported a model age that is younger than the producer's value by 162 (± 190) days. The model purification date from C-AAC (γ-counting data) is older by 461 (± 223) days. Within the uncertainties reported, this age did not overlap the archived production date from the manufacturer. This model date is not included in the average shown above for the $^{241}Am/^{241}Pu$ chronometer. Within the large uncertainty of 1.1 years, the $^{238}U/^{242}Pu$ chronometric age of August 16, 1970 from C-AAC is consistent with the ages from other chronometry systems.

Figure 4 shows a comparison of the model purification ages obtained for CRM 138. Analytical results along with the uncertainties reported by the different facilities are shown. The production date of this CRM based on information available from NBL is also shown (the uncertainty on the production date indicated is assumed to be about 6 months, factor of three higher than that for CRMs 136 and 137).

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For CRM 138, the $^{234}U/^{238}Pu$ chronometer yields an average model purification date of February 6, 1964 (± 764 days). This average model purification date is younger than the known production date of this CRM by 144 days. Uncertainties on the $^{234}U/^{238}Pu$ model ages reported by the facilities ranged from 373 days (LLNL) to 877 days (C-AAC). The $^{234}U/^{238}Pu$ model age from C-AAC is older by 870 (± 877) days and the C-NR model age is younger by 958 (± 797) days. All reported model purification dates reported by the facilities, overlap the manufacturer's reference value for the production date of this Pu isotopic standard. The $^{235}U/^{239}Pu$ chronometer yielded an average model purification date of April 24, 1964 (± 397 days) for CRM 138. This model purification date is younger than the known production age of this CRM by 222 days. Uncertainties on the $^{235}U/^{239}Pu$ model ages reported by the facilities ranged from 51 days (C-AAC) to 363 days (C-NR). Whereas the $^{235}U/^{239}Pu$ model ages from C-NR and JRC are consistent with the manufacturer's production date, the model ages from C-AAC and LLNL are younger by 539 days (within the uncertainty values of 51 days (C-AAC) and 194 days (LLNL) the $^{235}U/^{239}Pu$ model ages are not consistent with archived production date from NBL). The $^{236}U/^{240}Pu$ chronometer yielded an average model purification date of January 2, 1964 (± 477 days) for CRM 138. This model purification age is younger than the known production date of this CRM by 110 days. Uncertainties on the $^{236}U/^{240}Pu$ model ages reported by the facilities ranged from 51 days (C-

AAC) to 407 days (C-NR). Whereas two facilities (JRC and C-NR) reported model purification dates that are marginally older than the producer's value, the purification dates from LLNL and C-AAC are younger by 509 days (within the uncertainty values of 51 days (C-AAC) and 216 days (LLNL) the model ages are not consistent with archived production date from NBL). The larger deviation of the high-fidelity chronometers from the producers value for the production age of this standard support the large systematic bias in the $^{240}Pu/^{239}Pu$ isotope ratio of this standard [49]. The $^{241}Am/^{241}Pu$ chronometer yielded an average model purification date of September 11, 1962 (± 151 days) for CRM 138. This model purification date is older than the known production date of this CRM by 369 days. Uncertainties on the $^{241}Am/^{241}Pu$ model ages reported by the facilities ranged from 95 days (C-AAC, TIMS data) to 226 days (C-AAC, γ-counting data). The model purification ages from JRC and C-NR are consistent with the archived production date of this CRM. All $^{241}Am/^{241}Pu$ model ages are older than the archived production date from NBL. The γ-counting model age from C-AAC (indicated by 2* in Figure 4) is older than the producer's age by 592 (± 226) days and the JRC model age is older by 232 ± 179 days. Within the large uncertainty of 1.4 years, the $^{238}U/^{242}Pu$ model purification date of June 4, 1963 from C-AAC is consistent with the ages from other chronometry systems.

Figure 5 shows a comparison of the model purification ages obtained for CRM 126-A. The producer value for the age of this CRM is also shown.

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For CRM 126-A, the $^{234}U/^{238}Pu$ chronometer yields an average model purification date of May 22, 2001 (± 246 days). This average model purification date is older than the known production date of this CRM by 54 days. Uncertainties on the $^{234}U/^{238}Pu$ model ages reported by the facilities ranged from 135 days (LLNL) to 470 days (C-NR). All $^{234}U/^{238}Pu$ model purification dates overlap the production date of this Pu isotopic standard. The $^{235}U/^{239}Pu$ chronometer yield an average model purification age of March 18, 2001 (± 245 days) for CRM 126-A. This model purification date is older than the known production date of this CRM (from LANL records) by 119 days. Uncertainties on the $^{235}U/^{239}Pu$ model ages reported by the facilities ranged from 12 days (C-AAC) to 1096 days (JRC). All $^{235}U/^{239}Pu$ model purification dates overlap the purification date of this Pu isotopic standard. The $^{236}U/^{240}Pu$ chronometer yielded an average model purification age of February 15, 2001 (± 274 days) for CRM 126-A. This model purification age is older than the known production age of this CRM by 150 days. Uncertainties on the $^{236}U/^{240}Pu$ model ages reported by the facilities ranged from 12 days (C-AAC) to 584 days (JRC). All model ages overlap producer's value within the uncertainties stated. The $^{241}Am/^{241}Pu$ chronometer yielded an average model purification date of January 28, 2001 (± 83 days) for CRM 126-A. This model purification date is older than the known production age of this CRM by 168 days. Two facilities (C-AAC and C-NR) reported model ages that overlap the archived production dates. Model purification ages from JRC and LLNL yielded older ages than the production date from the producer. Within the large uncertainty of 1.5 years, the $^{238}U/^{242}Pu$ chronometric age of December 31, 1999 from C-AAC is consistent with the ages from other chronometry systems.

Comparison of the above model purification dates to lower fidelity chronometers proved to be largely consistent, demonstrating increased confidence in the model ages established for these CRM standards. It is interesting to note that in the case of CRMs 136, 137, and 138 the C-AAC $^{235}U/^{239}Pu$ and $^{236}U/^{240}Pu$ similarly deviate compared to the archived production dates. This shows that the younger ages are not due to laboratory contamination during the processing of the samples as it is impossible to contaminate both $^{235}U/^{239}Pu$ and $^{236}U/^{240}Pu$ chronometers to the same levels through contamination.

Consensus values for the model purification ages are given in **Table 7**. The chronometers averaged to establish the consensus values are indicated. Two times standard deviation of the purification ages included in deriving the consensus values is shown as the uncertainty of the model purification date. The difference between the consensus values for model purification ages and the archived pro-

duction dates are also indicated (column 4 of Table 7). As the uncertainties assigned to the consensus model purification ages are larger than the differences (listed in column 4), the consensus values are unbiased relative to the production ages.

Table 7 goes here as a two column insert

Concordant ages for the different chronometry systems at different facilities show that unit-to-unit heterogeneity is not present. These primary Pu isotopic standards are homogeneous and large differences between the different units are not observed. For U daughter isotopes produced from the different Pu parent isotopes, analytical data show absence of heterogeneity of both Pu and U element contents.

6. Contributors to Chronometric Uncertainties

As examples, the uncertainty budgets for the model ages calculated using analytical data from two different facilities were investigated to identify significant contributors to the overall uncertainty budget. **Table 8** summarizes the uncertainty budgets for the different chronometry pairs using C-AAC data. Uncertainty calculations following ISO GUM methodology [45, 46] using Workbench software [47] showed that the dominant contributors of uncertainty varied with the 1) chronometric relationship of interest, 2) material age, and 3) isotopic composition of the sample. For example, the $^{236}U/^{240}Pu$ and $^{235}U/^{239}Pu$ ratio uncertainties are dominated by the U assay value, but the Pu assay and ^{239}Pu half-life contributions are also important. The ^{239}Pu and ^{235}U isotopic abundance measurements did not contribute significantly to the uncertainty budget (these contributions were usually 1 to 2%). This is not surprising as C-AAC used TIMS analytical technique that yielded excellent precision in the major isotope ratio measurements of U and Pu. Considerations of half-life measurements and propagation of their uncertainty have been considered previously [48] revealing a clear need for further refinement in the current context to better constrain primary chronometric windows of interest. Interestingly, even within the primary chronometers, some distinct distributions of uncertainty drivers were noted for newer vs older materials. For example, for both the $^{236}U/^{240}Pu$ and $^{235}U/^{239}Pu$ high-fidelity chronometers the Pu assay becomes an insignificant contributor for the newer 126-A. For this newer standard, the U assay contribution decreases to 30% of the overall uncertainty whereas for the older CRMs (136, 137, and 138), the U assay accounts for >50% of the uncertainty in the model ages. For the newer material, the contribution of the ^{239}Pu and ^{240}Pu half-life increases at the expense of the assay contributions.

