

Fate of Plutonium at a Former Nuclear Testing Site in Australia

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1 The fate of plutonium released from nuclear
2 weapons tests

3

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15

16 **ABSTRACT**

17 A series of the British nuclear tests conducted on mainland Australia between 1953 and 1963
18 dispersed long-lived radioactivity and nuclear weapons debris, the legacy of which is a long-
19 lasting source of radioactive contamination to the surrounding biosphere. A reliable assessment
20 of the environmental impact of these types of radioactive contaminants and their implications for
21 human health requires an understanding of their physical/chemical characteristics on the
22 molecular scale. However, mainly due to the technical difficulties associated with the chemical
23 diversity of environmental samples, these contaminants have never been characterized
24 adequately. In this study, we identify the chemical form of plutonium (Pu), one of the most
25 problematic radionuclides dispersed, in the local soils collected from one of the former weapons
26 test sites, Maralinga. We herein reveal the first direct spectroscopic evidence that the Pu legacy
27 exists as particulates of fine Pu oxyhydroxide compounds, a very concentrated and low-soluble
28 form of Pu, which will serve as ongoing radioactive sources far into the future. We also verify
29 that the Pu in the particles originated in the so-called “*Minor trials*” that involved the dispersal of
30 weapon components by highly explosive chemicals, not in the nuclear explosion tests called
31 “*Major trials*”. The obtained results help us to understand the chemical transformation of the
32 original Pu materials dispersed in the semi-arid environment more than fifty years ago. These
33 findings further highlight the importance of the comprehensive physical/chemical
34 characterization of Pu contaminants for reliable environmental- and radiotoxicological
35 assessment, which is significantly influenced by the original physical/chemical form of the
36 contaminant.

37

38 INTRODUCTION

39 From 1953 to 1963, the British nuclear weapons testing programme conducted twelve nuclear
40 detonation tests (“*Major trials*”) and more than five hundred non-nuclear explosion tests (“*Minor*
41 *trials*”) in the Great Victoria Desert, South Australia (Fig. 1-(a)).¹⁻² These tests caused
42 radioactive contamination with nuclear weapons debris in the test sites and their surroundings.
43 After completion of official remediation operations in 2002, radionuclides including plutonium
44 (Pu) remain in activity concentrations that represent extensive environmental contamination with
45 deposition plumes extending for tens of kilometers outside the clean-up area.³ A reliable
46 assessment of the environmental fate of the remaining radioactive contamination and its potential
47 implication for human health requires detailed knowledge of their chemistry in the relevant
48 environment; little of which is understood, mainly due to technical difficulties associated with
49 the analysis of environmental samples with low activity concentrations and complex matrices.⁴
50 Here we report on a unique analytical approach combining radiochemical analysis with
51 synchrotron-based X-ray fluorescence microscopy (XFM) to comprehensively characterize the
52 Pu contaminants resulting from the nuclear weapons tests in Maralinga, Australia (Fig. 1-(a)).

53

54 Figure 1

55

56 EXPERIMENTAL

57 **Isolation of Pu-containing particle.** An initial screening of the soil samples to search for the
58 remaining Pu contaminants was performed by measuring ²⁴¹Am activity in the soils with gamma
59 spectrometry. The presence of ²⁴¹Am is largely the result of in-growth following neutron-capture

