Particulate plutonium released from the Fukushima Daiichi meltdowns

Eitaro Kurihara a, Masato Takehara a, Mizuki Suetake a, Ryohei Ikehara a, Tatsuki Komiya a, Kazuya Morooka a, Ryu Takami a, Shinya Yamasaki b, Toshihiko Ohnuki c, Kenji Horie d,e, Mami Takehara d, Gareth T.W. Law f, William Bower f, J. Frederick W. Mosselmans g, Peter Warnicke b, Bernd Grambow i, Rodney C. Ewing j, Satoshi Utsunomiya a,*

a Department of Chemistry, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
b Faculty of Pure and Applied Sciences and Center for Research in Isotopes and Environmental Dynamics, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan
c Laboratory for Advanced Nuclear Energy, Institute of Innovative Research, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan
d National Institute of Polar Research, 10-3, Midori-cho, Tachikawa-chi, Tokyo 190-8518, Japan
e Department of Polar Science, The Graduate University for Advanced Studies (SOKENDAI), Shonan Village, Hayama, Kanagawa 240-0193, Japan
f Radiochemistry Unit, Department of Chemistry, The University of Helsinki, Helsinki 00014, Finland
g Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, UK
h Swiss Light Source, Paul Scherrer Institute, 5232 Villigen, Switzerland
i SUBATECH, IMT Atlantique, CNRS-IN2P3, The University of Nantes, Nantes 44307, France
j Department of Geological Sciences and Center for International Security and Cooperation, Stanford University, Stanford, CA 94305-2115, USA

HIGHLIGHTS

• Debris nano-fragments were captured in the cesium-rich microparticles (CsMPs).
• Plutonium and U isotopes in CsMPs have been precisely determined.
• Plutonium oxides occur as a submicron-sized concentrate in uraninite matrix.
• Long-distance dispersion of Pu is mainly attributed to the transport of CsMPs.

ABSTRACT

Traces of Pu have been detected in material released from the Fukushima Daiichi Nuclear Power Plant (FDNPP) in March of 2011; however, to date the physical and chemical form of the Pu have remained unknown. Here we report the discovery of particulate Pu associated with cesium-rich microparticles (CsMPs) that formed in and were released from the reactors during the FDNPP meltdowns. The Cs-pollucite-based CsMP contained discrete U(IV) O2 nanoparticles, ~10 nm, one of which is enriched in Pu adjacent to fragments of Zr-cladding. The isotope ratios, 235U/238U, 240Pu/239Pu, and 242Pu/239Pu, of the CsMPs were determined to be ~0.0193, ~0.347, and ~0.065, respectively, which are consistent with the calculated isotopic ratios of irradiated-fuel fragments. Thus, considering the regional distribution of CsMPs, the long-distance dispersion of Pu is mainly attributed to the transport by CsMPs that have incorporated nanoscale fuel fragments prior to their dispersion up to 230 km away from the Fukushima Daiichi reactor site.
1. Introduction