Table 8 goes here as a two column insert

The $^{234}U/^{238}Pu$ model purification age uncertainty in these materials exhibited significant connection between resultant uncertainty and the isotopic composition of the Pu material, presumably due to the highly variable abundance of ^{238}Pu in each material. Specifically, model age uncertainties for this chronometer in CRM 126-A and CRM 138, both reflecting weapons grade Pu material and containing relatively low levels of the ^{238}Pu parent radionuclide, were dominated by the uncertainty in the ^{238}Pu abundance measurement (~98% of the uncertainty for this chronometer comes from this factor). In contrast, the $^{234}U/^{238}Pu$ model age uncertainties for CRMs 136 and 137, the two materials reflecting reactor grade Pu materials and broader isotopic distribution, were associated with contributions from many different components (^{238}Pu half-life: 2 to 20 %; isotopic measurement: 4 to 90%; Pu assay: 1 to 16%, U assay: 4 to 44 %).

For the older (48 to 55 years) CRMs 136, 137, and 138, a significant portion of the overall uncertainty (15 to 26%) in the $^{235}U/^{239}Pu$ and the $^{236}U/^{240}Pu$ model purification ages originate from the ^{239}Pu & ^{240}Pu half-life. The U content (51 to 59%) and Pu content (8 to 20%) also contribute significantly to the overall uncertainty of the model purification age using these two chronometers. The ^{239}Pu and ^{235}U isotope abundances contribute 2 to 6% of the uncertainty. In the $^{236}U/^{240}Pu$ chronometer, the isotopic abundances have a larger contribution of 16 to 22% of the overall uncertainty.

As expected, the partitioning of the uncertainty budget changes when different analytical methodology are used to determine the daughter/parent

abundances. For C-NR data, the uncertainty budgets for the different chronometers partition as summarized in **Table 9**. C-NR utilized MC-ICP-MS for Pu & U assay measurements as well as U isotopic abundance measurements and TIMS for Pu isotope abundance measurements. The Pu concentration measurements utilized a ^{242}Pu tracer which is not highly pure. The contributions from the spike are subtracted to derive the abundances of the other Pu isotopes. Uncertainty associated with the tracer calibration, therefore, dominates the uncertainty of the parent Pu isotope abundance measurements at C-NR. For the ^{234}U/^{238}Pu chronometer, the uncertainty is predominantly (90 to 99.8%) from the ^{238}Pu isotopic abundance measurement with ~7 to 8% of the uncertainty coming from ^{234}U abundance measurements and 1 to 2% coming from the ^{238}Pu half-life. For the ^{235}U/^{239}Pu chronometer, the uncertainty budget is dominated by the uncertainty in ^{239}Pu isotopic abundance measurement (90 to 100%), whereas ^{235}U abundance measurement and the ^{239}Pu half-life makes equal contributions in the range of ~5% to 0%. For the second high-fidelity chronometer (i.e., ^{236}U/^{240}Pu), ~80 to 99% of the uncertainty is due to the ^{240}Pu abundance measurement, with the ^{236}U abundance measurement contributing ~16 to 1% of the total uncertainty. For the high-burnup CRMs 136 and 137, the ^{240}Pu half-life contributes ~3% of the total uncertainty.

Table 9 goes here as a two column insert

Chronometers dependent upon the decay of ^{241}Pu consistently reflected uncertainties which were predominantly driven by the measurement of the progeny (90 to 99% uncertainty originating from Am assay value with the rest coming from the ^{241}Pu abundance measurement). This is not unexpected given the relatively low levels of ^{241}Pu in the materials investigated here, even with decades of elapsed time to promote progeny in-growth. For Am assay measurements using IDMS, the uncertainty budget is more evenly distributed between the Am assay uncertainty (54 to 97%) and ^{241}Pu abundance uncertainty (1% for CRM136 to 45% for CRM137).

That the model purification ages from these reference materials, especially the younger ages in CRMs 137 and 138 may point to systematic biases of the Pu standards and/or U isotopic standards used for calibration of the mass spectrometer instrumentation and for estimation of the mass fractionation effects. For CRM 138, bias of ~0.08% has been identified in the ^{240}Pu/^{239}Pu major ratio[49] and biases in the range of 0.02 to 0.05% have been identified in the major ratio of several U CRMs[50]. Biases of similar magnitude are possible in the major isotope ratios of other Pu CRMs and for minor ratios the systematic biases can be even larger (as observed for U CRMs from NBL). Systematic bias(es) between the two standards used in Am assay measurements using γ-spectrometry are also identified. The uncertainty quoted for Am measurements using γ-spectrometry is ~3.1% (for comparison, IDMS using TIMS yields Am contents with ~0.1% uncertainty). For the high-burnup CRMs 136 and 137, Am contents by γ-spectrometry are higher than the corresponding TIMS values (for CRM 136, an Am content of 18300 μg/g by γ-spectrometry and 17067 μg/g by ID-TIMS) by ~7.3%, whereas for CRM 138, the γ-spectrometry value is higher by ~4.2%. Bias in the range of 4.2 to 7.5% between the two Am standards used by γ-spec is a possible reason that need to be investigated.

7. Conclusions

An inter-comparison of the different $^{234}U/^{238}Pu$, $^{235}U/^{239}Pu$, $^{236}U/^{240}Pu$, and $^{241}Am/^{241}Pu$ model purification ages at four independent analytical facilities demonstrates that consistent ages across the different chronometry systems and across different analytical facilities can be obtained in 'age dating' of nuclear materials. Multiple analytical techniques and separation methodologies were evaluated and shown to yield ages that are broadly consistent with one another. Consensus model purification ages for four distinct Pu isotopic standards (CRMs 136, 137, 138, and 126-A), including the oldest known standard from the former National Bureau of Standards, are established using data from expert laboratories with proven track record of accomplishments in the nuclear safeguards area.

Chronometric study of these distinct plutonium materials incorporated a wide variety of considerations. In addition to the need for capable preparative and measurement strategies, the diverse set of possible material parameters potentially associated with real-world materials (quantity, form, isotopic composition, etc.) will clearly impact upon the ability to measure a given chronometer with desirable confidence on a case-by-case basis. In the current work, however, characterization of the selected reference materials clearly supports the ability to chronometrically investigate distinct Pu systems and to explore considerations of concordant/discordant material ages. Until new certified isotopic standards that are also certified for radiochronometric ages are available, the isotopic standards included in this inter-comparison study along with the consensus values can be used as quality control in nuclear forensic applications.

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Figure Captions:

Figure 1: Decay schematics, starting with the Pu parent isotopes, investigated in the present study.

Figure 2: Comparison of the model purification ages from the different chronometers for CRM 136. For each chronometer, numerals next to the symbols indicate the facility from which the data came from (1 represent JRC, 2 represent C-AAC (LANL), 3 indicate C-NR (LANL), and 4 indicate LLNL).

Figure 3: Comparison of the model purification ages from the different chronometers for CRM 137. For each chronometer, numerals next to the symbols indicate the facility from which the data came from (1 represent JRC, 2 represent C-AAC (LANL), 3 indicate C-NR (LANL), and 4 indicate LLNL).

Figure 4: Comparison of the model purification ages from the different chronometers for CRM 138. For each chronometer, numerals next to the symbols indicate the facility from which the data came from (1 represent JRC, 2 represent C-AAC (LANL), 3 indicate C-NR (LANL), and 4 indicate LLNL).

Figure 5: Comparison of the model purification ages from the different chronometers for CRM 126-A. For each chronometer, numerals next to the symbols indicate the facility from which the data came from (1 represent JRC, 2 represent C-AAC (LANL), 3 indicate C-NR (LANL), and 4 indicate LLNL).