60 and beta decay reactions from the parent ^{239}Pu . As a result, the activity concentrations of ^{241}Am
61 are proportional to those of ^{239}Pu ($^{239}\text{Pu}/^{241}\text{Am}$ ratios of 3.4 mean, 0.5 standard deviation) as
62 measured in the soils of the NW plume. This ratio can vary from plume to plume depending on
63 the composition of the original tested material.^{3,5} Among the collected fifty soil samples, one soil
64 sample containing the highest ^{241}Am activity concentration of 1.3 kBq/kg was selected for further
65 treatment to isolate Pu contaminants. The selected soil sample was then passed through a 125 μm
66 sieve to remove large sand particles and debris. Ten grams of the sieved sample was then
67 dispersed in 30 ml of lithium heteropolytungstate (LST) heavy liquid ($D = 2.9$ g/ml) for density
68 separation. The sample was centrifuged for 5 minutes at 2,000 rpm and the bottom sediments
69 containing heavy particles were collected. The centrifugation-sediment collection process was
70 repeated to ensure that the supernatant did not contain heavy particles. The resultant sediments
71 and supernatant were analysed by gamma spectrometry, which confirmed that the collected
72 sediments (0.32 g) held at least one particle showing high ^{241}Am activity. The collected
73 sediments were further dropped onto the top of a new LST solution to allow the sediments to
74 stratify only with gentle agitation. Four subsamples were obtained from this stratification
75 process, only the third densest of which contained almost all of the original ^{241}Am activity. This
76 subsample containing ^{241}Am was further split within small droplets of aqueous solution,
77 measured by gamma spectrometry, and repeated until a single particle (approximately 150-200
78 μm in diameter) was identified as a Pu-rich particle. The isolated particle was found to be highly
79 friable, and, when placed between thin glass slides, easily fragmented into smaller pieces (Fig.
80 S1 in SI). All fragments exhibited ^{241}Am activity approximately proportional to their respective
81 masses, and thus indicated the presence of Pu in similar per mass activity concentrations,
82 consistent with their origin from a single particle. The isolation process of the Pu particle

83 involved only physical sieving and use of LST solution and deionised water. As the Pu particle
84 was in a stable chemical form when collected, contact with LST solution (*i.e.*, Li⁺ and
85 polytungstate anions) and deionised water would not cause any further change in the chemical
86 composition of the particle. Additionally, the employed LST solution was almost saturated ($D =$
87 2.9 g/ml, where 2.95 g/ml is the maximum density at 298 K). Hence, the dissolution of other co-
88 existing minerals/soils during the LST density separation process and subsequent sorption of the
89 dissolved mineral/soil components on the particle surface is very unlikely. Therefore, the isolated
90 particle should reflect the current chemical form of Pu at the Taranaki test site.

91 **X-ray fluorescence microscopy and X-ray absorption spectroscopy.** Fragmented pieces of the
92 isolated particle (five pieces in total) were mounted on a Kapton tape and covered with Ultralene
93 X-ray fluorescence film (4 μm in thickness) for transport to the Australian Synchrotron. Figure
94 S3 in the SI shows optical microscope images of the fragments employed for XFM experiments.
95 XFM measurements were performed at the XFM beamline⁶ of the Australian Synchrotron under
96 ring operating conditions of 3 GeV and 200 mA with top-up mode. Scanning X-ray fluorescence
97 (XRF) mapping⁷ and X-ray absorption near edge structure (XANES) mapping in fluorescence
98 mode⁸ at the Pu L_{III}-edge (18.057 keV) were carried out under ambient conditions with a
99 Kirkpatrick-Baez (KB) mirror pair and the Maia detector.⁹ XANES mapping produces a XANES
100 spectrum from the X-ray fluorescence signal at selected pixels in a stack of images collected as a
101 function of incident beam energy. For XANES mapping measurements, X-ray absorption spectra
102 of Zr foil was acquired simultaneously in transmission mode for energy calibration (at the Zr K-
103 edge, defined as 17999.35 eV at the 1st inflection point) upstream of the KB mirrors. The
104 acquired data were treated and analysed with the software GeoPIXE (Version 6.6)¹⁰ and
105 WinXAS (Version 3.2).¹¹ The acquired X-ray fluorescence data were deconvoluted based on the

