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Anal. Chem., 2009, 81 (4), 1297-1306• DOI: 10.1021/ac802286a • Publication Date (Web): 16 January 2009

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Nuclear Archeology in a Bottle: Evidence of Pre-Trinity U.S. Weapons Activities from a Waste Burial Site

Jon M. Schwantes,* Matthew Douglas, Steven E. Bonde, James D. Briggs, Orville T. Farmer, Lawrence R. Greenwood, Elwood A. Lepel, Christopher R. Orton, John F. Wacker, and Andrzej T. Luksic

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During World War II, the Hanford Site in Washington became the location for U.S. plutonium production. In 2004, a bottle containing a sample of plutonium was recovered from a Hanford waste trench. Here, state-ofthe-art instrumental analyses, reactor model simulations, and investigative science techniques were used to provide insights as to the origin of this unknown sample, a process collectively termed as nuclear archeology. Isotopic age dating conducted on the sample in 2007 indicated the sample was separated from the spent fuel 61.6 ± 4.5 years earlier. The isotope ²²Na, a detectable product of a secondary nuclear reaction, proved useful as a powerful tool for nuclear forensic analysis as (1) an easily detectable signifier of the presence of α emitting actinides, (2) an indicator of sample splitting, and (3) a measure of the time since sample splitting. Analytical results of minor actinide isotopes and reactor model simulations confirmed the material originated from the X-10 reactor in Oak Ridge, TN. Corroborated by historical documents, we concluded this sample was part of the first batch of Pu separated at T-Plant, Hanford, the world's first industrial-scale reprocessing facility, on December 9, 1944. This sample represents the oldest known collection of man-made ²³⁹Pu in the world.

The frequency of smuggling events involving radioactive materials is supply driven and is on the rise world-wide.^{1,2} While

special nuclear materials from the nuclear fuel cycle have not significantly contributed to this increasing trend to date, it is likely that with the current nuclear renaissance and greater access to these materials by the public, smuggling events involving fissionable materials may rise in the near future. Perhaps the most effective tool investigators have against this type of smuggling is the successful application of nuclear forensic science.³ Nuclear forensics is defined as the science of identifying the source, pointof-origin, and/or routes of transit of nuclear and radiological materials associated with illegal activities for ultimately contributing to the prosecution of persons responsible for those activities.⁴ In many respects, the goals of nuclear archeology are identical to those of nuclear forensics, without the added constraints specifically associated with legal prosecution. As such, studies of nuclear archeology serve as an excellent means for advancing the science and demonstrating the capabilities of the nuclear forensics community. Moreover, depending upon the pedigree of the artifacts studied, fully characterized finds representing specific end members of various processes or reactors may be of direct use to forensics experts for comparative purposes against real interdicted sample materials of unknown origin.⁵⁻⁷ This work provides the public a rare glimpse at a real-world example of the science behind modern-day nuclear forensics and, in doing so, uncovers a sample of historical significance.

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Figure 1. Pictures of (a) excavated safe and contents and (b) glass bottle containing several hundred milligrams of Pu.

Background. The Hanford Site in Washington became the location for U.S. plutonium production during World War II. The Pu produced at this site was used in the first Pu nuclear weapon dropped on Nagasaki, Japan, on August 10, 1945, and in Trinity, the name given to the world's first test of a nuclear weapon on July 16, 1945. In December 2004, a safe containing several hundred milligrams of extremely low burnup Pu (a term typically associated with Pu produced as part of a weapons program) in a one gallon glass jug was unearthed by Washington Closure Hanford (WCH) personnel while excavating the 618-2 burial ground in the 300area of Department of Energy's Hanford site.^{8,9} The jug contained \sim 400 mL of slurry characterized as a white precipitate in a clear liquid. Pictures in Figure 1 document this find. In-field γ analysis conducted on the container detected the presence of only ²³⁹Pu. The minimum ^{239,240}Pu/²³⁸Pu and ²³⁹Pu/²⁴¹Am ratios were estimated to be at least 320:1, and 1000:1, respectively, based upon the detection limits of this analytical technique, indicating the Pu was produced from extremely low exposure fuel, consistent with early military reactor operations at Hanford. The absence of γ -emitting U or fission product isotopes in the spectra also suggested the Pu had been separated and purified prior to its disposal. Considering the potential historical significance of the find, WCH personnel coordinated with staff at Pacific Northwest National Laboratory (PNNL) to conduct further analysis of the sample. All of the liquid and $\sim 2\%$ of the solid from the container were repackaged into two 1 L polypropylene bottles on May 10, 2006, with one of the two bottles being transferred to PNNL. The majority of the solid material remained, caked to the walls of the original glass jug and was earmarked for disposal. We have coined the process of characterizing this sample as nuclear archeology.

EXPERIMENTAL SECTION

An analysis plan (Figure 2) was developed for processing the Pu sample. The pH of the liquid from the Pu sample was estimated



Figure 2. Analysis plan for Pu jug sample.

using 0-6 range pH paper prior to collecting samples for analyses. In all, a total of four samples were taken from the main bottle. This included a single 10 mL sample taken through a 0.45 μ m syringe filter for research and development purposes to investigate fission product (FP) contents using ICPMS and three replicate 15 mL slurry samples for the main set of analyses. The solid phase was suspended within the liquid just prior to taking each of the samples, since it was assumed the majority of the Pu was contained in the solid material of the slurry. After γ counting, each of the slurry samples, solid and liquid phases, were separated using disposable 0.2 μ m filter apparatuses (Nalgene Sterile Analytical Filter Units; Nalgene No. 130 4020). The filtrate was γ counted prior to splitting equally into four parts for IC, ICPMS, and ICP-OES analyses, respectively, leaving one part in reserve for archival purposes. Retentate on the filter membranes were transferred to Teflon conical tubes and dissolved overnight in 20

⁽⁸⁾ Washington Closure Hanford. Final Hazard Categorization and Auditable Safety Analysis for the Remediation of Six 300-FF-2 Operable Unit Solid Waste Burial Grounds; WCH-01683, rev. 2, November; Washington Closure Hanford: Richland, WA, 2005.