1 $$t = \frac{1}{(\lambda_P - \lambda_D)} \, ln\left[1 - \frac{N_D(t)}{N_P(t)} \bullet \frac{(\lambda_D - \lambda_P)}{\lambda_P}\right]$$ Eq (1)

Table 1: Certified Ratios and Date of initial characterization of the Pu standards included in the present study

Standard	Certified Ratios				Date of Certification
	$^{238}Pu/^{239}Pu$	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$	
CRM 136*	0.002747(83)	0.14507(23)	0.029326(59)	0.006796(36)	10/19/1971
CRM 137*	0.003606(78)	0.24141(37)	0.036594(79)	0.015592(52)	10/13/1971
CRM 138*	0.000120(11)	0.08642(12)	0.005111(11)	0.0003604(33)	8/8/1966
CRM 126-A	0.00013022(30)	0.062744(16)	0.00157886(76)	0.00038465(25)	7/30/2003

*The isotope ratios listed are as of January 1, 1982, as listed in the Certificate of Analysis dated August 19, 1982. These values are obtained by decay correcting the provisional (atom percent) values dated October 19, 1971 (for CRM 136), October 13, 1971 (for CRM 137), and September 1, 1972 (for CRM 138). Note that correlation plays a significant role in uncertainty calculations involving atom percent or weight percent abundances[39] (the uncertainty estimates shown above, for the certified isotope ratios, are calculated following a methodology that correctly incorporates such correlations[39]).

1 Table 2a: Details on the Analytical Methodology at LANL (C-AAC)

Sample Preparation	U	~1 g chunk of metal mechanically cleaned using a stainless steel brush until surface is shiny. Metal cut into pieces using hand dykes. One piece (~0.25 g) in a cleaned glass beaker is transferred to an attached open-front enclosure and dissolved in 6 mL of 6 M HCl, transferred into a 125 mL polypropylene bottle and diluted with 3 M HNO_3, swirled and aliquoted. CRMs 136, 137, and 138 were received as ~0.5 g Pu sulfate in a glass vial. Standard solutions were transferred to Al weighing dish and into glass beakers that were transferred to open-front enclosure and dissolved in 10 mL of 6 M HCl, transferred to 125 mL polypropylene bottle and diluted using 0.1 M HCl to the desired weight, swirled, and aliquoted.
	Pu	
Separation Technique	U	U separated using ~10 mg aliquots of Pu solution using Lewatit MP5080 anion exchange resin. Methodology: ~1mL 12 M HCl - 0.2 M HI to the sample, add ~8mL 12M HCl-0.2M HI to the column, add ~4mL of 0.1M HCl to elute the Uranium. Uranium is collected into a glass wheaton vial.
	Pu	Directly measured.
	Am	Am fractions separated using Lewatit MP5080 anion exchange resin. Methodology: Add ~1mL of 12M HCl to the sample, collect Am by adding ~4mL of 12M HCl to the column.
Quantification	U	Isotopic abundance characterized by TIMS, U assay characterized by IDMS using ^{233}U calibrated with CRM 111
	Pu	Isotopic abundance characterized by TIMS, Pu assay characterized by CPC
	Am	Am assay characterized by IDMS using ^{243}Am spike
Analytical Instrumentation	U	U and Pu isotope ratio measurements performed on Isoprobe-T; IDMS measurements performed on VG (Sector 54) instrument
	Pu	
	Am	VG (Sector 54) instrument

2

3

Table 2a: Details on the Analytical Methodology at LANL (C-AAC) contd.

Analytical Method	U	Isotope ratio measurements used mixed array detection strategies incorporating both 10^{11} and 10^{12} Ω amplifiers using Faraday detection system. Total evaporation methodology [40-42] was utilized for IDMS measurements, except Am assay which used ion counting strategies.
	Pu	
	Am	
Instrument Calibration	U	1 ug/g U was used to tune the instruments with maximum sensitivity and low signal variation; IRM-199 was used for mass bias correction; CRM 126-A used to check abundance sensitivity and mass bias.
	Pu	
QC Standard	U	CRM 126-A used as U-Iso and Pu-Iso accuracy standard. U930 used as QC standard for U-Iso measurements. For Pu-IDMS, a Pu Reference standard spiked with CRM 126-A was analyzed, and for U-IDMS a U reference sample was analyzed.
	Pu	
Sample consumption	U/Pu	Per analysis, the following amounts of the samples were consumed: 200 ng U and 30 ng Pu (isotopics).
Corrections Applied	U/Pu	Isotope ratio data were corrected for mass bias, peak tailing, method blank.
Abundance Sensitivity	U/Pu	Determined using NU isotopic standard CRM 112-A.
Analytical Blank	U	Ranged from 1.4 to 216.9 ppt.
	Pu	< 2 ppt Pu. Results are corrected using this measured blank.
	Am	Am: < 10 ppq ^{243}Am.

Table 2b: Details on the Analytical Methodology at C-NR

Sample Preparation	U	A 1 ug Pu aliquot of the ”working solutions” of the Pu standards (see below) was purified for U assay. A separate 1 ug Pu aliquot used for U isotope ratios. Duplicate aliquots of the standards were purified and analyzed.
	Pu	Process blanks were introduced at the start of the dissolution of the Pu standards. CRMs 136, 137, and 138 were dissolved in 8M HNO_3 and diluted to primary solutions with concentrations of ~500 ug Pu per gram (of solution) using 3M HNO_3 + 0.005M HF. CRM 126A was dissolved in 6M HCl and diluted to a primary solution of ~1000 ug Pu per gram using 3M HCl + 0.005M HF. "Working solutions" with concentrations of ~ 5 ug Pu per gram of solution were made by diluting with 3M HNO_3 + 0.005M HF for CRMs 136, 137, and 138 and 3M HCl + 0.005M HF for CRM 126A. The ”working solutions” were transferred to a radiological hood with a lower blank for chemical processing/separation and diluted using serial dilutions to create tertiary dilutions with picogram-level Pu concentrations. Duplicate aliquots of the standards were purified and analyzed.
	Am	A dilution, at ~ 20 ng Pu/g, was prepared from the ~ 5 ug Pu / g ”working solution”. Picogram-level Am aliquots were taken for purification. Duplicate aliquots of the standards were purified and analyzed.
Separation Technique	U	The U was purified using two LaF_3 precipitations of a 1 ug Pu aliquot. Following LaF_3 precipitations, a final purification was done using a Eichrom UTEVA column in 3M HNO_3, with 9M HCl and 5M HCl washes, and eluted from the resin using 0.1M HCl.
	Pu	Picogram-level Pu aliquots were taken from tertiary dilutions of the standards and Am and U were removed using a 2-column purification using BioRad AG-MP-1 resin. The Pu was loaded in 8M HNO_3 + $NaNO_2$, the column was washed with HCl and 8M HNO_3, and then Pu was eluted using HBr.
	Am	Am was separated from a 5 ng total Pu aliquot using a BioRad AG-1x8 resin 4-column purification. The first and second columns are an 8M HNO_3 column to remove Pu, the third column is a 9M HCl column to remove U, and the final purification sorbs Am in acetone-HCl for final purification and elutes in HCl.

Table 2b: Details on the Analytical Methodology at C-NR contd.

Quantification	U	Abundances of ^{234}U, ^{235}U, ^{236}U, and ^{238}U were quantified by IDMS using an in-house ^{233}U spike calibrated (every six months) against CRM U960.
	Pu	Abundances of ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu were quantified by IDMS using a ^{242}Pu spike made from SRM 4334G calibrated (yearly) against IRMM-081a ^{239}Pu standard.
	Am	Abundances of ^{241}Am was quantified by IDMS using a ^{243}Am spike made from SRM 4332E. The ^{243}Am spike concentration is calibrated yearly using SRM 4322C ^{241}Am standard.
Analytical Instrumentation	U	U assay and isotopic measurements were made by MC-ICP-MS using a Thermo Neptune Plus.
	Pu	Pu assay measurements were made by MC-ICP-MS using a Thermo Neptune Plus. Pu isotopic abundances were measured by MICTE-TIMS using an IsotopX Phoenix.
	Am	^{241}Am assay measurements were made using a Thermo Element XR single-collector magnetic sector ICPMS
Analytical Method	U	U IDMS used a static routine with ^{233}U and ^{235}U on Faradays. U isotope measurements used a static routine with ^{233}U, ^{234}U, ^{236}U, and ^{238}U on ion counters and ^{235}U on a Faraday collector.
	Pu	Pu IDMS used a static routine with ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu all measured on ion-counters. Pu isotope compositions measured by MICTE-TIMS.
	Am	^{241}Am assay measurements were made using a Thermo Element XR single-collector magnetic sector ICPMS
Instrument Calibration	U	CRM U970 and CRM U500 as mass bias and gain standards.
	Pu	For Pu IDMS, IRMM-081A used as a QC standard. Pu isotope measurements used IRMM-081A as a QC standard.
	Am	Am IDMS used CEA ^{243}Am as a QC – consensus value from LLNL-LANL-ORNL round robin was used.