The nuclear disaster that occurred at the Fukushima Daiichi Nuclear Power Plant (FDNPP) in March 2011 released $10^{19}$ Bq of radioactivity into the environment; this included fission products (Xe, I, and Cs) (Bueseler et al., 2017; Steinhauser et al., 2014) and trace quantities of actinides, such as U and Pu (Sakaguchi et al., 2014; Yamamoto et al., 2014; Zheng et al., 2012, 2013). In the reactor units #1–3, a large fraction of nuclear fuel, which is mainly composed of UO$_2$, melted and caused the failure of each unit’s reactor pressure vessel (RPV) (Nagase et al., 2016). The melting fuel mixed with various structural materials, such as concrete and steel, and cooled to remain as “debris” inside the reactors. The amount of U and Pu released from the FDNPP have been estimated to be $6.1 \times 10^5$ and $2.0 \times 10^6$% of the core inventory, respectively (Sakaguchi et al., 2014; Zheng et al., 2013). The Pu radioactivity in surface soils in the vicinity of the FDNPP was determined to range from 0.003 to 3.924 Bq/kg (Yamamoto et al., 2014). The comparatively small amount of released Pu was previously ascribed to the low volatility of U and Pu in nuclear fuel (Grabow and Poinssot, 2012). Despite the limited amount of Pu in the environment surrounding the FDNPP, the occurrence of Pu isotopes (half-lives of 239Pu, 235Pu, 240Pu, and 241Pu were 87.74 years, 2.411 x 10^3 years, 5653 years, and 14.35 years, respectively) have been a concern because of the high effective dose conversion coefficient for these isotopes in the event of internal exposure ($1.5 \times 10^{-3}$ Sv/Bq for 239Pu, 238Pu, and 237Pu, $1.6 \times 10^{-2}$ Sv/Bq for 240Pu, and 1.4 x 10^{-2} Sv/Bq for 242Pu) (ICRP, 2012). Also, 32 of the 548 fuel assemblies in reactor unit 3 were a metal oxide fuel (MOX fuel); U oxide mixed with ~3.9 wt% of Pu, (U,Pu)O$_2$.

Before the FDNPP meltdowns, the average isotope ratios of 235U/238U, 240Pu/239Pu, and 242Pu/239Pu in the irradiated fuels of units 1–3 were calculated to be 0.0172–0.0193, 0.319–0.355, and 0.0612–0.0654, respectively (Nishihara et al., 2012). Note that these values are only representative isotope compositions averaged across the entire fuel inventory before meltdowns. A significant heterogeneity likely occurred in the isotopic and chemical composition of the fuel debris during, and possibly after the meltdowns.

Although intrinsic U and Pu oxide microparticles have been previously characterized in various contaminated environments utilizing micro-focused X-ray analysis (e.g., Batuk et al., 2015; Eriksson et al., 2005; IAEA, 2011; Ikeda-Ohno et al., 2016; Salbu et al., 2001), reports on the form of U and Pu released from the FDNPP has been limited by the extremely low bulk Pu concentration in regional soils, which is at the level of global radioactive fallout from the testing of nuclear weapons (Igarashi et al., 2019). However, the recent discovery of U oxides and fuel debris microparticles associated with FDNPP derived Cs-rich microparticles (CsMPs) in the vicinity of the site (Ochiai et al., 2018) raises the possibility that Pu might have been released together with U in particulate form to the surrounding environment. The CsMPs are generally composed of Si, Fe, Zn, and Cs; they are sparingly soluble and have high radioactivity per unit mass ($10^{11}$ Bq/g), and their size ranges from submicron to tens of microns (Furuki et al., 2017; Suetake et al., 2019; Utsunomiya et al., 2019). The $^{134}\text{Cs}^{137}\text{Cs}$ radioactivity ratio can be used to assign the source reactor because of the homogenized isotopic composition of the volatilized Cs ($>670$ °C) within the damaged reactors, where temperatures approached ~2200 K. The $^{134}\text{Cs}^{137}\text{Cs}$ radioactivity ratio of CsMPs is typically slightly over ~1 (Furuki et al., 2017), which agrees well with the ratios for units 2 (~1.08) and 3 (~1.05). The CsMPs formed inside the reactor were released, and dispersed over an area ~10,000 km$^2$ in the Fukushima prefecture and Kanto region of eastern Japan (Adachi et al., 2013; Furuki et al., 2017; Ikehara et al., 2018, 2020; Utsunomiya et al., 2019; Yamasaki et al., 2016).