106 Dynamic Analysis matrix transform method¹² to obtain elemental concentration maps as a
107 function of incident beam energy. Pu L_{III}-edge X-ray absorption spectra were produced based on
108 the total counts of the observed Pu L fluorescence lines (Fig. S4 in SI) on a selected region
109 covering the whole area of each sample fragment. The data treatment for the extended X-ray
110 absorption fine structure (EXAFS) region was performed with the software WinXAS¹¹ according
111 to the standard procedure.¹³ Theoretical phase and amplitude for EXAFS theoretical fitting were
112 calculated by a program code FEFF8.20¹⁴ based on the crystal structures of metallic Pu and
113 PuO₂.¹⁵

114

115 **RESULTS AND DISCUSSION**

116 **History of plutonium legacy at the Taranaki test site, Maralinga.** Soil samples were collected
117 in September 2010 at a distance of 2.0 km from the former firing pad of the Taranaki site, one of
118 the test sites at Maralinga (Figs. 1-(b) and -(c)). At the Taranaki site, in addition to one “*Major*
119 *trial*” in 1957, twelve “*Minor trials*” were conducted between 1960 and 1963.² These tests
120 dispersed more than 22 kg of Pu, resulting in four contaminated plumes radiating from the test
121 site.² The sampling point is situated within the northwest (NW) plume (Fig. 1-(c)), where the
122 main radioactive contamination was caused by the Minor trial “*Vixen B2 – Round 5*” undertaken
123 in May 1961.^{2, 16} The “*Vixen B*” trials involved the burning and detonation of nuclear weapon
124 components with high-explosives to ascertain the potential for accidents to trigger nuclear
125 explosions.² A “limited number of fissions” during testing were reported,² suggesting that the
126 original Pu materials employed for the trials was presumably metallic Pu with fissile ^{239,241}Pu

127 isotopes. Hence, the Pu in the soils gathered at the Taranaki site could have originated from
128 nuclear detonation, limited nuclear fission, or non-nuclear high-explosive dispersal events.

129

130 **Identification of plutonium legacy.** The collected soil samples were first analyzed by gamma
131 spectrometry and autoradiography to find Pu debris in the soil mixture. After a repetitive process
132 including sample fractionation, gamma spectrometry and autoradiography, a single particle with
133 approximately 40 Bq-²⁴¹Am, a major daughter nuclide of ²³⁹Pu, was successfully isolated. The
134 gamma-ray spectrum of this particle indicated the absence of fission products (FPs) (Fig. S2 in
135 SI), suggesting that the Pu in the isolated particle did not undergo fission reactions and, hence, it
136 is likely to originate in “*Minor trials*”, not from “*Major trials*”.

137 Because of the physical/chemical complexity and diversity, the chemical analysis of
138 environmental samples is always a challenging task.⁴ Synchrotron-based XFM is an emerging
139 and powerful tool to comprehensively characterize not only environmental samples¹⁷ but also
140 biological and geological samples,¹⁸ providing the information on elemental distribution,
141 oxidation states and local structural arrangement of the target atoms in a non-destructive manner.
142 Shown in the upper-left of Fig. 2 is an optical microscope image of one fragment of the isolated
143 Pu particle. The X-ray fluorescence spectrum of this fragment was found to be primarily
144 composed of Ca K-, Fe K-, Pb L-, U L- and Pu L-lines (Fig. S4 in SI), suggesting the dominant
145 presence of these elements in the fragment. No major FPs of Pu isotopes (e.g., noble metals or
146 lanthanides) were detected, being consistent with the results of gamma spectrometry (Fig. S2 in
147 SI). The XFM images of the fragment (Fig. 2) further reveal that Pb and Pu are more
148 concentrated inside the fragment, while Ca, Fe and U are distributed mainly on the outer surface
149 of the fragment. These elemental distributions, together with the XFM results for other fragments

150 from the same Pu particle (Figs. S5-S10 in SI), point to the fact that the isolated Pu particle
151 forms the “*core-shell*” structure composed of the Pu+Pb core surrounded by the external shell
152 containing Ca, Fe and U (Fig. S12 in SI).