Table 2c: Details on the analytical methodology at JRC

Sample Preparation	U	A master solution of ~20 mg Pu sulfate standard in 15 ml of 8 M HNO_3 in a Teflon vial was prepared by heating on a hot plate set at 80 ºC for 12 h. The CRM 126-A Pu metal was cleaned by the electric method prior to dissolution. The whole sample was dissolved cautiously in 12 M HCl on a hot plate for 8 h to yield a solution with ~2 mg/g Pu concentration.
	Pu	
Separation Technique	U	U was separated from 5-20 µg of Pu using TEVA Resin. Conditions: 3 M HNO_3/0.02 M $NH_2.OH.HNO_3$ added to the sample, + 60 µl 3 M $NaNO_2$. Wash: 3 ml 3 M HNO_3, load and wash were collected in a PE vial.
	Pu	Directly measured. Sample taken in the same time as for U and Am
	Am	Gamma spectrometry was also used to measure the $^{241}Am/^{241}Pu$ ratio. The $^{235}U/^{239}Pu$ and $^{236}U/^{240}Pu$ ages were measured directly without chemical separation.
Quantification	U	The ^{234}U, ^{235}U, ^{236}U, and ^{238}U isotopic abundances were quantified by IDMS using a ^{233}U spike (in-house ^{233}U isotopic standard was calibrated against EC NRM 101 U metal by TIMS).
	Pu	The ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu isotopic abundances were quantified by IDMS using a ^{242}Pu spike (IRMM-085).
	Am	The ^{241}Am isotopic abundance was quantified by IDMS using a ^{243}Am spike (NIST 4332E).
Analytical Instrumentation	U	Element 2 (single collector) HR-ICP-MS attached to a glove-box.
	Pu	
	Am	Element 2 (single collector) HR-ICP-MS attached to a glove-box, HPGe γ-spectrometry

Table 2c: Details on the Analytical Methodology at JRC cont'd.

Analytical Method	U	Sequential determination on the SEM (ion counting) detector of the Element 2 HR-ICP-MS. Th and Np levels were measured/checked.
	Pu	
	Am	
Instrument Calibration	U	1 ng/g U was used to tune the instruments with maximum sensitivity and low signal variation; NBS U-010 was used to measure the mass bias; Unat was used (100 ng/g concentration) to check the abundance sensitivity.
	Pu	
QC Standard	U	IRMM-185 was used to check accuracy. Results were compared with certified values and TIMS results.
	Pu	
Sample consumption (per analysis)	U	1 to 5 ng U.
	Pu	2 ng Pu.
Corrections Applied	U/Pu/Am	Isotope ratio data were corrected for mass bias, peak tailing, method blank.
Abundance Sensitivity	U/Pu/Am	Natural U at a concentration of 100 ng/g was used to measure the $(m+2)/m$ value.
Analytical Blank	U	< 1 ppt @^{234}U, ^{235}U, ^{236}U; ^{238}U < 20 ppt). Results are corrected using this measured blank.
	Pu	< 2 ppt Pu. Results are corrected using this measured blank.
	Am	Am: < 10 ppq ^{243}Am.

Table 2d: Details on the Analytical Methodology at LLNL (for additional info see [43])

Sample Preparation	U	Aliquots of 10 or 20 ppm solutions were used for U.
	Pu	Master solutions of CRM 136, 137 and 138 were prepared by dissolving ~150 mg of Pu sulfate in 2 M HNO3, and serially diluted with 0.5 M HNO_3, to produce 10 ppm (Pu element) dilutions for CRM 136 and 137, and a 20 ppm (Pu element) dilution of CRM 138. These solutions were further diluted to 20 ppb, and aliquots of the 20 ppb dilutions were used for Pu ID analysis. CRM126A was gravimetrically dissolved and diluted to concentrations of 10 ppm and 175 ppb.
	Am	Am analyses utilized 20 ppb or 175 ppb dilutions.
Separation Technique	U	Aliquots of ~ 10-20 µg of Pu were spiked with a ^{233}U for U assay by IDMS. U was separated from Pu using a LaF_3 precipitation (Pu is incorporated into a fluoride precipitate while U remains in the supernate). The supernate was decanted, dried, dissolved in 4 M HNO_3, and loaded on a 0.6 mL TEVA resin bead. Uranium was eluted from the TEVA resin by rinsing with 4 M HNO_3. Final purification of U used a 0.6 mL UTEVA resin bed. The sample in 4 M HNO_3 is loaded on the column; rinsed with 4 M HNO_3, 9 M HCl and 5 M HCl, and then U was eluted in 0.1 M HCl.
	Pu	A weighed aliquot was spiked with ^{244}Pu for assay by IDMS. Plutonium was purified using a two-column procedure. First, Pu was dissolved in 8 M HNO_3 + $NaNO_2$ and loaded on 1.4 mL AG 1-X8 anion resin bed. The column was rinsed with 8 M HNO_3 and 9 M HCl. Plutonium was eluted using 9 M HCl + HI. For the second column, Pu was dissolved in 4 M HNO_3 + $NaNO_2$ and loaded on a 0.6 mL TEVA-resin bed. The column was rinsed with 4 M HNO_3 and then 9 M HCl. The Pu was eluted in 9 M HCl, followed by 0.1 M HCl + 0.005 M HF and then 0.1 M HCl + HI.
	Am	Approximately 30 ng of Pu was spiked with ^{243}Am for Am assay by IDMS. A three stage anion exchange purification was used. First, the sample in 8 M HNO_3 was loaded on a 1.4 mL AG-1X8 anion resin bed, and Am was eluted by rinsing with 8 M HNO_3. Next, the sample was dissolved in 9 M HCl + HNO_3, and loaded on a 1.0 mL AG 1-X8 anion resin bead. The Am was eluted by rinsing with 9 M HCl. Last, Am was dissolved in a 75:25 mixture of acetone and concentrated HCl and loaded on a 1.0 mL AG 1-X8 anion resin bead. The column was rinsed in the acetone-HCl solution, and then Am was eluted in concentrated HCl.

Table 2d: Details on the Analytical Methodology at LLNL contd.

Quantification	U	U isotopic abundances were quantified by IDMS using an in-house ^{233}U spike calibrated against CRM 112A.
	Pu	Abundances of ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu were quantified by IDMS using a ^{242}Pu spike calibrated against CRM 126-A. ^{238}Pu abundance was quantified by α-spectrometry (Ortec ULTRA-AS);
	Am	^{241}Am quantified by IDMS using a ^{243}Am spike made from SRM 4332D
Analytical Instrumentation	U/Pu/Am	Nu Plasma HR MC-ICP-MS, alpha-spectrometry using Ortec ULTRA-AS ion-implanted Si detectors
Analytical Method	U	Static analysis routine with all masses on Faradays;
	Pu	Two-cycle mixed collector array (^{239}Pu and ^{240}Pu measured on Faraday and ^{240}Pu, ^{241}Pu, ^{242}Pu, and ^{244}Pu measured on ion counters); Alpha-spectrometry for ^{238}Pu using Ortec ULTRA-AS ion-implanted Si detectors;
	Am	Static multi-ion counting routine measuring ^{241}Am and ^{243}Am simultaneously; ^{243}Am SRM 4332D
Instrument Calibration	U	CRM U010 used for U mass bias corrections
	Pu	CRM 137 used for mass bias and collector gain corrections; For α-spectrometry, ^{238}Pu/^{239}Pu ratios were calculated from background-subtracted integrals of peaks associated with ^{238}Pu (5.499 and 5.456 MeV) and ^{240}Pu + ^{239}Pu (5.168, 5.124, 5.157, 5.144, 5.106 MeV), along with the ^{240}Pu/^{239}Pu determined by mass spectrometry
	Am	CRM U010 was used as a reference standard for correction of instrumental mass bias and relative detector gains
QC Standard	U/Pu	CRM U630/ CRM 138, 126-A, IRMM-086
Sample consumption (per analysis)	U/ Pu	40 µg Pu for U isotope composition; 10-20 µg Pu for U-IDMS; 20 ng Pu for Pu-IDMS
Corrections Applied	U/Pu/Am	mass bias, peak tailing, instrument background, and collector gains

