Supplementary Information

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

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ABSTRACT: A brief history of the primary plutonium isotopic reference materials investigated here is included. Table S1 shows the certified isotope ratios of the Pu certified reference materials investigated here. Figure S1 shows the decay schematics utilized in this investigation for estimating the model purification (radio-chronometric) ages. Uncertainty budgets for the different radio-chronometric ages using C-AAC and C-NR data are shown as Tables S2 and S3.

Brief History of the Plutonium Isotopic Standards

Three of the four Pu isotopic reference materials investigated here were originally named by National Bureau of Standards (NBS – US certifying body and predecessor to National Institute of Standard and Technology, NIST) as Standard Reference Materials (SRMs) 946, 947, and 948[31-33]. 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[34], 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[a]. The material was purified via ion exchange chemistry between March and April 1970 (to remove americium and impurities), and converted to plutonium sulfate tetrahydrate[35]. 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[a]. 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[31-32].

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[35] 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 purification for CRM 126-A material appears to have occurred at LANL in early July 2001.

Table S1 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, SRMs 946, 947, and 948 is referenced using their modern names CRMs 136, 137, and 138.

Table S1: 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[b] (the uncertainty estimates shown above, for the certified isotope ratios, are calculated following a methodology that correctly incorporates such correlations[b]).

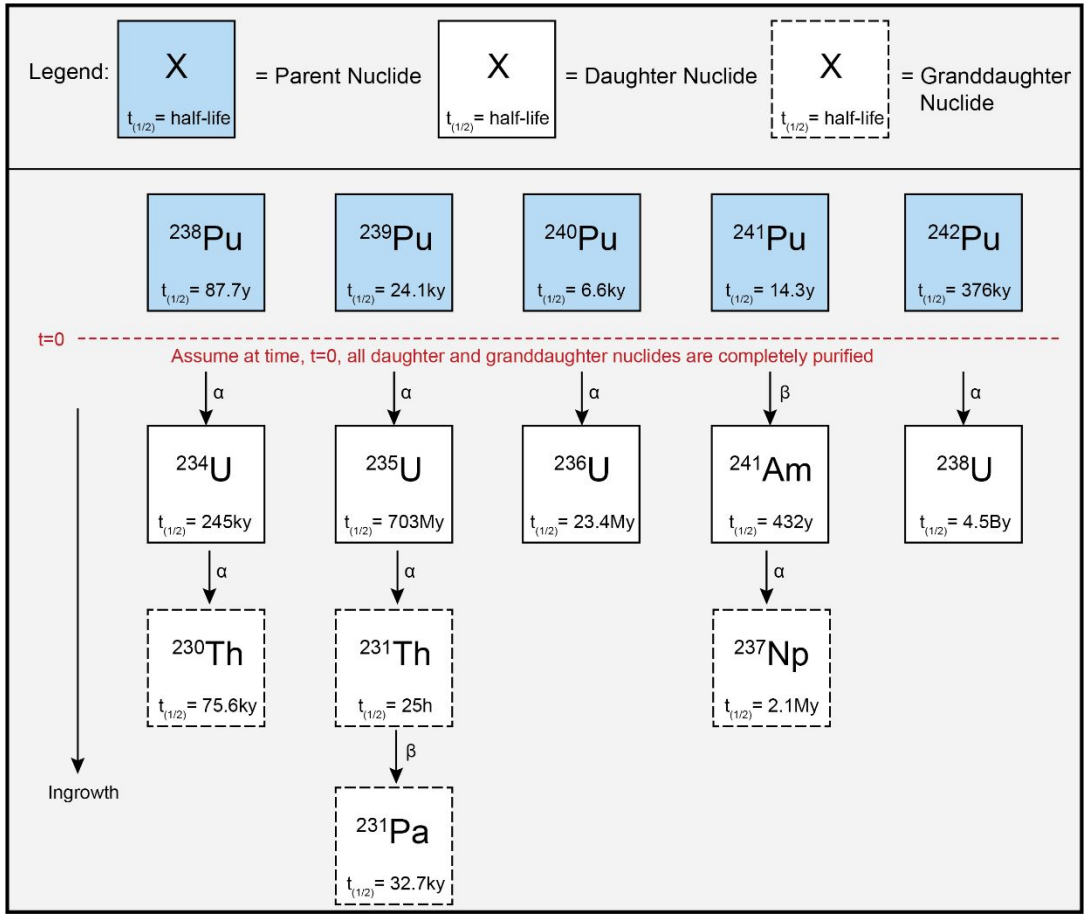

Figure S1: Decay schematics, starting with the Pu parent isotopes, investigated in the present study. Half-lives applicable to the decay are indicated. Even though 2nd and 3rd generation chronometers are shown, only the primary chronometric pairs are investigated in this study.

Table S2: 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 S3: 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).

[a]Nash K. L.; Lumetta G. Standard and Advanced Separation: PUREX Processes for Nuclear Fuel Reprocessing 2011, Woodhead Publishing, Knovel E-Books (Knovel Corporation)

[b]Mathew K. J.; Thomas M. Advances in Nuclear Nonproliferation Technology & Policy Conference, 2016, American Nuclear Society, Santa Fe, NM, USA, LA-UR-16-22161.