⁽⁹⁾ Bechtel Hanford Inc. 300-FF-2 Remedial Action 618-2 Self-Assessment Report; Interoffice Memorandum CCN 123003, Bechtel Hanford Inc.: Richland, WA, 2005.

mL of a roughly 2:1 mixture of saturated boric acid and 10 M HNO₃. After removing the first of three membranes from the dissolver solution, counting via a handheld α detector revealed significant activity was left on the membrane. As a result, dissolver solutions for replicates 2 and 3 were heated below boiling to enhance dissolution. The relative effectiveness of the dissolution process was estimated by difference from γ spectra for the filter membrane and the dissolved retentate solutions. After counting, the retentate solutions were split into five equal samples, holding one of the five in reserve and utilizing each of the rest for α counting, IC, ICPMS, and ICP-OES analyses.

Nuclear Counting Methods. The in situ object counting system (or ISOCS, by Canberra Industries Inc.) was utilized for initial in situ γ counting of the Pu sample in the field. In the laboratory, γ energy analysis (GEA) using high-purity Ge coaxial counters was used for rapidly quantifying ²³⁹Pu, detecting the presence of γ -emitting FPs and activation products (AP), and for material balance purposes during phase separation and elemental purification. γ spectrometry was also the primary method for quantifying ²⁴¹Am (the strongest line being 59.5 keV, with a 35% branching ratio). α energy analysis (AEA) was used to quantify ²³⁸Pu content in the three redissolved retentate solutions. To do this, it was first necessary to separate ²³⁸Pu $(E_{\rm a} = 5.499 \text{ MeV})$ from ²⁴¹Am $(E_{\rm a} = 5.486 \text{ MeV})$, which has an α decay of similar energy. Separation was accomplished by a proven, previously published anion separation method.¹⁰ γ spectrometry confirmed the separation of Pu and Am was quantitative (to within the limits of detection of the counting method), identifying no γ lines associated with ²⁴¹Am in the spectrum of the ²³⁸Pu fraction. Subsequently, the Pu fractions of three replicate samples were electrodeposited out of an aqueous sulfate solution onto a stainless steal planchet following a previously published method.¹¹ These samples were counted using a new Si-diode surface barrier detector in order of increasing activity. This was done to ensure the lowest possible background was obtained and also to minimize cross contamination between replicates.

Inductively Coupled Plasma-Optical Emission Spectrophotometry. Filtrate and retentate samples in triplicate and one dissolution blank sample were analyzed by ICP-OES. Calibration of the ICP-OES was done following the manufacturer's recommended calibration procedure and using multianalyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards (MCVA and MCVB) were used to verify acceptance of the two-point calibration curves obtained for each analyte and also used for continuing calibration verification. These measurements were conducted in accordance with ASO-QAP-001, which was the controlling quality assurance (QA) plan. Instrument calibrations, quality control (QC) checks and blanks, postspikes, replicate, and serial dilution were conducted during the analysis run.

Ion Chromatography Analysis. Major anions present within the Pu sample were quantified by ion chromatography (IC) using a Dionex model ICS-2500 modular system with a conductivity detector. Samples were prepared by simple dilution using distilled, deionized water. The dilution factors ranged from $100 \times to 2500 \times$ (needed to span the concentration of anions present in the sample matrix). No other sample preparation other than simple dilution was performed.

Inductively Coupled Plasma Mass Spectrometry. Pu sample filtrate and retentate replicates were analyzed by ICPMS for fission yield elements and total and isotopic U and Pu. Prior to analysis, chemical separation of U and Pu was required and undertaken following a previously published methodology.¹² Briefly, an aliquot of each solution was spiked with ²³³U (10 ng). Pu in the solution was reduced using hydroxylamine-hydrochloride to the trivalent state and loaded onto a pre-packed TRU resin (Eichrom, Inc.) column. The TRU column retains U, while Pu(III) and most matrix components pass through to waste. A subsequent elution with oxalic acid strips the U from the column.

The isolation of Pu prior to analysis was accomplished in the following manner.¹² First, an aliquot of the solution was spiked with ²⁴⁴Pu (10 pg). Plutonium in the solution was then reduced using hydroxylamine-hydrochloride to the trivalent state and separated from U by loading it onto a TRU (Eichrom, Inc.) column. The Pu fraction was collected and oxidized to the tetravalent state using HNO₃. This solution was then loaded onto a new TRU column and washed with HNO₃. Tetravalent Pu was held up on the column, while the remaining matrix components eluted through the column. Plutonium was subsequently stripped from the column using oxalic acid.

ICPMS analysis began by first screening samples for U and Pu levels within a diluted ($\sim 10000 \times$) aliquot of the unspiked samples prior to separation. This solution was also evaluated for trace amounts of fission product elements, of which none were found. Quantitative analysis of the spiked and separated U and Pu fractions for each of the filtrate and retentate replicates and blank sample followed the screening run.

Reactor Burnup Code Modeling. All reactor burnup modeling was conducted using *BURN*, a PNNL-proprietary code that simulates the effect of neutron irradiation of nuclear materials. The primary function of *BURN* is to track isotopic changes in the actinides, though it also tracks a broad spectrum of fission products in a variety of reactors. *BURN* performs a one-group point-depletion calculation, similar to *ORIGEN-ARP*,¹³ using reactor-specific one-group cross sections. Outputs from *BURN* calculations have been compared with other calculational models, including *WIMS5*,¹⁴ as well as being benchmarked against a variety of isotopic data. Unpublished benchmarking studies with historical plutonium isotopic measurements taken of irradiated fuel from the Hanford light water-cooled production reactors indicated *BURN* was capable of reproducing ²⁴⁰Pu/²³⁹Pu ratios to within less than 5% of the measured values.