Another type of radioactive particle released from unit 1 of the FDNPP has been identified (Igarashi et al., 2019); however, this has not been defined as a CsMP because of its comparatively low Cs content (which is undetectable with energy dispersive X-ray analysis (EDX)). As a consequence, this type of particles was not investigated in the present study. Compared with CsMPs, the other type of particle is different in its physico-chemical properties; namely, they have a much lower Cs content and a different matrix composition, with a slightly lower $^{134}\text{Cs}^{137}\text{Cs}$ radioactivity ratio of ~0.9. They are also larger (~several hundred μm) and are found in a limited area of distribution in the north-northwest zone close to the FDNPP. This distribution is linked to the direction of blast materials from the hydrogen explosion of unit 1. The presence and isotopic signatures of Pu in this other type of radioactive particle have been recently investigated by dissolution techniques (Igarashi et al., 2019). Based on a whole digestion and solution analysis, the Pu isotopes were determined to be $^{240}\text{Pu}^{238}\text{Pu}$ of 0.330–0.415 and $^{241}\text{Pu}^{239}\text{Pu}$ of 0.162–0.178 with large uncertainties; 9–23% (Igarashi et al., 2019), and thus it was difficult to be used as an explicit isotopic signature for Pu.

Compared with the large radioactive particle derived from unit 1 distributed only within a limited area near FDNPP, CsMPs of a smaller size were distributed across a wide area in the Kanto region (up to 230 km away from FDNPP). The relation between CsMPs and long-range Pu transport has been inferred in a previous study (Yamamoto et al., 2014), but the previous studies failed to detect Pu in the CsMPs (Igarashi et al., 2019; Yamamoto et al., 2014). The purpose of the present study is to elucidate the dispersion and release mechanisms of FDNPP-derived Pu into the environment and to better understand the properties of the debris, in particular any occurrence of Pu. This is based on a combination of advanced analyses of Pu and U isotopic signatures, speciation and elemental distribution measurements, and characterization of the internal texture and structural characteristics of individual CsMPs that have been released from the FDNPP units 2 or 3.

2. Samples and methods

2.1. Samples

Soil samples were collected at an aquaculture center (AQC) and a paddy field in Ottozawa (OTZ), Okuma town, within ~4 km of the FDNPP (Fig. 1). Surface soils of the dimension of 20 cm x 20 cm x ~5 cm depth were sampled from areas without vegetation. All of the collected soils were air dried and sieved through 2 mm Tetron mesh to remove pebbles and plants. Soil particles <2 mm were used for the present experiments. Isolation of three CsMPs was completed for three soil samples collected from the two locations, which were labeled as AQC1, AQC2, and OTZ.
2.3. Gamma spectrometry

The procedure for separating CsMPs from soil samples followed the method developed in our previous study (Furuki et al., 2017). First, the soil samples were sieved through a 114-μm mesh. The samples were dispersed on an Al plate and covered with a plastic sheet; an imaging plate (IP; Fuji film, BAS-SR 2025) was then placed on the samples for 5–25 min. The autoradiograph was recorded with a pixel size of 100 μm using an IP reader (GE, Typhoon FLA 5100). After identifying the positions of intense radioactive spots, droplets of pure water were added to the positions and then taken up using a pipette to make a suspension with a small amount of soil particles. The procedure was repeated until the suspension did not contain a significant amount of soil particles. CsMPs are sparingly soluble because of the Si glass matrix (Suetake et al., 2019), as such, this procedure would not have affected the chemical properties of the CsMPs. Subsequently, the position containing a highly radioactive spot was sampled using double-sided carbon tape. The piece of carbon tape with the radioactive particle was cut into smaller pieces using a blade. The small pieces were scanned again by autoradiography before a scanning electron microscopy (SEM) observation. The pieces were placed on an Al plate and coated with carbon using a carbon coater (SANYU, SC-701C) prior to SEM analysis. The CsMP was found using an SEM (Shimadzu, SS550 and Hitachi, SU6600) equipped with energy dispersive X-ray spectrometry (EDX, EDAX Genesis). The acceleration voltage was 5–25 kV for imaging details of the surface morphology and 15–25 kV for elemental analysis, including area analysis and elemental mapping.

