Helmholtz-Zentrum Dresden-Rossendorf (HZDR)



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

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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.

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 trials") in the Great Victoria Desert, South Australia (Fig. 1-(a)).¹⁻² These tests caused 41 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 deposition plumes extending for tens of kilometers outside the clean-up area.³ A reliable 45 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

and beta decay reactions from the parent ²³⁹Pu. As a result, the activity concentrations of ²⁴¹Am 60 are proportional to those of ²³⁹Pu (²³⁹Pu/²⁴¹Am ratios of 3.4 mean, 0.5 standard deviation) as 61 62 measured in the soils of the NW plume. This ratio can vary from plume to plume depending on the composition of the original tested material.^{3,5} Among the collected fifty soil samples, one soil 63 sample containing the highest ²⁴¹Am activity concentration of 1.3 kBg/kg was selected for further 64 65 treatment to isolate Pu contaminants. The selected soil sample was then passed through a 125 µm sieve to remove large sand particles and debris. Ten grams of the sieved sample was then 66 dispersed in 30 ml of lithium heteropolytungstate (LST) heavy liquid (D = 2.9 g/ml) for density 67 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 sediments (0.32 g) held at least one particle showing high ²⁴¹Am activity. The collected 72 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 process, only the third densest of which contained almost all of the original ²⁴¹Am activity. This 75 76 subsample containing ²⁴¹Am was further split within small droplets of aqueous solution, 77 measured by gamma spectrometry, and repeated until a single particle (approximately 150-200 78 um 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 ²⁴¹Am 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 (XRF) mapping⁷ and X-ray absorption near edge structure (XANES) mapping in fluorescence 97 98 mode⁸ at the Pu L_m-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 WinXAS (Version 3.2).¹¹ The acquired X-ray fluorescence data were deconvoluted based on the 105

Dynamic Analysis matrix transform method¹² to obtain elemental concentration maps as a 106 function of incident beam energy. Pu L_m-edge X-ray absorption spectra were produced based on 107 108 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 absorption fine structure (EXAFS) region was performed with the software WinXAS¹¹ according 110 to the standard procedure.¹³ Theoretical phase and amplitude for EXAFS theoretical fitting were 111 calculated by a program code FEFF8.20¹⁴ based on the crystal structures of metallic Pu and 112 PuO_{2} .¹⁵ 113

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 trial" in 1957, twelve "Minor trials" were conducted between 1960 and 1963.² These tests 119 120 dispersed more than 22 kg of Pu, resulting in four contaminated plumes radiating from the test site.² The sampling point is situated within the northwest (NW) plume (Fig. 1-(c)), where the 121 122 main radioactive contamination was caused by the Minor trial "Vixen B2 – Round 5" undertaken in May 1961.^{2, 16} The "Vixen B" trials involved the burning and detonation of nuclear weapon 123 124 components with high-explosives to ascertain the potential for accidents to trigger nuclear explosions.² A "limited number of fissions" during testing were reported,² suggesting that the 125 original Pu materials employed for the trials was presumably metallic Pu with fissile ^{239,241}Pu 126

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

129

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

137 Because of the physical/chemical complexity and diversity, the chemical analysis of environmental samples is always a challenging task.⁴ Synchrotron-based XFM is an emerging 138 139 and powerful tool to comprehensively characterize not only environmental samples¹⁷ but also biological and geological samples,¹⁸ providing the information on elemental distribution, 140 141 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 presence of these elements in the fragment. No major FPs of Pu isotopes (e.g., noble metals or 145 146 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

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

153

154 Figure 2

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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 (XANES) region is not consistent with that for Pu-metal,¹⁹ the original Pu compound dispersed at 158 the site, but rather similar to those for oxide compounds, such as PuO_2 (inset of Fig. 3).¹⁹ The 159 160 XANES absorption edge and peak positions of the fragment, both of which are indicative of the oxidation states and chemical compositions,²⁰ are comparable with those of Pu(IV) compounds, 161 such as PuO₂¹⁹ or oxyhydroxides²¹ (Fig. 3). The extended X-ray absorption fine structure 162 163 (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

Transformation of original plutonium materials. In the "Vixen B" trials, the explosions were 170 171 reportedly triggered by a high-explosive chemical, such as TNT², which can generate temperatures over 3,000 °C.²² The initial Pu component (i.e., metallic Pu) was, therefore, subject 172 173 to a high temperature environment during explosion, which prompted the instant oxidation to PuO₂, the highest oxidation state and most stable form of Pu oxide compounds.²³ Other lower Pu 174 oxides, such as Pu₂O₃, are unstable and eventually transformed into PuO₂.²⁴ The metallic Pu is 175 176 also known to be self-ignitable in the air at temperatures exceeding 500 °C, resulting in the formation of PuO₂.²⁵ Based on these facts, it is reasonable to posit that the initial Pu component 177 178 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 eventually transformed into PuO_{2+x}^{24} , which can be more accurately described as PuO_{2+x}^{24} . 182 $_{v}(OH)_{2v}$: $zH_{2}O$.²¹ The chemical interaction of these Pu compounds with local minerals and soils 183 184 could potentially occur via, for instance, the dissolution of Pu into water. However, both PuO₂ and $PuO_{2+x-y}(OH)_{2y}$; zH_2O are expected to be sparingly soluble²⁶ in the local climate conditions at 185 186 Maralinga,² suggesting that the chemical form of Pu would be unlikely to be affected by prolonged exposure to the local minerals and soil environment. Hence, $PuO_{2+x-y}(OH)_{2y}$: zH_2O is 187 188 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 as compared with PuO₂,^{19,21} which is consistent with our XANES data in Figs. 2 and S13 in SI. 190 191 The Pu oxyhydroxides could be poorly structured due to the partial oxidation of Pu(IV) to higher oxidation states.^{21, 27} This could account for the EXAFS results indicating lower coordination 192

193 numbers for Pu O and Pu Pu shells in the fragments as compared with those in PuO_2 (Table S1 194 in SI).

195

196 Figure 4

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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 isotopes, indicating that the Pb probably originates either in Pb-metal/alloy tampers¹ which 201 202 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 constituents from local soils, which are reported to be rich in these elements,²⁸ on the surface of 205 206 the core particle.

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

concentrated internal Pu sources.³⁰ This scenario can explain the elevated Pu activity 214 215 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 protection³¹ is based largely on the uptake of dissolved Pu forms which behave differently from 217 218 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 nonrefractory particulates of Pu oxides from non-nuclear accidents.³⁴ These different forms of Pu 230 231 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.





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

83.9 µm Elastic Pb Fe Ca Ca, Fe Pb, U, Pu Pu 0 (wt%) 0 (wt%)

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.



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).



Figure 4. A scenario explaining the possible chemical transformation of Pu weapon componentsreleased in the semi-arid environment by non-nuclear detonation events.

286 ASSOCIATED CONTENT

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

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295 Author Contributions

296 The manuscript was written through contributions of all authors. All authors have given approval

to the final version of the manuscript.

298 Notes

299 The authors declare no competing financial interest.

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- 307 data of reference Pu compounds.
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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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