Table 3: Model purification dates calculated from the different chronometers using JRC data

Chronometer	Measured Daughter/Parent Atom Ratio*	*Uc* (*k* = 2)	Model Purification Date**	*Uc* (*k* =2) years	Measured Daughter/Parent Atom Ratio	*Uc* (*k* = 2)	Model Purification Date*	*Uc* (*k* =2) years
	CRM 136				CRM 137			
$^{234}U/^{238}Pu$	0.41264	0.0132	10/15/1970	1.2	0.3955	0.027	5/22/1972	2.5
$^{235}U/^{239}Pu$	1.2608E-3	1.31E-5	8/18/1970	0.46	1.2494E-3	2.82E-6	1/15/1971	0.11
$^{236}U/^{240}Pu$	4.5893E-3	6.16E-5	2/13/1971	0.6	4.6187E-3	1.65E-5	10/30/1970	0.18
$^{241}Am/^{241}Pu$	7.1878	0.154	11/10/1970	0.65	7.0759	0.562	2/24/1971	0.52
	CRM 138				CRM 126-A			
$^{234}U/^{238}Pu$	0.49017	0.017	12/28/1963	1.5	0.14023	8.04E-3	7/5/2000	0.9
$^{235}U/^{239}Pu$	1.4494E-3	1.55E-5	12/20/1963	0.55	4.857E-4	8.58E-5	3/17/2000	3
$^{236}U/^{240}Pu$	5.3002E-3	2.54E-5	4/23/1963	0.27	1.8123E-3	1.63E-4	1/4/2000	1.6
$^{241}Am/^{241}Pu$	10.259	0.21	1/26/1963	0.49	1.2017	0.0316	11/24/2000	0.38

*The daughter/parent ratios shown are w.r.t a reference date of March 11, 2015.

**Dates are specified in the mm/dd/yyyy format

Table 4: Model purification dates calculated from the different chronometers using C-AAC (LANL) data

Chronometer	Measured Daughter/Parent Atom Ratio*	Uc (k = 2)	Model Purification Date**	Uc (k =2) years	Measured Daughter/Parent Atom Ratio	Uc (k = 2)	Model Purification Date*	Uc (k =2) years
	CRM 136				CRM 137			
$^{234}U/^{238}Pu$	0.4374	0.0012	5/31/1970	0.12	0.4318	0.0042	11/26/1970	0.37
$^{235}U/^{239}Pu$	1.3151E-3	3.1E-6	8/12/1970	0.12	1.3024E-3	2.7E-6	1/20/1971	0.11
$^{236}U/^{240}Pu$	4.846E-3	1.3E-5	7/25/1970	0.13	4.799E-3	1.1E-5	1/2/1971	0.12
$^{238}U/^{242}Pu$	8.54E-5	1.7E-6	2/14/1970	0.97	8.46E-5	1.9E-6	8/16/1970	1.1
$^{241}Am\ (\gamma)/^{241}Pu$	8.49	0.26	12/29/1968	0.59	8.29	0.25	6/11/1969	0.61
$^{241}Am/^{241}Pu$ (MS)	7.915	0.088	4/25/1970	0.21	7.71	0.11	10/21/1970	0.28
	CRM 138				CRM 126-A			
$^{234}U/^{238}Pu$	0.545	0.029	4/28/1961	2.4	0.1204	4.6E-3	4/15/2001	0.82
$^{235}U/^{239}Pu$	1.4701E-3	3.5E-6	3/23/1965	0.14	4.0607E-4	3.5E-7	7/19/2001	0.034
$^{236}U/^{240}Pu$	5.418E-3	1.3E-5	3/8/1965	0.14	1.4949E-3	1.6E-6	7/12/2001	0.034
$^{238}U/^{242}Pu$	9.77E-5	2.5E-6	6/4/1963	1.4	2.9E-5	2.7E-6	12/31/1999	1.5
$^{241}Am(\gamma)/^{241}Pu$	12.13	0.37	1/31/1962	0.62	1.062	0.098	12/19/2000	1
$^{241}Am/^{241}Pu$ (MS)	11.64	0.15	11/23/1962	0.26	n.a	n.a.	n.a.	n.a.

*The daughter/parent ratios shown are w.r.t a reference date of April 28, 2016. **Dates are specified in the mm/dd/yyyy format

Table 5: Model purification dates calculated from the different chronometers using C-NR (LANL) data

Chronometer	Measured Daughter/Parent Atom Ratio*	Uc (k = 2)	Model Purification Date**	Uc (k =2) years	Measured Daughter/Parent Atom Ratio	Uc (k = 2)	Model Purification Date*	Uc (k =2) years
	CRM 136				CRM 137			
$^{234}U/^{238}Pu$	0.450	0.012	1/27/1971	1.09	0.442	0.0095	9/23/1971	0.90
$^{235}U/^{239}Pu$	0.001368	0.000013	7/1/1970	0.46	0.001350	0.000010	2/13/1971	0.36
$^{236}U/^{240}Pu$	0.005067	0.000059	3/9/1970	0.58	0.005015	0.000047	9/4/1970	0.48
$^{241}Am/^{241}Pu$	8.54	0.16	6/22/1970	0.35	8.36	0.14	11/24/1970	0.31
	CRM 138				CRM 126-A			
$^{234}U/^{238}Pu$	0.505	0.026	4/30/1966	2.18	0.134	0.011	2/4/2002	1.28
$^{235}U/^{239}Pu$	0.001586	0.000029	12/4/1962	0.99	0.000476	0.000019	6/23/2001	0.67
$^{236}U/^{240}Pu$	0.00588	0.00012	7/7/1962	1.11	0.001759	0.000073	5/25/2001	0.69
$^{241}Am/^{241}Pu$	12.565	0.345	12/21/1962	0.55	1.218	0.053	5/29/2001	0.51

*The daughter/parent ratios shown are w.r.t a reference date of January 15, 2018.

**Dates are specified in the mm/dd/yyyy format

Table 6: Model purification dates calculated from the different chronometers using LLNL data

Chronometer	Measured Daughter/Parent Atom Ratio*	Uc (k = 2)	Model Purification Date**	Uc (k =2) years	Measured Daughter/Parent Atom Ratio	Uc (k = 2)	Model Purification Date*	Uc (k =2) years
	CRM 136				CRM 137			
$^{234}U/^{238}Pu$	0.4563	0.0068	10/24/1969	0.59	0.4421	0.0061	1/17/1971	0.54
$^{235}U/^{239}Pu$	1.3600E-3	1.00E-5	2/19/1970	0.37	1.3390E-3	1.10E-5	11/20/1970	0.37
$^{236}U/^{240}Pu$	5.0120E-3	4.10E-5	1/25/1970	0.40	4.9310E-3	3.80E-5	11/2/1970	0.38
$^{241}Am/^{241}Pu$	8.53	0.17	11/3/1969	0.39	8.24	0.17	7/1/1970	0.39
	CRM 138				CRM 126-A			
$^{234}U/^{238}Pu$	0.512	0.012	10/4/1964	1.02	0.1323	3.30E-3	8/31/2001	0.37
$^{235}U/^{239}Pu$	1.504E-3	1.50E-5	2/18/1965	0.53	4.540E-4	3.00E-6	8/12/2001	0.10
$^{236}U/^{240}Pu$	5.549E-3	6.10E-5	1/5/1965	0.59	1.673E-3	1.30E-5	7/28/2001	0.13
$^{241}Am/^{241}Pu$	12.47	0.30	6/17/1962	0.47	1.188	0.032	1/14/2001	0.30

*The daughter/parent ratios shown are w.r.t a reference date of May 24, 2017.

**Dates are specified in the mm/dd/yyyy format

Table 7: Consensus value for the model purification ages for the Pu standards

Standard	Model Purification Date	Uncertainty (days)[€]	Δ from production age (days)	Chronometers included
CRM 136	5/23/1970	146	55	$^{234}U/^{238}Pu$, $^{235}U/^{239}Pu$, $^{236}U/^{240}Pu$, $^{241}Am/^{241}Pu$
CRM 137	12/25/1970	295	102	$^{234}U/^{238}Pu$, $^{235}U/^{239}Pu$, $^{236}U/^{240}Pu$, $^{241}Am/^{241}Pu$
CRM 138	10/11/1963	536	27	$^{234}U/^{238}Pu$, $^{235}U/^{239}Pu$, $^{236}U/^{240}Pu$, $^{241}Am/^{241}Pu$
CRM 126-A	3/14/2001	100	122	$^{234}U/^{238}Pu$, $^{235}U/^{239}Pu$, $^{236}U/^{240}Pu$, $^{241}Am/^{241}Pu$

[€]Uncertainties shown are the expanded uncertainties (= 2* standard deviation) of the model purification dates estimated by combining all data from all chronometry systems. With the exception of CRM 126-A, in all cases, within the uncertainties suggested, the "Model Purification Date" overlap the archived production date from the reference material producer (NBL).