153

154 Figure 2

155

156 The chemical state of Pu in the fragment was further investigated by X-ray absorption
157 spectroscopy. The spectral shape of the fragment in the X-ray absorption near-edge structure
158 (XANES) region is not consistent with that for Pu-metal,¹⁹ the original Pu compound dispersed at
159 the site, but rather similar to those for oxide compounds, such as PuO₂ (inset of Fig. 3).¹⁹ The
160 XANES absorption edge and peak positions of the fragment, both of which are indicative of the
161 oxidation states and chemical compositions,²⁰ are comparable with those of Pu(IV) compounds,
162 such as PuO₂,¹⁹ or oxyhydroxides²¹ (Fig. 3). The extended X-ray absorption fine structure
163 (EXAFS) spectrum further indicates the presence of Pu□O and Pu□Pu arrangements around the
164 Pu atoms in the fragment, which is consistent with the structure of oxide or oxyhydroxide
165 compounds (Fig. S15 and Table S1 in SI). This also excludes the possible presence of
166 intermetallic Pu compounds in the fragment, such as Pu□Pb compounds.

167

168 Figure 3

169

170 **Transformation of original plutonium materials.** In the “*Vixen B*” trials, the explosions were
171 reportedly triggered by a high-explosive chemical, such as TNT,² which can generate
172 temperatures over 3,000 °C.²² The initial Pu component (i.e., metallic Pu) was, therefore, subject
173 to a high temperature environment during explosion, which prompted the instant oxidation to
174 PuO₂, the highest oxidation state and most stable form of Pu oxide compounds.²³ Other lower Pu
175 oxides, such as Pu₂O₃, are unstable and eventually transformed into PuO₂.²⁴ The metallic Pu is
176 also known to be self-ignitable in the air at temperatures exceeding 500 °C, resulting in the
177 formation of PuO₂.²⁵ Based on these facts, it is reasonable to posit that the initial Pu component
178 was transformed into PuO₂ immediately after the explosion and blasted over the test site as fine
179 particles, as illustrated in Fig. 4. Subsequently, the scattered PuO₂ particles underwent local
180 weathering including the interaction with moisture from ambient humidity over more than fifty
181 years before sampling. PuO₂ is susceptible to moisture even under atmospheric conditions and
182 eventually transformed into PuO_{2+x},²⁴ which can be more accurately described as PuO_{2+x}.
183 _y(OH)_{2y}·zH₂O.²¹ The chemical interaction of these Pu compounds with local minerals and soils
184 could potentially occur via, for instance, the dissolution of Pu into water. However, both PuO₂
185 and PuO_{2+x}._y(OH)_{2y}·zH₂O are expected to be sparingly soluble²⁶ in the local climate conditions at
186 Maralinga,² suggesting that the chemical form of Pu would be unlikely to be affected by
187 prolonged exposure to the local minerals and soil environment. Hence, PuO_{2+x}._y(OH)_{2y}·zH₂O is
188 likely to be the final form of Pu in the particulate debris remaining at the Taranaki site. This
189 oxyhydroxide form of Pu shows a characteristic high-energy shift in the XANES peak position
190 as compared with PuO₂,^{19,21} which is consistent with our XANES data in Figs. 2 and S13 in SI.
191 The Pu oxyhydroxides could be poorly structured due to the partial oxidation of Pu(IV) to higher
192 oxidation states.^{21,27} This could account for the EXAFS results indicating lower coordination

193 numbers for Pu□O and Pu□Pu shells in the fragments as compared with those in PuO₂ (Table S1
194 in SI).

195

196 Figure 4

197

198 As shown in Fig. 2, the distribution of Pb coincides with that of Pu. This suggests that Pb is an
199 intrinsic component of the particle core and not derived from natural accumulation after the
200 explosion. The gamma-ray spectrum of the fragments confirmed the absence of radioactive Pb
201 isotopes, indicating that the Pb probably originates either in Pb-metal/alloy tampers¹ which
202 surrounded the explosive core of the device, or in the shielding/construction materials of the
203 firing devices² blasted with the Pu fuel component. The Ca, Fe and U forming the outer layer of
204 the Pu particle are likely to originate in the evaporation of moisture containing dissolved
205 constituents from local soils, which are reported to be rich in these elements,²⁸ on the surface of
206 the core particle.