Input requirements for *BURN* include ingoing isotopics (generally fresh fuel specifications) and power history details, either described in terms of power level or flux level. A selection of the appropriate reactor type is required in order that the proper onegroup cross sections are utilized. Output from the code include

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 (11) Film Andrea Control Control

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ISOCS						
isotope	activity (Bq)	error (±)	quantity (atoms)	error (±)	mass (g)	error (±)
²³⁹ Pu	$1.12 imes 10^9$	$3.57 imes 10^8$	1.23×10^{21}	3.92×10^{20}	4.86×10^{-1}	1.56×10^{-1}
GEA						
isotope	filtrate (Bq)	2σ (Bq)	retentate (Bq)	2σ (Bq)	
²² Na ²³⁵ U ²³⁹ Pu ²⁴¹ Am	$\begin{array}{c} 2.45 \times 10^2 \\ 1.76 \times 10^1 \\ \mathrm{bd}^a \\ \mathrm{bd}^a \end{array}$	$1.52 imes 10^1 \ 2.10 imes 10^0 \ { m bd}^a \ { m bd}^a$	1.51×10 1.21×10 6.60×10 6.78×10)3)2)3)3	$\begin{array}{c} 1.44 \times 10^{3} \\ 5.33 \times 10^{1} \\ 3.60 \times 10^{8} \\ 3.11 \times 10^{3} \end{array}$	
GEA w/time sample	isotope	date	Quantity (atoms)	2σ (atoms)	
slurry slurry slurry	²² Na ²² Na ²² Na	July 1, 2007 December 12, 2007 July 18, 2008	3.42×1 3.01×1 2.64×1	10 ¹⁰ 10 ¹⁰ 10 ¹⁰	$\begin{array}{c} 1.47 \times 10^9 \\ 6.94 \times 10^8 \\ 3.47 \times 10^8 \end{array}$	
AEA isotope	retentate (B	q/sample)	2σ (Bq/sample)			
^{239,240} Pu ²³⁸ Pu	4.62×10^{-4}	10^{1} 10^{-3}	$3.53 imes 10^{0} \ 3.27 imes 10^{-4}$			

actinide and select fission product isotopics resulting from the irradiation (generally the composition of the resultant spent fuel) specified, as well as the reactivity (k-effective) of the irradiated material.

RESULTS AND DISCUSSION

The pH of the solution was measured prior to dissolution with 0-6 pH paper, indicating the pH of the sample was between 1-1.5. This was consistent with the expected matrix of a sample originating at the end of the flow sheet of the BiPO₄ process consisting of a LaF₃ solid phase in dilute nitric acid matrix.

Nuclear Counting. Results summarizing ISOCS, GEA, and AEA analyses are shown in Table 1. ISOCS analyses identified the presence of only ²³⁹Pu within the Pu sample. Limits of detection by ISOCS for ²⁴⁰Pu and ²⁴¹Pu isotopes are also listed. However, GEA conducted in the laboratory was able to identify the presence of ²³⁵U and ²²Na within the filtrate and ²³⁹Pu, ²⁴¹Am, ²³⁵U, and ²²Na within the retentate of the sample. ²³⁹Pu and ²³⁵U activities were consistent with ICPMS results within the analytical errors associated with each method. ²⁴¹Am, a daughter product of ²⁴¹Pu, was only detected in the retentate fraction. α energy analysis was used to quantify ²³⁸Pu. Since AEA is not capable of resolving peaks associated with ²³⁹Pu (average a energy of 5.143 MeV) and ²⁴⁰Pu (average a energy of 5.15 MeV), peaks from these two isotopes are summed and treated together. Results are reported in terms of ²³⁸Pu/^{239,240}Pu activity ratios to eliminate the need for tracers and correcting data for separation and electroplating yields. A representative spectrum of the results is shown in Figure 3, illustrating the importance of low-background, high-resolution, α counting capabilities for resolving the rather small ²³⁸Pu peak from the immense peak of 239,240Pu.

ICP-OES, ICPMS, and IC Results. ICP-OES was used to analyze for the presence of transition elements. Results from ICP-



Figure 3. α spectra of the retentate solution showing the ^{239,240}Pu peak at 5.2 MeV and the ²³⁸Pu peak at 5.5 MeV.

OES are presented in Table 2. Actinide isotopes within the Pu sample were quantified using ICPMS. Results from these analyses are presented in Table 3. IC was used to analyze the sample for the presence of major anions (F^- , Cl^- , SO_4^{2-} , PO_4^{3-} , etc.). These results are presented in Table 4. Nitrate concentration within the retentate replicates were not reported since a nitric acid solution was used to dissolve the solid retentate from the filter membrane. Data in Table 4 have been adjusted for all instrument dilutions.

Age Dating. Uranium isotopic ratios within the sample were distinctly different from those found in nature. These uranium isotopes originated from two possible sources: (1) from contamination, either due to incomplete separation during reprocessing or from the natural environment introduced at some point in the disposal path or (2) in situ production from the decay of Pu parent isotopes. Uranium from contamination sources, whether from incomplete separation or from the environment, would have had essentially identical isotopic abundances as early U.S. military Pu