2.4. Secondary ion mass spectrometry

134Cs and 137Cs radioactivities of the three CsMPs were determined using gamma spectrometry. The radioactivity of an additional microparticle with a size of ~400 μm obtained from the surface soil in Fukushima was precisely determined at the radioisotope center in Tsukuba University, Japan, and utilized as a standard point specimen for 134Cs and 137Cs, which was used in a previous study (Furuki et al., 2017). The radioactivity of the point source standard was 23.9 Bq for 134Cs and 94.6 Bq for 137Cs as of September 29, 2015. The measurement of radioactivity was performed on CsMPs and the point source standard using a gamma spectrometer equipped with a low background type germanium detector GMX30200 (EG&G ORTEC Ltd.) in Tsukuba University, Japan and Ge semiconductor detector GMX40 (SEIKO E&G) at the Center for Radioisotopes in Kyushu University, Japan. The acquisition times were 4800 s for AQC using GMX30200 and 65,878 s for OTZ using GMX40.

2.5. Synchrotron analysis

After performing SIMS analysis, X-ray fluorescence (XRF) mapping and discrete-area X-ray absorption near-edge spectroscopy (XANES) was completed at beamlines 118, at Diamond Light Source, UK, and X05LA at the Swiss Light Source. In both instances, AQC1 was mounted on carbon tape and double contained in Kapton windowed radioactive sample holders for analysis. At beamline 118 (double-crystal monochromator), the synchrotron micro-beam was focused to a horizontal width of ~2 μm. XRF mapping was performed with an incident beam energy of 18.1 keV. Uranium and Pu L-edge XANES data were collected in fluorescence mode at ambient temperature with minimum step sizes of 0.1 eV and 0.5 eV over the absorption edges of U and Pu, respectively. Fluorescence data were collected using the beamline’s 4 element Vortex Silicon Drift Diode (SDD). Uranium (IV/VI) reference standards were the research teams own, with data collected on beamline B18 at the Diamond Light Source (calibrated using in-line Y foil). The U(IV) standard is a crystalline uraninite (UO2) powder and the U(VI) standard is a crystalline metaschoepite (UO2·nH2O) powder. Plutonium standards were not run.

At beamline X05LA (double-crystal monochromator), the synchrotron micro-beam was focused to a horizontal width of ~1 μm. On-the-fly XRF maps, windowed for Fe, Zn, Zr, Mn, Sr, and U were collected at incident beam energies of 18.0 and 18.1 keV. Pu L-edge XANES data were collected in fluorescence mode at ambient temperature with a step size of 0.5 eV over the absorption edge. Fluorescence data was collected using the beamlines’ single-element Ketek SDD. At both beamlines, Y and Zr foils were used to calibrate the U and Pu absorption edges, respectively. XRF mapping data were processed using PyMCA (Solé et al., 2007). Although µXRF analysis was not used for quantitative elemental analysis in the present study, the synchrotron-based XRF facilities used at both beam-lines can typically analyze U and Pu down to concentrations of several 10s of ppm. Maps were normalized for comparability by subtracting the base noise level from the maps and dividing the maps by the maximum pixel intensity. XANES data were aligned and normalized using Athena (Demeter Suite) (Ravel and Newville, 2005).

2.6. Transmission electron microscopy (TEM) analysis and the specimen preparation

High-resolution TEM (HRTEM) with energy dispersive X-ray analysis (EDX) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were performed using a JEOI JEM-ARM200F with an acceleration voltage of 200 kV at the Ultramicroscopy Research Center (URC) of Kyushu University. The spatial resolution is ~0.11 nm. The JEOI Analysis Station software was used to control the STEM-EDX mapping. To minimize the effect of sample drift, a drift-correction mode was used during acquisition of the elemental map. The detection limit of EDX analysis is typically ~0.1 wt%. The STEM probe size was ~0.13 nm, generating ~140 pA of current when 40 μm of the condenser lens aperture was inserted. The collection angle of the HAADF detector was ~97–256 mrad.
A focused ion beam (FIB) system (FEI, Quanta 3D FEG 200i Dual Beam) was utilized to prepare thin foils of AQC1 after SIMS and synchrotron X-ray analysis. The ion source was Ga, while W deposition was used to minimize damage by the ion bombardment covering a rectangle area of ~3 × 8 μm size (Fig. S1a). The current and acceleration voltage of the ion beam were adjusted to be 100 pA to 30 nA and 5–30 kV depending on the progress of thinning and sample properties such as hardness and size. The thinned piece of size of ~2 × 6 × 8 μm was attached to the semilunar-shaped Cu grid for FIB and further thinned to ~200 nm thickness by an ion beam at 5 or 8 kV.