207 **Implication for radioecology.** The low solubility of the Pu(IV) oxyhydroxide/oxide particles
208 characterized in this study would reduce Pu mobility in abiotic media. However, it does not
209 prevent its absorption into living organisms. In the mammals inhabiting the studied site, the Pu
210 was absorbed across biological membranes into muscle, liver and bone, at significant activity
211 concentrations.²⁹ As the Pu particles at the site were friable, any fragmentation will increase
212 potential for uptake by inhalation and lodgement of sub-µm Pu particles deep in the lung.
213 Clearance of such particles from the organism can be slow, leading to persistent and highly

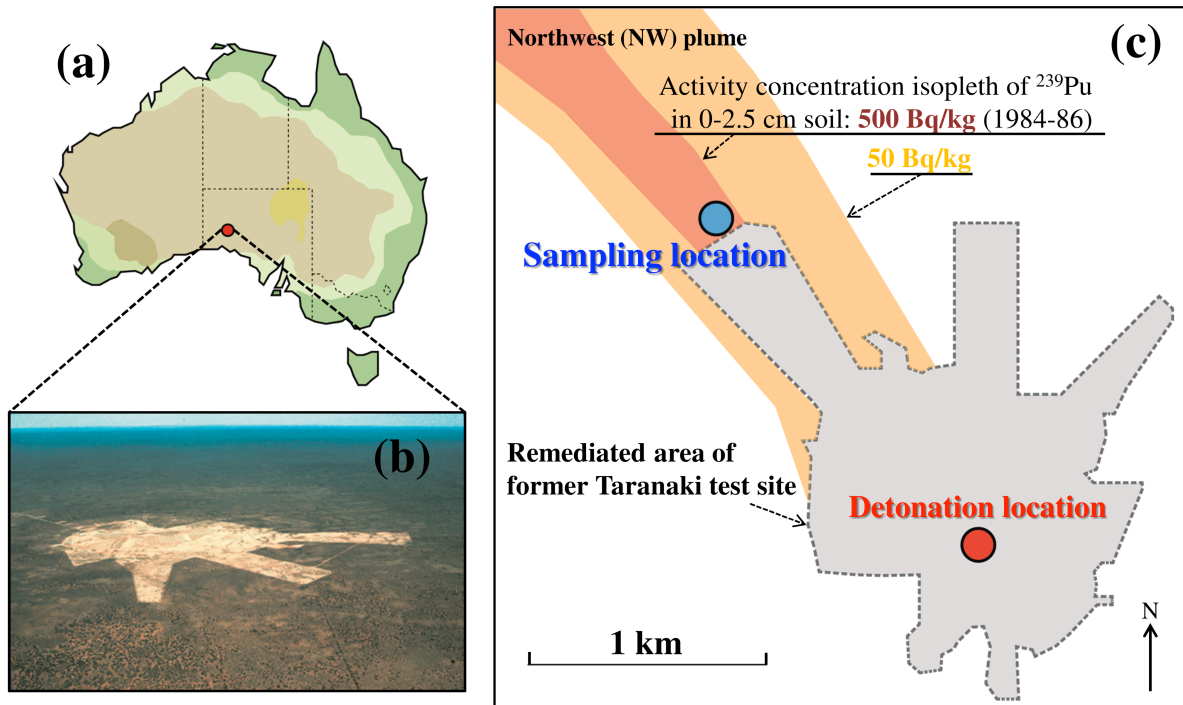
214 concentrated internal Pu sources.³⁰ This scenario can explain the elevated Pu activity
215 concentrations observed in some mammals at the Taranaki test site,²⁹ which could also
216 potentially occur in case of human uptake. However, the current guidance on radiation safety and
217 protection³¹ is based largely on the uptake of dissolved Pu forms which behave differently from
218 that of particulates during exposure and uptake. In those cases where particles have been
219 considered, lung deposition and clearance have been a major concern, with sparse information on
220 the physical/chemical characteristics of Pu contaminants, due in large part to the difficulty of
221 evaluating the *in-vivo* behavior of complex Pu particulates.