Table 2. Results from ICP-OES Analyses on the Pu Sample

element	filtrate (mg)	2σ (mg)	retentate (mg)	2σ (mg)	jug total (mg)	2σ (mg)	fraction in solid phase (%)
Ag	$5.60 imes 10^{-4}$	$9.24 imes 10^{-5}$	bd	bd	$5.60 imes 10^{-4}$	$9.24 imes 10^{-5}$	0
Al	$9.21 imes 10^{-1}$	$1.02 imes 10^{-1}$	$7.25 imes 10^{\circ}$	$3.06 imes 10^{-1}$	$8.17 imes 10^{\circ}$	$4.09 imes 10^{-1}$	89
As	$6.88 imes 10^{-2}$	$1.28 imes10^{-2}$	$7.63 imes 10^{\circ}$	$2.00 imes 10^{-1}$	$7.69 imes 10^{\circ}$	$2.13 imes 10^{-1}$	99
В	$3.07 imes 10^{-1}$	$1.22 imes 10^{-2}$	bd	bd	$3.07 imes 10^{-1}$	$1.22 imes 10^{-2}$	0
Ba	$1.99 imes 10^{-3}$	$2.31 imes 10^{-4}$	$2.85 imes 10^{-1}$	$2.36 imes10^{-2}$	2.87×10^{-1}	$2.38 imes 10^{-2}$	99
Be	$2.09 imes 10^{-4}$	$2.26 imes 10^{-5}$	$6.33 imes 10^{-3}$	$6.33 imes 10^{-4}$	$6.54 imes10^{-3}$	$6.56 imes10^{-4}$	97
Bi	$5.80 imes 10^{-2}$	$7.04 imes10^{-3}$	4.24×10^{1}	$2.00 imes 10^{\circ}$	$4.25 imes 10^1$	$2.01 imes 10^{\circ}$	100
Ca	$7.79 imes 10^{-1}$	$9.03 imes10^{-2}$	$8.60 imes 10^{0}$	$4.71 imes 10^{-1}$	$9.38 imes 10^{\circ}$	$5.62 imes 10^{-1}$	92
Cd	bd	bd	$3.58 imes10^{-2}$	$1.18 imes10^{-3}$	$3.58 imes10^{-2}$	$1.18 imes10^{-3}$	100
Ce	bd	bd	3.21×10^1	$1.77 imes 10^{\circ}$	3.21×10^1	$1.77 imes 10^{\circ}$	100
Co	$1.34 imes10^{-3}$	$4.07 imes 10^{-5}$	2.06×10^{-1}	$1.53 imes10^{-2}$	2.07×10^{-1}	$1.54 imes10^{-2}$	99
Cr	5.82×10^{-1}	$6.54 imes10^{-2}$	$2.81 imes 10^{\circ}$	1.77×10^{-1}	$3.39 imes10^{0}$	2.42×10^{-1}	83
Cu	1.03×10^{-2}	1.17×10^{-3}	4.87×10^{-1}	1.65×10^{-2}	4.97×10^{-1}	1.77×10^{-2}	98
Dv	bd	bd	5.83×10^{-2}	9.43×10^{-3}	5.83×10^{-2}	9.43×10^{-3}	100
Eu	bd	bd	4.75×10^{-2}	1.18×10^{-3}	4.75×10^{-2}	1.18×10^{-3}	100
Fe	1.02×10^{1}	1.26×10^{0}	4.83×10^{1}	$2.47 \times 10^{\circ}$	5.85×10^{1}	3.73×10^{0}	82
ĸ	5.41×10^{0}	6.01×10^{-1}	hd	bd	5.00×10^{0}	6.01×10^{-1}	0
Ia	5.08×10^{-2}	6.25×10^{-3}	340×10^{3}	1.18×10^{2}	3.40×10^3	1.18×10^2	100
Li	1.30×10^{-3}	1.32×10^{-4}	bd	hd	1.30×10^{-3}	1.32×10^{-4}	0
Mo	7.64×10^{-1}	8.63×10^{-2}	6.50×10^{-1}	236×10^{-1}	$1.00 \times 10^{-1.00}$	3.22×10^{-1}	46
Mn	4.12×10^{-1}	5.00×10^{-2}	1.86×10^{0}	8.25×10^{-2}	2.27×10^{0}	1.33×10^{-1}	82
Mo	2.11×10^{-3}	4.11×10^{-4}	8.62×10^{-1}	1.41×10^{-2}	8.64×10^{-1}	1.00×10^{-2} 1.46×10^{-2}	100
Na	1.40×10^{1}	1.72×10^{0}	4.89×10^{1}	3.18×10^{0}	6.04×10^{1}	4.90×10^{0}	8
Nd	hd	hd	hd	bd	bd	hd	N/A
Ni	9.80×10^{-2}	1.15×10^{-2}	6.77×10^{-1}	1.18×10^{-2}	7.75×10^{-1}	2.33×10^{-2}	87
P	1.58×10^{-1}	1.10×10^{-2} 1.91 × 10 ⁻²	2.08×10^{0}	1.10×10^{-1} 1.18×10^{-1}	2.24×10^{0}	1.37×10^{-1}	93
Ph	2.87×10^{-3}	3.61×10^{-4}	$2.00 \times 10^{-2.00}$	0.00×10^{0}	2.24×10^{0} 2.47×10^{0}	3.64×10^{-4}	100
Pd	2.07×10	bd	$2.47 \times 10^{-2.47}$ 2.26×10^{-0}	5.80×10^{-2}	$2.47 \times 10^{-2.47}$ 2.26×10^{0}	5.04×10^{-2} 5.89×10^{-2}	100
Rh	bd	bd	bd	bd	bd	bd	N/A
Ru	bd	bd	3.08×10^{-1}	1.71×10^{-3}	3.08×10^{-1}	1.71×10^{-3}	100
S	3.49×10^{0}	3.03×10^{-1}	3.50×10^{10}	4.71×10 2.26×10^{-1}	3.95×10^{1}	4.71×10^{-1} 6.20 × 10 ⁻¹	91
Sh	5.43×10^{-3}	1.08×10^{-3}	5.00 × 10 bd	2.50×10 bd	5.33×10^{-3}	1.08×10^{-3}	0
50	1.42×10^{-2}	1.00×10^{-3}	0.77×10^{0}	2.26×10^{-1}	$0.42 \times 10^{-0.00}$	1.00×10 2.28×10^{-1}	100
50	$1.40 \times 10^{-0.00}$	2.24×10 1.12 × 10 ⁰	9.77×10^{-1}	$2.50 \times 10^{-1.00}$	5.76×10^{1}	2.30×10 2.77×10^{0}	100
Sn	5.13×10^{-2}	1.12×10 1.82×10^{-3}	4.04×10 3.05×10^{0}	1.03×10^{-1}	3.00×10^{-0}	2.77×10^{-1}	100
Sn	1.33×10^{-3}	1.03×10^{-4}	5.05 × 10 bd	1.10 × 10 bd	1.21×10^{-3}	1.20×10 1.71×10^{-4}	100
Te	1.31 × 10 bd	1.71×10	bd	bd	1.31 × 10 bd	1.71 × 10 bd	
	bd	bd	118×101	1.65×10^{0}	110×10^{1}	1.65×10^{0}	100
Th	00 1.d	00 1.1	4.10×10 1 E0 × 10 ⁰	1.03×10^{-2}	4.10×10 1 50 × 100	1.03×10^{-2}	100
	$DU = 7.40 + 10^{-3}$	DU 0.1010-4	1.50×10^{-1}	1.07×10^{-3}	1.30×10^{-1}	7.07×10^{-3}	100
11	7.40×10^{-3}	8.18×10^{-3}	1.09×10^{-1}	1.77×10^{-1}	1.17×10^{-1}	2.59×10^{-5}	94
11	1.24×10^{-2}	3.47×10^{-4}	$0.33 \times 10^{\circ}$	2.12×10^{-1}	$0.33 \times 10^{\circ}$	2.16×10^{-1}	100
V	3.56×10^{-6}	3.64×10^{-4}	7.25×10^{-2}	1.18×10^{-1}	7.61×10^{-2}	1.54×10^{-5}	95
W	DCI 1 1	DCI 1 1	$1.21 \times 10^{\circ}$	1.01×10^{-1}	$1.21 \times 10^{\circ}$	1.01×10^{-1}	100
Y Zu	DCI 1 25 · · 10=?	DCI	2.83×10^{-1}	1.18×10^{-3}	2.83×10^{-1}	9.67×10^{-3}	100
Zn Zu	1.35 × 10 ²	1.11×10^{-3}	3.20×10^{-1}	$4./1 \times 10^{-2}$	3.33×10^{-4}	4.82×10^{-2}	96
Zr	DCI	DCI	1.84×10^{4}	1.06×10^{6}	1.84×10^{4}	1.06×10^{5}	100
hd helov	w detection limit	N/A not applic	able				