Table 8: Uncertainty budget for the model purification dates (C-AAC data) from the different chronometers.

Chronometer	Standard			
	CRM 126-A	**CRM 136**	**CRM 137**	**CRM 138**
^{234}U/^{238}Pu	99.8 % ^{238}Pu abundance	20% ^{238}Pu half-life 13% ^{238}Pu abundance 16% Pu assay 44% U assay 7% ^{234}U abundance	2% ^{238}Pu half-life 90% ^{238}Pu abundance 1% Pu assay 4% U assay 4% ^{234}U abundance	97 % ^{238}Pu abundance 3% ^{234}U abundance
^{235}U/^{239}Pu	68% ^{239}Pu half-life 31% U assay	21% ^{239}Pu half-life 20% Pu assay 55% U assay 2% ^{239}Pu abundance	26% ^{239}Pu half-life 9% Pu assay 59% U assay 6% ^{235}U abundance	21% ^{239}Pu half-life 20% Pu assay 56% U assay
^{236}U/^{240}Pu	50% ^{240}Pu half-life 31% U assay 16% ^{236}U abundance 3% ^{240}Pu abundance	15% ^{240}Pu half-life 18% Pu assay 51% U assay 8% ^{240}Pu abundance 8% ^{236}U abundance	17% ^{240}Pu half-life 8% Pu assay 53% U assay 15% ^{240}Pu abundance 7% ^{236}U abundance	16% ^{240}Pu half-life 20% Pu assay 55% U assay 5% ^{240}Pu abundance 5% ^{236}U abundance
^{241}Am/^{241}Pu	99.8% Am assay (γ)	Am assay (γ, 99.6%) Am assay (MS, 97%)	Am assay (90%, γ) (55%, MS) ^{241}Pu (9%, γ) (45%, MS)	Am assay (95%, g) (70%, MS) ^{241}Pu abundance (5%, g) (28%, MS)

Table 9: Uncertainty budget for the model ages (C-NR data) measured from the different chronometers.*

Chronometer	Standard			
	CRM 126-A	CRM 136	CRM 137	CRM 138
$^{234}U/^{238}Pu$	99.8 % ^{238}Pu abundance	2% ^{238}Pu half-life 90% ^{238}Pu abundance 8% ^{234}U abundance	1% ^{238}Pu half-life 91% ^{238}Pu abundance 7% ^{234}U abundance	99 % ^{238}Pu abundance
$^{235}U/^{239}Pu$	100% ^{239}Pu abundance	5% ^{239}Pu half-life 90% ^{239}Pu abundance 5% ^{235}U abundance	4% ^{239}Pu half-life 90% ^{239}Pu abundance 6% ^{235}U abundance	1.7% ^{239}Pu half-life 97% ^{239}Pu abundance 1.6% ^{235}U abundance
$^{236}U/^{240}Pu$	1% ^{236}U abundance 99% ^{240}Pu abundance	3% ^{240}Pu half-life 81% ^{240}Pu abundance 15% ^{236}U abundance	3% ^{240}Pu half-life 80% ^{240}Pu abundance 16% ^{236}U abundance	1% ^{240}Pu half-life 94% ^{240}Pu abundance 5% ^{236}U abundance
$^{241}Am/^{241}Pu$	5% ^{241}Am abundance 94% ^{241}Pu abundance	37% ^{241}Am abundance 58% ^{241}Pu abundance 5% ^{241}Pu half-life	45% ^{241}Am abundance 49% ^{241}Pu abundance 6% ^{241}Pu half-life	24% ^{241}Am abundance 72% ^{241}Pu abundance 4% ^{241}Pu half-life

* Pu assay is the dominant contributor to uncertainties in C-NR data, as a ^{242}Pu activity tracer that is not highly pure is used. Spike subtraction adds uncertainty from converting activity of the tracer to mass and from the calibration of this less than ideal tracer (ideal tracer would be ^{244}Pu).

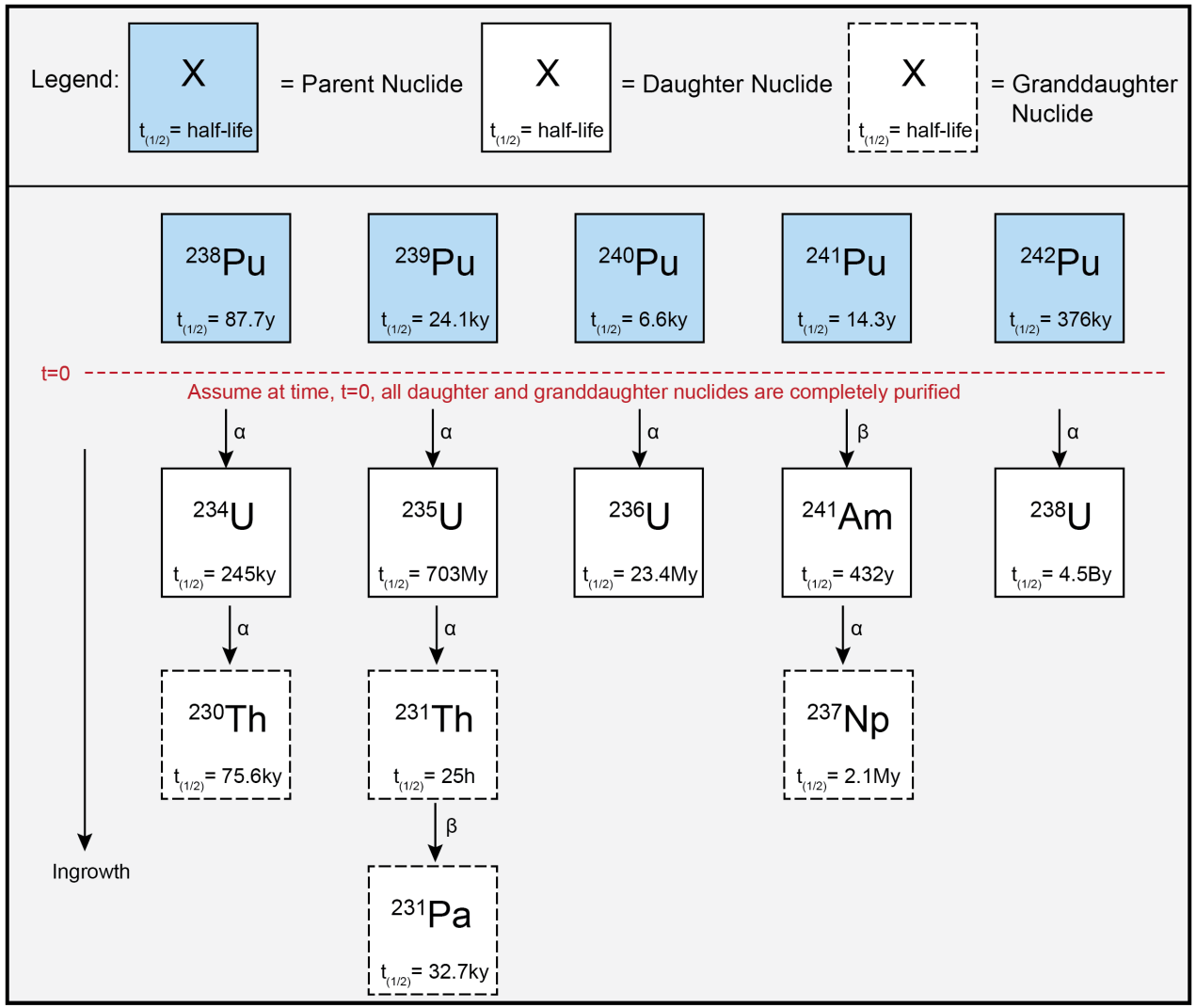

Figure 1: Decay schematics, starting with the Pu parent isotopes, investigated in the present study.