222 This study provides spectroscopic evidence that the Pu legacy in the particles obtained at the
223 Taranaki test site originates from unfissioned Pu fuel components, which is a unique source of
224 Pu contamination as compared not only with those found at most other nuclear test sites, but also
225 with worldwide fallout, reactor accidents or waste disposal. For instance, the first nuclear test
226 near Alamogordo, New Mexico, left glassy residues containing fissioned Pu components,³²
227 known as “*Trinitite*”, while the Pu legacy from underground nuclear tests at the Nevada Test
228 Sites (NTS) was associated with mobile colloids facilitating the groundwater transport of
229 fissioned Pu nuclides.³³ Other non-test-related releases of Pu into the environment include non-
230 refractory particulates of Pu oxides from non-nuclear accidents.³⁴ These different forms of Pu
231 contaminants would behave differently in the environment, resulting in different pathways of
232 their potential introduction to the human body. With a strong advantage of using synchrotron-
233 based X-ray microscopy/spectroscopy for the comprehensive characterization of particulate
234 contaminants, this study highlights the importance of identifying the physical/chemical
235 characteristics of each Pu contaminant for the reliable assessment of their environmental fate and
236 potential implication for humans.

237 **FIGURES**

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241

242 **Figure 1.** Geographical location of Maralinga (red circle) on an Australian map (a), and an aerial
243 photo (b)* and a local map (c) of the Taranaki test site at Maralinga. *Reprinted with permission
244 from the Department of Communications, Information Technology and the Arts, the
245 Commonwealth of Australia (2002).

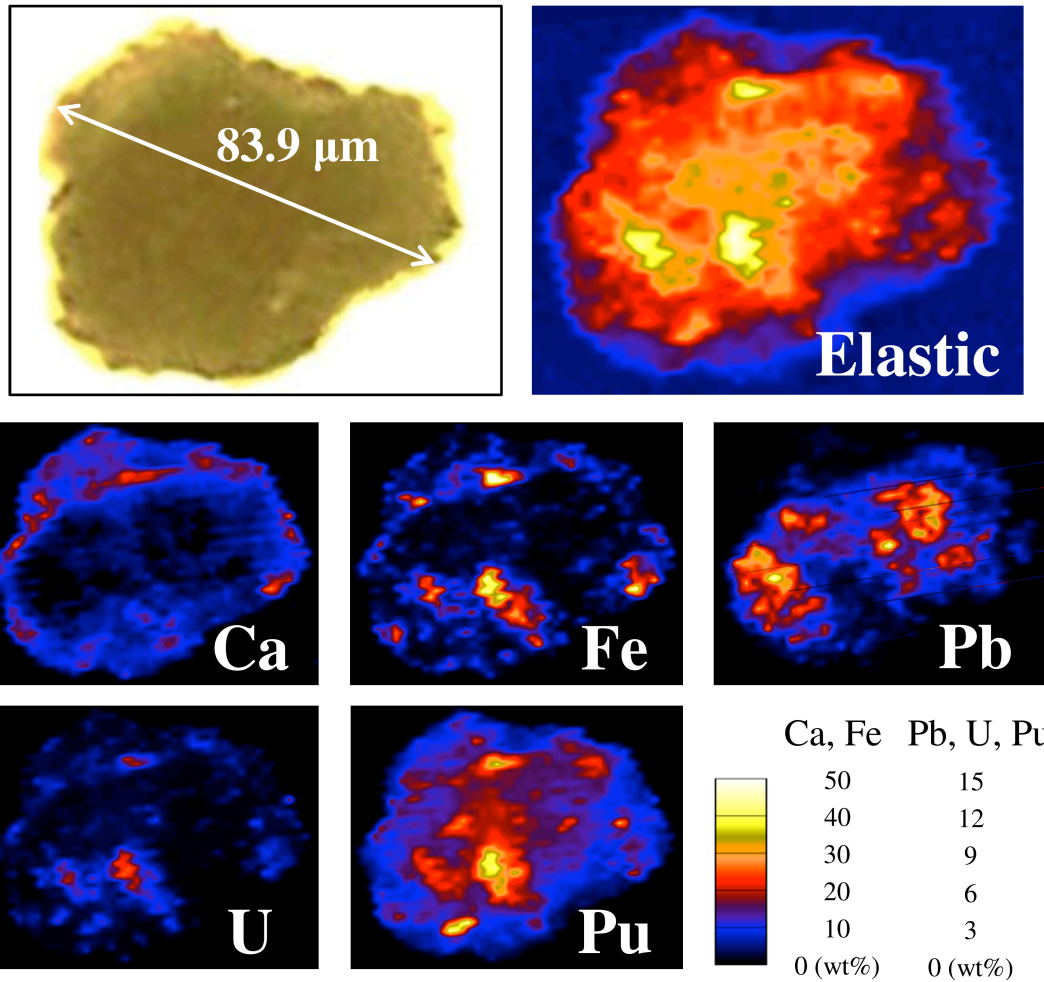
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252 **Figure 2.** Optical microscope- (top left) and X-ray fluorescence microscope (XFM) images of a
253 fragment of the isolated Pu particle deposited at the Taranaki test site.