production reactors were burning natural U fuel.¹⁵ Reactor burnup simulations based on historical operator records confirmed that reactor operations would not have significantly altered the U isotopics within the fuel. These simulations also supported the conclusion that essentially all of the ²³⁸U within the sample originated from contamination, while essentially all of the ²³⁶U within the sample originated from the radioactive decay of ²⁴⁰Pu. However, isotopes ²³⁴U and ²³⁵U were influenced by both contamination and in situ production. With the use of the ²³⁸U activity in conjunction with the published natural U isotopic abundances for normal terrestrial sources, ^{16,17} the sources of ²³⁴U and ²³⁵U found in the sample were delineated and indicated that 75.6 ± 6.3 % of ²³⁴U and 99.5 ± 0.1 % of ²³⁵U came from in situ production from the decay of their respective parent isotopes, $^{238}\mathrm{Pu}$ and $^{239}\mathrm{Pu}.$

Once the in situ production source for U isotopes was known, the elapsed time since the Pu was separated from the U could be calculated using three independent parent/daughter pairs of isotopes including, ²³⁸Pu/²³⁴U, ²³⁹Pu/²³⁵U, and ²⁴⁰Pu/²³⁶U. Care was taken in our calculations to remove effects from the possible fractionation between U and Pu that may have occurred during repackaging in 2006. For each pair of Pu and U isotopes utilized, the number of parent (x = P) and daughter (x = D) atoms (N_x) within the sample at the time of analysis are related by the following equation:

$$fN_{\rm D} = N_{\rm P} (\mathrm{e}^{\lambda_{\rm P} \Delta t} - 1) \tag{1}$$

where *f* is the fractionation factor, the fraction of daughter atoms unaccounted for relative to the parent atoms during analysis, $\lambda_{\rm P}$ is the decay constant for the parent isotope, and Δt is the

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isotope	filtrate (mg)	2σ (mg)	retentate (mg)	2σ (mg)	total (mg)	2σ (mg)	
[²³⁸ Pu] ^a	nm ^c	nm^c	$1.48 imes 10^{-4}$	$2.20 imes 10^{-5}$	$1.48 imes 10^{-4}$	$2.20 imes 10^{-5}$	
[²³⁹ Pu]	$1.51 imes 10^{-3}$	2.33×10^{-5}	4.86×10^{2}	$1.72 imes 10^{\circ}$	$4.86 imes 10^2$	$1.72 \times 10^{\circ}$	
$[^{240}Pu]$	5.76×10^{-7}	$8.00 imes 10^{-8}$	$1.87 imes10^{-1}$	$4.24 imes10^{-3}$	$1.87 imes10^{-1}$	$4.24 imes10^{-3}$	
$[^{241}Pu]^{b}$	bd^d	bd^d	9.29×10^{-5}	$1.85 imes 10^{-5}$	9.29×10^{-5}	$1.85 imes 10^{-5}$	
^{[234} U]	4.03×10^{-5}	1.69×10^{-6}	8.25×10^{-5}	9.64×10^{-6}	1.23×10^{-4}	1.30×10^{-5}	
[²³⁵ U]	2.76×10^{-1}	6.92×10^{-4}	5.83×10^{-1}	1.10×10^{-3}	8.59×10^{-1}	1.74×10^{-3}	
[²³⁶ [1]	3.97×10^{-4}	7.41×10^{-6}	8.38×10^{-4}	1.94×10^{-5}	1.24×10^{-3}	2.74×10^{-5}	
[²³⁸ U]	1.86×10^{-1}	6.84×10^{-4}	3.64×10^{-1}	4.66×10^{-4}	5.50×10^{-1}	1.15×10^{-3}	
isotope ratio	filtrate	24	J	retentate	2σ		
$238 \mathbf{D_{11}} / 239 \mathbf{D_{11}} (1)$	nm ^c	nm ^c	2 -	17×10^{-7}	3.54×10^{-8}		
240 D , /239 D ,	2 62 × 10 ⁻	4 2.12	10-5 20	24×10^{-4}	3.34×10^{-5}		
241 D (239 D (2)	5.05 × 10 1.1d	2.12 × 1.1d	10 3.0	24×10^{-7}	2.00×10^{-8}		
234II /238II	DU	4 0.59.	10-6	59×10^{-4}	3.77×10^{-5}		
235 U / 238 U	2.17×10	- 9.58 ×	10° Z.	58×10^{-100}	4.05×10^{-5}		
236 U / 238 U	$1.50 \times 10^{\circ}$	1./1×	10 2 1.0	$59 \times 10^{\circ}$	2.23×10^{-1}		
230U/230U	2.15×10^{-1}	7.36 ×	10 ° 2.4	11×10^{-3}	3.08×10^{-4}		
^a By AFA ^b By CFA ^c nm not measured ^d hd helow detection limit							

Table 4. IC Results of Filtrate and Retentate of the Pu Sample

filtrate (mg)	2σ (mg)	retentate (mg)	$2\sigma~({\rm mg})$			
F	$4.44 imes 10^2$	$1.13 imes 10^1$	$3.02 imes 10^4$	$9.66 imes 10^2$		
SO_4	$1.58 imes10^2$	$2.83 imes 10^{\circ}$	1.67×10^{3a}	$1.41 imes 10^2$		
PO_4	7.00×10^{0a}	$5.66 imes10^{-1}$	<	$1.00 imes 10^3$		
NO_3	$5.56 imes10^3$	$1.13 imes10^2$				
Cl	$2.06 imes 10^2$	$3.39 imes10^{0}$	$2.15 imes 10^{3a}$	$8.25 imes 10^2$		
^a Below quantifiable limit, above method detection limit.						