The above analysis was performed in the order of SIMS > μ-focus X-ray analysis > TEM, so that the CsMPs containing U and Pu can be efficiently analyzed. Due to the limited size of the samples compared with the SIMS ion probe, AQC2 and OTZ were entirely consumed during SIMS analysis and the further analyses could not be performed. The μ-focus X-ray analysis and TEM were competed only for sample OTZ1.

3. Results and discussion

3.1. Occurrence of U and Pu in the CsMPs revealed by the advanced nano-scale analyses

In the present study, three CsMPs, labeled as AQC1, AQC2, and OTZ, were isolated from the surface soils sampled within 3.9 km of the FDNPP (Fig. 1 and Table 1). Secondary electron images from scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) elemental maps, and the resulting spectra revealed a morphology and major element composition (Si, Fe, Zn, Cs, and O) typical of CsMPs reported in the literature (Furuki et al., 2017; Ikehara et al., 2018; Ochiai et al., 2018) (Fig. 2a–c). AQC1 occurs as an aggregate of smaller CsMP particles, while AQC2 and OTZ are individual microparticles. In all EDX spectra, Al concentrations may have been enhanced due to background soil materials. The amount of the other major and minor elements such as Fe, Zn, and Sn are similar to that of CsMPs previously reported (Furuki et al., 2017).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>KU-CsMP No.</th>
<th>Latitude—longitude</th>
<th>Distance from FDNPP (km)</th>
<th>Soil type</th>
<th>Sampling date</th>
</tr>
</thead>
<tbody>
<tr>
<td>AQC1</td>
<td>AQC6</td>
<td>37°24′27.626″N, 141°01′55.801″E</td>
<td>1.0</td>
<td>Surface soil of field</td>
<td>2012/3/16</td>
</tr>
<tr>
<td></td>
<td>KU-161</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AQC2</td>
<td>AQC8</td>
<td>37°24′27.626″N, 141°01′55.801″E</td>
<td>1.0</td>
<td>Surface soil of field</td>
<td>2012/3/16</td>
</tr>
<tr>
<td></td>
<td>KU-171</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OTZ</td>
<td>OTZ25</td>
<td>37°25′05.570″N, 141°00′21.661″E</td>
<td>3.9</td>
<td>Surface soil of field</td>
<td>2017/7/27</td>
</tr>
<tr>
<td></td>
<td>KU-309</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1

Information on the sampling for CsMPs characterized in the present study. KU-CsMP number and KU-soil number represent a label of CsMP and soil samples in the Kyushu University sample archive.

Fig. 2. Results of scanning electron microscopy including elemental maps and EDX spectra from three CsMPs; (a) OTZ, (b) AQC1, and (c) AQC2. The images are secondary electron images in (a) and (b), and a back-scattered electron image in (c). The red square in (b) indicates the position of the EDX analysis with a rastered electron beam. The area outlined by the white dotted line indicates the etched hole that resulted from SIMS analysis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
et al., 2017; Imoto et al., 2017; Utsunomiya et al., 2019), and they are derived from structural materials such as stainless steel, Zr–Sn alloy claddings, and primary cooling water (that contained Zn) (Abe et al., 2014). In the CsMPs, the total radioactivities of $^{134}$Cs and $^{137}$Cs per unit mass are in the order of $10^{11}$ Bq/g, and the $^{134}$Cs/$^{137}$Cs radioactivity ratios range from 1.05 to 1.17 after decay-correction to March 11th, 2011. This demonstrates that the CsMPs originated from the volatilized Cs stemming from molten fuel inside the damaged FDNPP reactor units 2 or 3 (Table 2). In general, the CsMPs were considered to form through molten core–concrete interaction at the concrete pedestal of the primary containment vessel, where the volatilized Cs, stemming from molten fuel, was condensed with vaporized silica (Furuki et al., 2017).