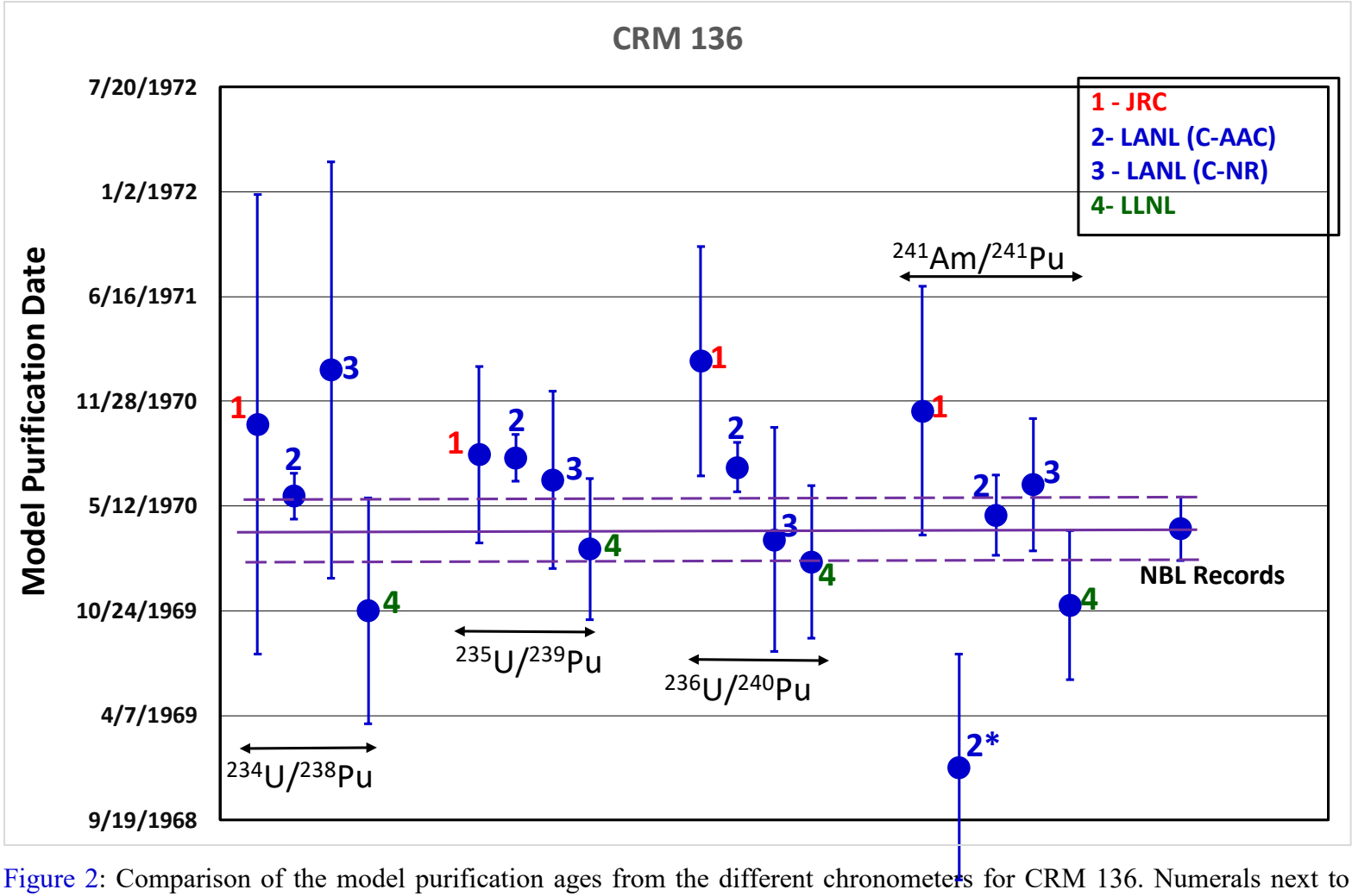

Figure 2: Comparison of the model purification ages from the different chronometers for CRM 136. Numerals next to the symbols indicate the facility: 1 represent JRC, 2 represent C-AAC (LANL), 3 indicate C-NR (LANL), and 4 indicate LLNL. For the $^{241}Am/^{241}Pu$ age from C-AAC, two values represented by 2 and 2* represent TIMS and γ-spec data, respectively.

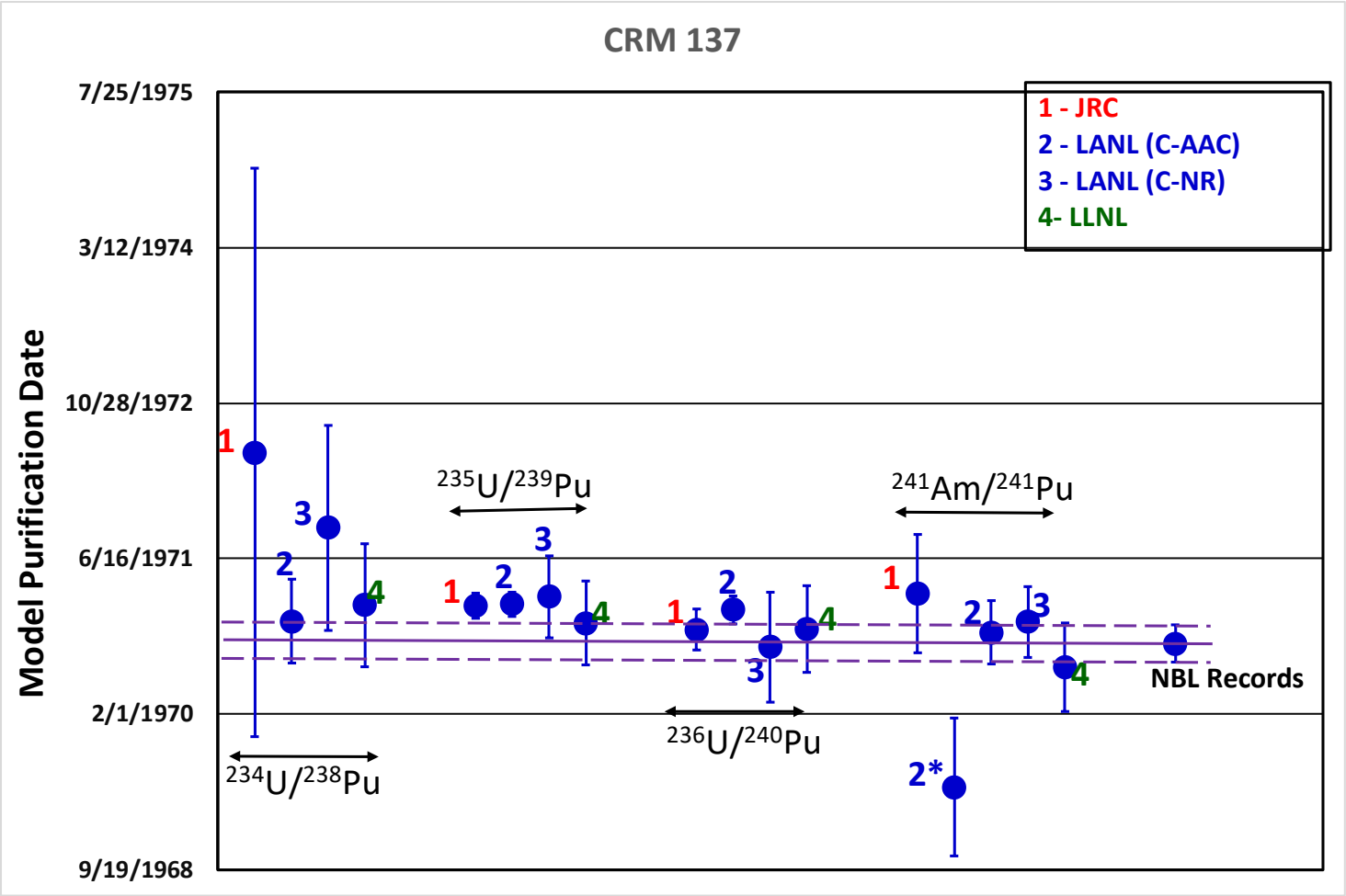

Figure 3: Comparison of the ages from the different chronometers for CRM 137. Numerals next to the symbols indicate the facility: 1 represent JRC, 2 represent C-AAC (LANL), 3 indicate C-NR (LANL), and 4 indicate LLNL. For the $^{241}Am/^{241}Pu$ age from C-AAC, two values represented by 2 and 2* represent TIMS and γ-spec data, respectively.