duration in time from analysis to the last separation performed on the sample. While fractionation between elements may be significant, little fractionation would be expected between isotopes of the same element. As such, the fractionation factor, *f*, may be canceled out by deriving the following ratios from eq 1 written for each of the three parent/daughter pairs of Pu and U isotopes.

$$\frac{N_{234}}{N_{235}} = \frac{N_{238}(e^{\lambda_{238}\Delta t} - 1)}{N_{299}(e^{\lambda_{239}\Delta t} - 1)}$$
(2)

$$\frac{N_{236}}{N_{235}} = \frac{N_{240}(e^{\lambda_{240}\Delta t} - 1)}{N_{239}(e^{\lambda_{239}\Delta t} - 1)}$$
(3)

$$\frac{N_{234}}{N_{236}} = \frac{N_{238}(e^{\lambda_{238}\Delta t} - 1)}{N_{240}(e^{\lambda_{240}\Delta t} - 1)}$$
(4)

Subscripts 234 through 236 and 238 through 240 reference the daughter U isotopes and the parent Pu isotopes of the same mass numbers, respectively. Equations 2–4 were used to solve for Δt independently for each of the six separate measurements (including three replicates each from the filtrate and retentate samples). Estimates for Δt from each of the ratios were self consistent, with the best values generated from eq 2, indicating the Pu within the sample had last been separated from the U 61.6 ± 4.5 years prior to analysis in July 2007.

With the age of the sample known, the extent of U fractionation was estimated by comparing the predicted amounts of U isotopes that should have been produced based on Pu measurements to direct measurements of daughter isotopes. Here, it was determined that the fractions of ²³⁴U, ²³⁵U, and ²³⁶U residing in the solid phase were underestimated by a factor of 3.4. This was caused by in situ production occurring within solid phases that were essentially inaccessible to the liquid phase. Measurements for the U daughter isotopes, once corrected for contamination and fractionation, agreed to within 1% of their calculated production based on measurements of Pu parent isotopes.

Forensics Signatures from Secondary Nuclear Reactions. GEA revealed the presence of the relatively short-lived ²²Na isotope within the sample. The mechanism for the formation of ²²Na ($t_{1/2} = 2.6$ years) within fluoride matrixes in the presence of α -emitting actinides has been well documented in the literature^{18–23} following the reaction pathway of ¹⁹F(α ,n)²²Na. The production rate for this reaction is a function of the physical characteristics of the fluoride matrix, the production rate and energy of the α particles, and the proximity of the α particles to the ¹⁹F atoms. Equation 5 provides a mathematical model for the production of ²²Na within simple actinide fluoride solids.

$$\frac{\mathrm{d}N_{22}}{\mathrm{d}t} = \sum_{i} R_i N_i - \lambda_{22} N_{22} \tag{5}$$

where N_i is the number of atoms of each α -emitting isotope, R_i is the production rate (atoms of ²²Na/atom N_i /s) specific to the α -emitting isotope, *i*, and N_{22} and λ_{22} are the number of atoms and the decay constant for ²²Na, respectively. The reaction rate constants (R_i) derived for actinide fluorides^{19,20,23} were used here as they should also be applicable to lanthanide fluoride solids that contain minor amounts of α -emitting actinides,

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Figure 4. Predicted and measured ²²Na content with time within the Pu sample from 1945–2038.

since particle interaction probabilities and α -particle mean free paths for both fluoride solids are nearly identical.²⁴ With caution, the production model presented in eq 5 may also be extended to systems containing hydrated, rather than crystalline, lanthanide solids (e.g., such as the Pu jug sample), with the expectation that R_i within a hydrated matrix may be depressed relative to a crystalline matrix due to competing interactions between α particles and waters of hydration within the solid matrix.

Considering both the abundances of the major actinide isotopes within the jug sample and their corresponding rate constants for the ¹⁹F(α ,n)²²Na reaction (R_i), it was deduced that the α decay of ²³⁹Pu drives essentially all production of ²²Na within this sample. In this case, eq 5 may be simplified to

$$\frac{\mathrm{d}N_{22}}{\mathrm{d}t} = RN_{239} - \lambda_{22}N_{22} \tag{6}$$

where *R* is the rate constant for the ¹⁹F(α ,n)²²Na reaction from α particles emitted by ²³⁹Pu and *N*₂₃₉ are the number of atoms of ²³⁹Pu (3.64 × 10²⁰ atoms) accessible to and in equilibrium with the liquid phase (30% of the total based on U/Pu fractionation estimates) within the sample. With the use of this equation and the published value for *R* in ²³⁹PuF₄ solids,²³ the production of ²²Na within the Pu jug sample was modeled from December 1944 to 2038 (Figure 4).

Uncorrected model simulations of the ²²Na activity agreed to within a factor of 2 of GEA measurements (solid purple line in Figure 4), which was significant considering rate constants derived from solid crystalline actinide fluorides were applied here for a system of hydrated lanthanum fluoride slurry without correction. The solid blue line in Figure 4 represents model results fit to the first of the ²²Na measurements taken in time following the repackaging event in 2006. To illustrate the trend in the data, dashed lines representing the predicted ²²Na activity in time for instances where repackaging would have transferred 5% or 10% of the solid phase, instead of the actual 1.6%, were also provided in Figure 4. The fact that the adjusted (blue) model line runs through data points from subsequent ²²Na measurements in time provides some credence to the validity of the model describing the ¹⁹F(α ,n)²²Na reaction within this system.

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Four distinct regions can be identified from the ²²Na activity plot with time in Figure 4. Region 1 represents the in-growth phase where ²²Na atoms are produced faster than they decay away. Regions 2 and 4 represent steady-state phases where the ²²Na production is equal to its rate of decay. Region 3 represents a re-equilibration phase for the ²²Na after this isotope had been separated from the majority of the Pu as a result of repackaging in 2006. In this phase, more ²²Na atoms decay away than are produced by the small residual of Pu still remaining with the liquid.