Synchrotron micro-focus X-ray fluorescence ($\mu$XRF) mapping was successfully performed on AQC1. Mapping of the whole particle showed that the distribution of Fe was slightly different to Zn (Fig. 3a). Further detailed mapping of the area outlined by the white dotted rectangle in the Fe map of Fig. 3a also revealed heterogeneously localized distributions of U, Zr, Sr (Sr masked any Pu signal) and Mn within AQC, implying that the melted fuel fragment reacted heterogeneously with Zr-containing fuel cladding at the micron-scale. Indeed, prior work has characterized nanoparticles of (U, Zr) oxide solid solution containing a wide range of U/Zr ratios (Ochiai et al., 2018). Iterative-target factor analysis (ITFA) (Rossberg et al., 2003) of the U L$_3$-edge $\mu$XANES (Fig. 3b), collected from the point indicated by red arrow (Fig. 3a), and comparison with U(Iv) and U(VI) standards, suggests that the U predominantly occurs as U(IV) oxide (i.e. there was no meaningful spectral contribution from U(VI)) (Fig. 3b).

Plutonium $\mu$XRF mapping was attempted; however, it was hampered due to interference from Sr. Within the U distribution map, the three spots with highest U intensity (indicated by the arrows in Fig. 3a) were further analyzed in an attempt to obtain X-ray absorption spectra at the Pu L$_3$-edge. In the three areas of highest U, two spots (indicated by the white arrows) did not show a Pu absorption edge; in contrast, the area indicated by the red arrow had enough Pu to permit collection of an absorption edge, albeit of low quality (Fig. 3c). Given the noise in the data and to ensure reproducibility, the Pu L$_3$-edge XANES spectrum was collected from the same point in the sample at both micro-focus beamlines used in this study (Fig. 3c). This highlights Pu occurrence within the CsMP and represents the first Pu XANES spectrum collected from Fukushima soils, where Pu is present at levels similar to global fallout. While the low signal to noise ratio precludes confident evaluation of the Pu speciation in the CsMP inclusion, the shape of the spectrum at least indicates that the Pu occurs as a Pu oxide (e.g. Ankudinov et al., 1998; Conradson et al., 2004), and not as Pu metal, which has a reduced XANES amplitude (e.g. Clark and Hobart, 2019; Ikeda-Ohno et al., 2016).

A thin foil for TEM observation was then made from the part of AQC1 indicated by a red rectangle in Fig. 3a using a focused ion-beam system to investigate textural and structural characteristics. A cross sectional view in HAADF-STEM images and EDX elemental maps of major elements revealed that AQC consists of a variety of nano-phases including Cs-pollicite (Cs–Fe silicate), ilmenite (Fe–Ti oxide), magnetite (Fe oxide), and chromite (Fe–Cr oxide), based on the diffraction pattern and composition (Fig. 2b and Fig. S1b – e). Although a typical CsMP comprises a SiO$_2$ glass matrix with Fe, Cs, and Zn, Cs-pollicite is a zeolite phase that can form within CsMPs when the Cs concentration is extremely high (~10 wt%; Imoto et al., 2017). Closely associated with the Fe oxides, several U oxide nanoparticles were also found as indicated by yellow and red arrows in Fig. 4a, which are labeled from U1 to U4 (Fig. 4b and Fig. S2). A high-resolution HAADF-STEM image of U

![Table 2](image)

**Table 2**

Size and radioactivity of CsMPs used in this study. The radioactivity of CsMPs was decay-corrected to March 11, 2011.