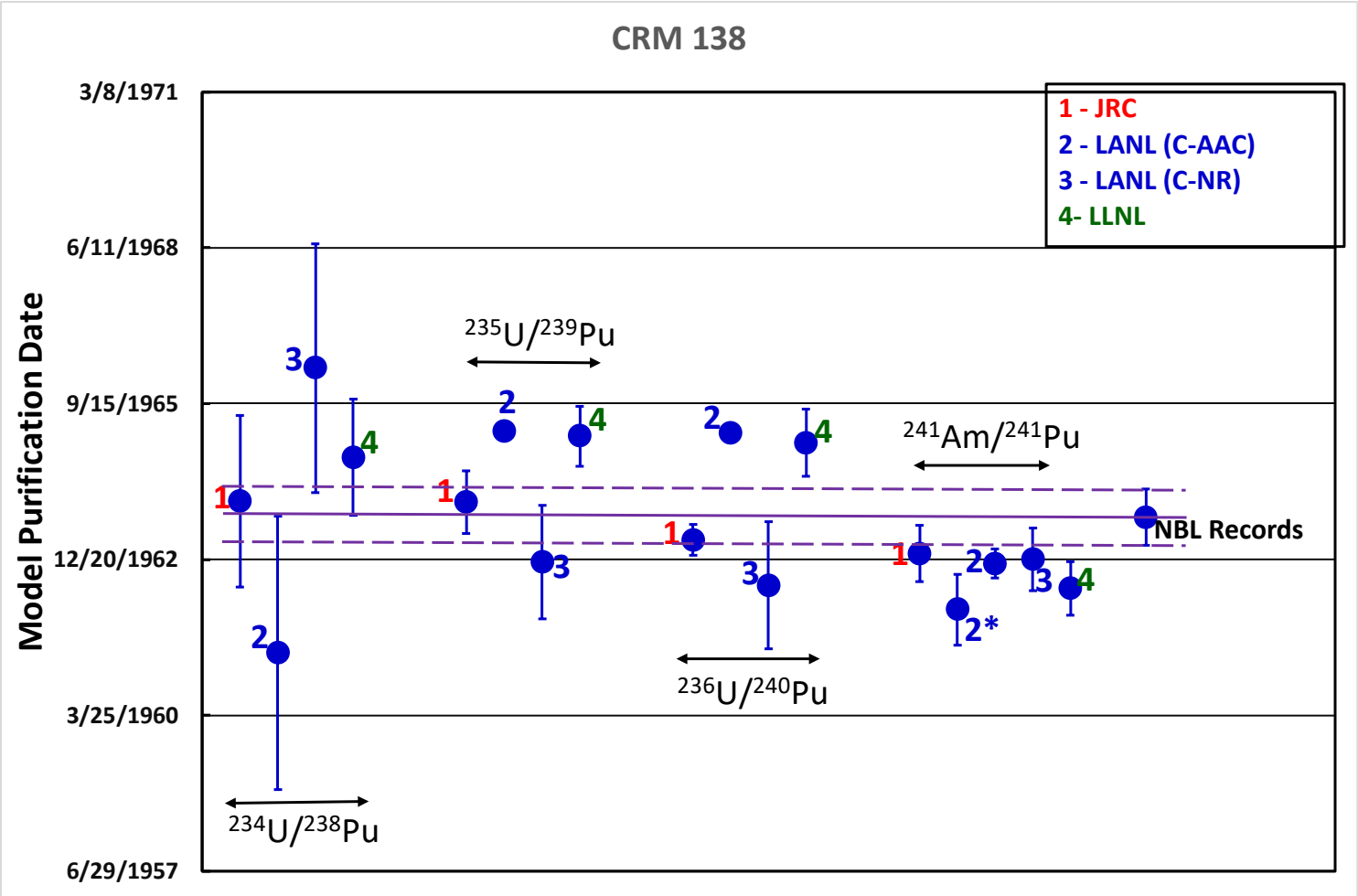

Figure 4: Comparison of the ages from the different chronometers for CRM 138. Numerals next to the symbols indicate the facility: 1 represent JRC, 2 represent C-AAC (LANL), 3 indicate C-NR (LANL), and 4 indicate LLNL. For the $^{241}Am/^{241}Pu$ age from C-AAC, two values represented by 2 and 2* represent TIMS and γ-spec data, respectively.

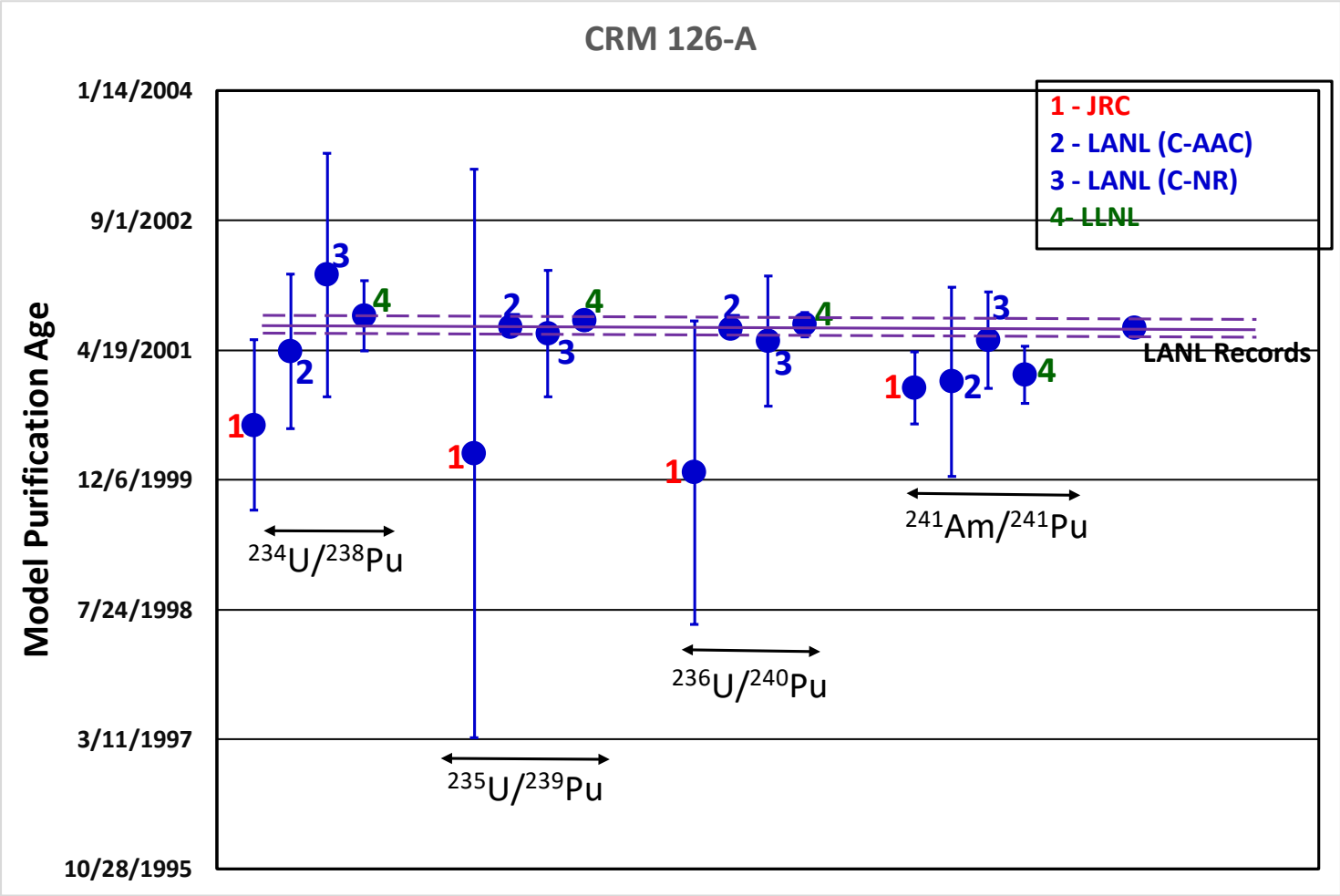

Figure 5: Comparison of the ages from the different chronometers for CRM 126-A. Numerals next to the symbols indicate the facility: 1 represent JRC, 2 represent C-AAC (LANL), 3 indicate C-NR (LANL), and 4 indicate LLNL.