Isotopes like ²²Na that are produced from secondary nuclear reactions involving radioactive material may be useful to investigators when a sample of unknown history containing such material is discovered. With the use of the Pu jug as an example, the ²²Na activity becomes an easy to detect (γ energy, 1275 keV; branching ratio, 99.4%) signature for ²³⁹Pu under steady-state conditions (regions 2 and 4 of Figure 4). In addition, with the assistance of an accurate production model for ²²Na, the total Pu within the sample prior to repackaging can be estimated prior to reaching steady-state conditions (i.e., within region 1) if it is known a priori when ²²Na production began. Alternatively, the time since ²²Na production began may be estimated during the in-growth period (region 1) if the amount of Pu within the sample (prior to repackaging) is known. However, it is region 3 of Figure 4 that is of most interest to the nuclear forensics community. Here the Pu jug after repackaging (2006) resembles what might be expected from an interdicted sample that, unknown to the investigator, had been separated from the majority of the Pu prior to confiscation. In such a case, a decrease in the ²²Na activity with time would suggest the confiscated sample may have been portioned off from a greater amount of Pu that had escaped interdiction. Moreover, assuming steady-state conditions between the ²²Na and ²³⁹Pu prior to splitting, the shape of the ²²Na activity curve with time after splitting (repackaging) is rather unique, defined by the amount of Pu residing with the ²²Na both before and after splitting. As such, the measured total ²²Na activity and the rate of change in this activity with time after splitting may be used to estimate (1) the total amount of Pu that resided with the ²²Na prior to splitting (Pu_T), and (2) the time that has elapsed since splitting ($\tau_{\rm E}$).

With the use of only information collected on the Pu sample after splitting, eq 6 was used to predict the number of ²²Na atoms as a function of $\tau_{\rm E}$ and Pu_T. These results were compared to GEA measurements of the total ²²Na activity after splitting (repackaging). The relative accuracy of fit $(1/\varepsilon)$ to model predictions with the measured values were calculated using eq 7 and are shown in Figure 5a as a function of $\tau_{\rm E}$ and Pu_T.

$$\frac{1}{\varepsilon} = 1 - \frac{\left|\frac{\text{(Modeled} - \text{Measured})}{\text{Measured}}\right|}{E_{\text{max}}} \times 100 \tag{7}$$

Where E_{max} is the maximum error in the dataset. Figure 5a shows good agreement between measured values and model predictions of the total ²²Na activity in the areas of the figure that are colored dark red, corresponding to instances when the predicted Pu_T and τ_{E} are, in parallel, both relatively high, relatively low, or relatively moderate, respectively.



Figure 5. (A) Comparison of model predictions of total ²²Na with measurements as a function of Pu_T and τ_{E} . (B) Comparison of model predictions to measured of rates of decrease in ²²Na activity with time as a function of Pu_T and τ_{E} . (C) Sum of $1/\varepsilon_{rel}$ from parts A and B as a function of Pu_T and τ_{E} .

A similar comparison may be made between the predicted and measured rates of decrease in ²²Na activity with time. In this case, the rate of decrease in ²²Na activity changes as a function of time after splitting based upon the Pu remaining in the system after splitting and Pu_T. The rate of decrease of ²²Na may be calculated from at least two GEA measurements of ²²Na activity in time. Figure 5b shows accuracy of fit (using eq 7) estimates for the predicted rate of change in ²²Na activity with time as a function of τ_E and Pu_T. As in Figure 5a, best model fits to the experimentally determined data in Figure 5b (the rate of decrease of ²²Na with time) are shown in dark red. Here, the best model fits to experimental data in Figure 5b occurred when the combined predicted Pu_T and τ_E were either correspondingly high and low, low and high, or mutually moderate, respectively.

Together, results of the comparisons presented in parts a and b of Figure 5 offer orthogonal information regarding the true history of the Pu sample. The sum of $1/\varepsilon$ as a function of τ_E and Pu_T in Figure 5a,b is represented in graphical form in Figure 5c, indicating the model fits best to measured results when values for Pu_T and τ_E are centered around a few hundred milligrams and a few years, respectively. These values are consistent with the known history of the Pu sample and illustrate how products from secondary nuclear reactions might be of use to the nuclear forensics community.

Trace Evidence of Reprocessing. Major contaminants found within the sample were consistent with the reprocessing method used to separate the Pu. In the 1940s, the bismuth phosphate process was the only industrial-scale reprocessing method in use



Figure 6. Trace contaminants within the Pu sample in decreasing order of prevalence.

within the U.S.²⁵ This process used a series of co-precipitation steps with BiPO₄ and LaF₃ to extract Pu from U and fission products in dissolved spent nuclear fuel.²⁶ Figure 6 shows the contaminants found in the sample in order of decreasing concentration. Contaminants that correspond to the list of reagents of the bismuth phosphate process have been color coded, along with components likely leached from the glass container and/or emanating from the cladding material. Figure 6 indicates many of the contaminants present at the highest concentrations within the sample were likely added as reagents during reprocessing.

Identity of Reactor of Origin. By 1950 (the latest possible date the sample could have been reprocessed based on age dating), there were a total of 11 production, process, and research reactors in operation within the U.S., of which the fuel from four of these reactors were routinely being reprocessed for Pu.²⁷ These include the prototype X-10 reactor located in Oak Ridge, Tennessee, and three graphite-moderated, light water-cooled production reactors at the Hanford site in Washington.^{28,29} A fourth, low-power reactor was also in operation during this time at the Hanford site (the 305 reactor) but was exclusively used for fuel clad testing.

Plutonium isotopic ratios from the Pu sample were consistent with model estimates expected from the X-10 reactor in the 1940s.²⁹ These isotopic measurements indicated the Pu sample was exposed to fuel burnup levels much lower than 220 MWd/ MTU (megawatt-day/metric ton uranium), the nominal burnup

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Figure 7. Comparison of measured Pu isotopic ratios from the sample (solid red squares) with predicted ratios within spent fuel from X-10 reactor at 3.6 and 3.7 MWd/MTU (solid and dashed blue lines, respectively) and B-reactor operations (dashed grey line) in the 1940s. The model line for the B-reactor represents ratios that would have been produced at the lowest recorded power level (17.2 MWd/MTU) for that reactor. The area above the B-reactor model line represents the possible range of isotopic ratios that could have been produced at power levels above the lowest recorded value. The value of the 242/239 ratio for the sample was found to be below the limit of detection (identified by the open red square) of the analytical technique used.