<table>
<thead>
<tr>
<th>CsMP</th>
<th>Particle size (µm)</th>
<th>Radioactivity (Bq)</th>
<th>$^{134}$Cs/$^{137}$Cs radioactivity ratio</th>
<th>Radioactivity per unit mass (Bq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$^{134}$Cs</td>
<td>$^{137}$Cs</td>
<td></td>
</tr>
<tr>
<td>AQC1</td>
<td>17.8–27.9</td>
<td>11.76 (±1.30)</td>
<td>11.24 (±2.43)</td>
<td>1.12</td>
</tr>
<tr>
<td>AQC2</td>
<td>4.6–5.0</td>
<td>11.24 (±1.8)</td>
<td>11.34 (±0.04)</td>
<td>1.17</td>
</tr>
<tr>
<td>OTZ</td>
<td>2.6–2.8</td>
<td>12.72 (±0.035)</td>
<td>11.39 (±0.195)</td>
<td>1.12</td>
</tr>
</tbody>
</table>

![Fig. 3](image)

**Fig. 3.** Results of synchrotron X-ray analysis. (a) Synchrotron micro-focus X-ray fluorescence ($\mu$XRF) elemental maps for the entire area of AQC1 outlined by the orange dotted rectangle in Fig. 2b, revealing the distribution of Fe and Zn, collected at beamline X05LA at the Swiss Light Source. The horizontal beam size was ~1 µm. High-resolution (step size 0.5 µm) $\mu$XRF elemental maps of U, Zr, Mn, and Sr for the area indicated by the white dashed square in the Fe map. (b) Uranium L$_3$-edge X-ray absorption near-edge structure (XANES) of a discrete point within AQC1, indicated by the red arrow in the U L$_3$ map. The spectrum is plotted alongside U(Iv) and U(VI) oxide standards. (c) Discrete-area Pu L$_3$-edge XANES collected from the point within AQC1 indicated by the red arrow in the U L$_3$ map. The XANES spectra from the point indicated by the white arrows in the U L$_3$ map did not show any Pu absorption edge. The two normalized and energy calibrated Pu L$_3$-edge spectra are presented, one collected from each beam-line used in the study. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
indicated by the red arrow revealed a periodic array of U atoms corresponding to the (111) plane of uraninite (Fig. 4c), indicating that U dioxide nanoparticles were encapsulated during the formation of the CsMP, as reported in our previous study (Ochiai et al., 2018) and as indicated from the U L$_3$-edge XANES (Fig. 3b). The scattered occurrence of uraninite nanoparticles within AQC is consistent with the heterogeneous U distribution observed in the μXRF map (Fig. 3a), which does not correlate with the distribution of other elements within CsMP.

Based on the results obtained from TEM, XRF elemental mapping, and XANES analyses, U predominantly occurs as U(IV) oxide in the CsMP, with small Pu oxide-enriched areas also present. As such, the particle appears to be a debris fragment with fuel composition that has been minimally affected by the subsequent alteration owing to its encapsulation in the CsMP. With increasing burn-up, actinides such as Np, Pu, and Am substitute for U in UO$_2$ matrix (Konings et al., 2015); thus, the trace Pu is distributed within the UO$_2$ matrix. The maximum value of burn-up: 40 GWd/tHM for both units 2 and 3 (Nishihara et al., 2012), is high enough to have Pu concentrates at fuel edge sites due to the higher burn-up (Bruno and Ewing, 2006; Burns et al., 2012; Ewing, 2015). Hence, the slightly enhanced Pu concentration, likely at ppm level, detected by μXANES within the UO$_2$ matrix is plausibly derived from a Pu concentrate at the rim of irradiated fuel, where a U, Zr oxide eutectic formed as inferred from localized Zr occurrence (Fig. 3) and also characterized in another CsMP utilizing TEM (Ochiai et al., 2018). Because the nuclear fuel fragment was not subjected to significant alteration, the initial state of Pu(IV) that substitutes for U in the irradiated UO$_2$ (Ewing, 2015; Konings et al., 2015) has likely remained in its initial state, which is consistent with the XANES data that indicates Pu is present as an oxide.