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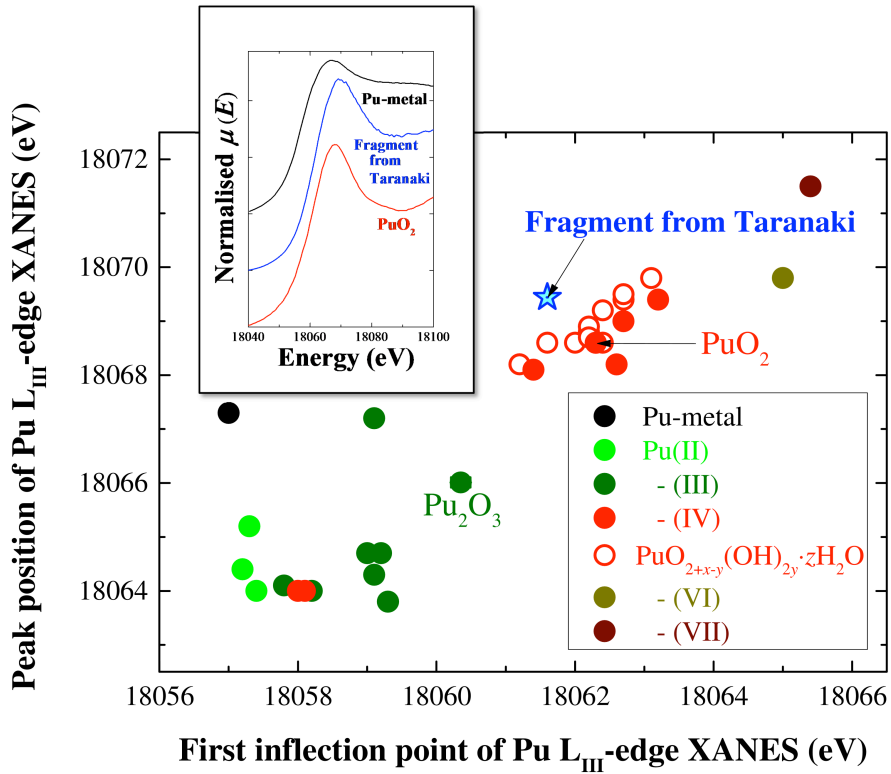
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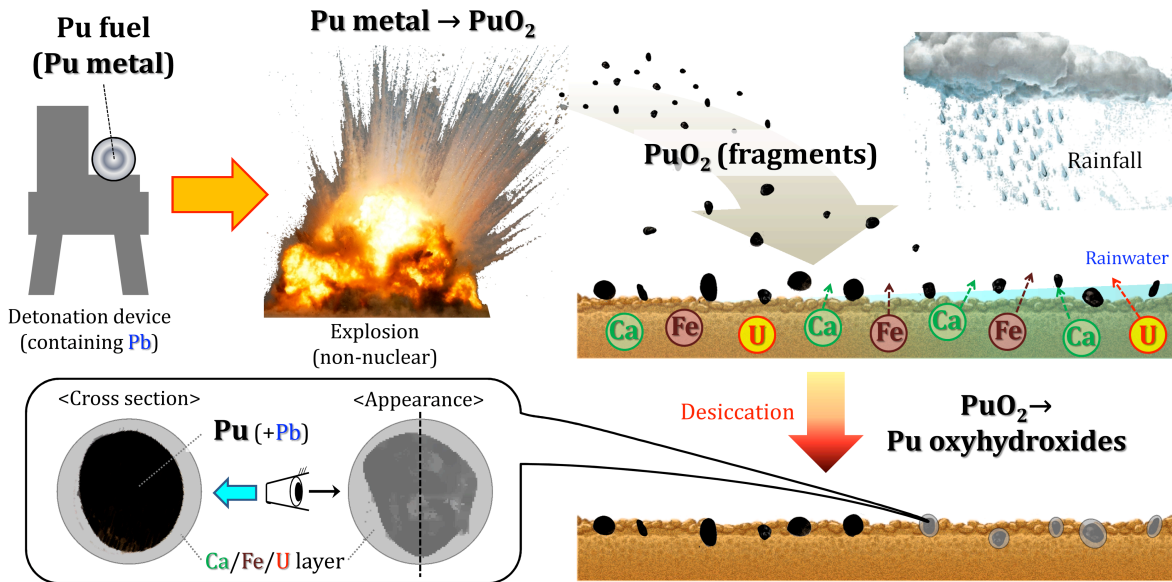