level of the Hanford production reactors in the 1940s. However, lower burnup levels were recorded during the initial start-up process for the production reactors at Hanford. The lowest recorded burnup level for any of the fuel ejected from the production reactors at Hanford occurred on November 6, 1944 with two channels ejected at a reported burnup of 1.976 MWD per channel, or 17.2 MWd/MTU.²⁸ From burnup model predictions, this would have produced 0.13 \pm 0.007 wt % ²⁴⁰Pu, still significantly higher than the measured 0.039 ± 0.0038 wt % ²⁴⁰Pu content in the Pu sample. During this same time, operator declarations from the X-10 reactor indicated this reactor consistently ran at a much lower burnup level of 3.6 MWd/ MTU.²⁹ Predictions at this burnup level modeled after the X-10 reactor design were also conducted. Figure 7 summarizes these results, comparing the measured Pu isotopics within the sample to those predicted for both the B-reactor running at a power level of 17.2 MWd/MTU and the X-10 reactor running at 3.6 MWd/ MTU. Noteworthy, predicted Pu isotopic ratios for the X-10 reactor are comparable to, but slightly lower than, measurements. We considered these predictions to be in good agreement, both in magnitude and trend, with measured data from the sample. The minor discrepancy between the measured ratios and X-10-modeled results are likely due to small errors in the operator declarations of the burnup level at the reactor. During this time, burnup levels of the reactors were deduced from the effluent temperatures of the coolant exiting the core. Unlike the Hanford production reactors, the X-10 reactor was gas cooled, which made these measurements somewhat less precise. An analysis of the burnup code to the power level was conducted by pushing simulations to higher power levels until a fit to the analytical results of the ²⁴⁰Pu/ ²³⁹Pu ratio was achieved. The results of the model at this higher power rating are also shown in Figure 7. These results indicated a match between experimental and predicted ²⁴⁰Pu/²³⁹Pu ratios was obtained at a power level for the X-10 reactor of 3.7 MWd/ MTU, within 5% of the declared power level of the X-10 reactor.²⁹ Simulations at 3.7 MWd/MTU also resulted in very close fits to the ²³⁸Pu/²³⁹Pu and the ²⁴¹Pu/²³⁹Pu experimentally determined ratios, providing increased confidence that the Pu within the sample was produced in the X-10 reactor.

Historical and Current Significance. Identifying X-10 as the reactor of origin for the sample was not immediately intuitive, considering the location where this material was discovered. However, a few archived documents retrieved during this investigation help to develop a near full history of the sample. Documentation was found detailing the disposal of a safe in 1951, with contents matching that of the safe uncovered in 2004.^{30–32} These records indicated the safe was sealed in April 1945 prior to disposal, after the inside of the safe was contaminated with radioactivity. Shipping manifests from 1944 also describe the transfer of 96 slugs of X-10 fuel to Hanford in September of that year.³³ These slugs contained a total of \sim 113 kg of irradiated uranium and an estimated 400 mg of Pu. The purpose of the shipment was to provide Pu for testing T-Plant operations. T-Plant and the B-reactor, the world's first industrial-scale reprocessing facility and production reactor, respectively, were constructed in parallel, with completion of T-Plant preceding the first ejection of fuel from the B-reactor core by a few weeks.³⁴ To bridge this scheduling gap, Pu from the X-10 reactor was initially used to test T-Plant operations. Operator records from T-plant indicated the first full-scale test of the facility occurred on December 9, 1944, with the introduction of the only batch of X-10 Pu ever processed by the plant.³⁵ The second (which occurred on December 12), and all subsequent batches of Pu separated by T-Plant, originated from Hanford production reactors. Therefore, we conclude the Pu in the sample uncovered at the 618-2 burial site at Hanford in December 2004 was part of the first batch of Pu separated by the world's first industrial-scale reprocessing facility. This $\sim 400 \text{ mg}$ sample represents the oldest known collection of ²³⁹Pu in the world and the second oldest known collection of the man-made element. The oldest known sample, a microgram quantity of ²³⁸Pu weighed 2 years after its discovery by Art Wahl and Glen Seaborg in 1940, is currently on display at the Smithsonian museum in Washington, DC.36

CONCLUSION

We have used state-of-the-art instrumental analyses, reactor model simulations, and investigative science techniques to provide insights as to the origin of this unknown sample discovered in a

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DOE waste trench in 2004, a process collectively termed as nuclear archeology. Isotopic age dating conducted in 2007 indicated the sample was separated from the fuel pellet 61.6 ± 4.5 years earlier. Here, we illustrated for the first time how ²²Na, a detectable product of a secondary nuclear reaction, might be employed during nuclear forensic analysis. Analytical results of minor actinide isotopes and reactor model simulations confirmed the material originated from the X-10 reactor in Oak Ridge, TN. Corroborated by historical documents, we were able to conclude this sample was part of the first batch of Pu separated at T-Plant, Hanford, the world's first industrial-scale reprocessing facility, on December 9, 1944. This sample represents the second oldest known collection of man-made Pu in the world.

Aside from the historical significance of this find, this work provides the public a rare glimpse at a real-world example of the science behind and power of modern-day nuclear forensics. While it is not fast or inexpensive, when baseline information about sources is available, the outcome can be very illuminating. The characterization of this sample and others like it can provide that baseline information necessary for comparing against interdicted samples of unknown origin.

ACKNOWLEDGMENT

We would like to formally acknowledge Mr. Matthew Haas and Mr. John Darby with Washington Closure Hanford for assisting us in procuring this sample, Dr. William J. Weber for his thoughtful technical review, and Mr. Robert E. Allen for his editorial review. This research was conducted at the U.S. Department of Energy's Pacific Northwest National Laboratory, which is operated for DOE by Battelle under Contract DE-AC05-76RL1830.

NOTE ADDED AFTER ASAP PUBLICATION

After ASAP publication on January 16, 2009, the authors provided the following additional information: Glen Seaborg's group detected the first isotope of Pu (²³⁸Pu) during a series of experiments conducted at the cyclotron at UC Berkeley in 1940. Shortly after that, the first visible sample of ²³⁹Pu was produced by the group and is currently on display at the Smithsonian. That sample holds the distinction as the oldest sample of plutonium in the world. Our sample holds the distinction as the oldest located reactor-produced sample of Pu in the world. The new version of this manuscript posted ASAP on January 28, 2009.

Received for review November 7, 2008. Accepted December 30, 2008.

AC802286A

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