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Figure 3. (Upper inset) Pu L_{III}-edge XANES spectra for the fragment of the isolated Pu particle shown in Fig. 2 (blue) and reference compounds of metallic Pu (Pu_{0.965}Ga_{0.035}, black)¹⁹ and PuO₂ (red).²¹ (Main figure) A plot of XANES first inflection points versus their peak positions at Pu L_{III}-edge for a series of Pu compounds with different oxidation states. The energy of the data was calibrated according to the first inflection point of Zr foil (defined as 17999.35 eV).

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276 **Figure 4.** A scenario explaining the possible chemical transformation of Pu weapon components
277 released in the semi-arid environment by non-nuclear detonation events.

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286 ASSOCIATED CONTENT

287 **Supporting Information.** Gamma spectrum, X-ray fluorescence spectra, X-ray fluorescence
288 microscopic images and X-ray absorption spectra of the isolated Pu particle, additional
289 descriptions of experimental details and interpretation of experimental data. This material is
290 available free of charge via the Internet at <http://pubs.acs.org>.

291

292 AUTHOR INFORMATION

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295 **Author Contributions**

296 The manuscript was written through contributions of all authors. All authors have given approval
297 to the final version of the manuscript.

298 **Notes**

299 The authors declare no competing financial interest.

300

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307 data of reference Pu compounds.

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421 **Table of Contents Graphic and Synopsis**



422

423 The plutonium legacy from a former nuclear weapons test in Australia was characterized as a
424 particulate form of Pu(IV) oxyhydroxides, which would be a potential source of long-term
425 internal radiation if lodged within an organism.

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