### 3.2. Plutonium and U isotope ratios in the CsMPs

Secondary ion mass spectrometry (SIMS) was successfully applied to determine U and Pu isotopes in the three CsMPs (Table 3). During SIMS analysis, the ionized isotopes were detected either in non-oxide ion or oxide ion form. Oxide form means an element bound to oxygen such as $^{235}$U$^{16}$O, of which the total mass of 251 is measured. The non-oxide form of ionized isotopes was detected for two analytical spots in AQC1, one spot in AQc2, and one spot in OTZ, while oxide ions were only detected for two spots in AQC1 and one spot in AQC2, due to the limited sample volume for OTZ (the OTZ CsMP was consumed by the first set of analysis detecting the non-oxide ion form and could not be used for the second set of analysis detecting the oxide ion form). As revealed in Fig. 5 and Table 3, isotope ratios in non-oxide and oxide form revealed almost identical values for $^{235}$U/$^{238}$U and $^{239}$Pu/$^{238}$U, but the greater number of ions were counted for the oxide form. The $^{235}$U/$^{238}$U isotope ratios of the four analyzed spots are 0.01935 (±0.00009), 0.01935 (±0.00006), 0.01935 (±0.00011), and 0.01925 (±0.00012).
CsMPs (Ochiai et al., 2018). Despite that the burnup of the irradiated fuel at the time of nuclear disaster ranged from 3.3 to 40 GWd/tHM for unit 2 and from 4.5 to 40 GWd/tHM for unit 3 (Nishihara et al., 2012), because the Pu concentration was as high as ~2.8 wt% (Nishihara et al., 2012) and occupied 32 of the 548 fuel assemblies of fuel rods so that the U isotopic ratio was homogenized, or the burnup of U oxide analyzed by SIMS in the present study is coincidentally close to the average value of the irradiated fuels in FDNPP at the time of meltdown.

In general, a series of Pu isotopes are produced mainly through the following sequence of nuclear reactions in reactors (Choppin et al., 2002):

$$\beta^- \quad 239\text{Pu}(n,\gamma)^{240}\text{Pu}(n,\gamma)^{241}\text{Am}(n,\gamma)^{242}\text{Am} \rightarrow ^{242}\text{Pu}$$

In which the time in parentheses represents the half-life of the respective radionuclide. The analyzed Pu isotopes are listed in Table 3. Because the isotope ratio of $^{239}\text{Pu}^{235}\text{U}$ was almost identical between non-oxide and oxide forms (Fig. 5b), the following discussion describes Pu-oxide ion ratios simply as a Pu isotope ratio. Plutonium isotope ratios of two spots in AQC1 are plotted in Fig. 5c and exhibit clear difference from the values of global fallout (Kelley et al., 1999). The isotope ratio of $^{240}\text{Pu}^{235}\text{U}$ was determined to be 0.3492 (±0.0040) for AQC1-spot1, 0.3441 (±0.0033) for AQC1-spot2, and 0.3313 (±0.0114) for AQC2, which are close to those of the average Pu vector calculated using ORIGEN2 for the irradiated fuels at the time of disaster in the FDNPP (Nishihara et al., 2012). This is consistent with the results analyzed for bulk soils and litter samples in previous studies (Zheng et al., 2012, 2013). The other results calculated using ORIGEN ARP (Kirchner et al., 2012; Schwantes et al., 2012) and CASMO5 (Yamamoto et al., 2018) revealed slightly higher $^{240}\text{Pu}^{235}\text{U}$Pu isotope ratios. The isotopic ratio of $^{242}\text{Pu}^{239}\text{U}$ was determined to be 0.0668 (±0.0033), 0.0651 (±0.0011), and 0.0622 (±0.0059), which are plotted within the range of the calculated ratios by ORIGEN2 (Nishihara et al., 2012), ORIGEN ARP (Kirchner et al., 2012; Schwantes et al., 2012), and CASMO5 (Yamamoto et al., 2018). For comparison, the Pu isotope ratios were calculated using ORIGEN ARP for the MOX fuels irradiated for 171 days prior to the meltdowns with input data of the fuel at the time of loading (Nishihara et al., 2012), because the Pu concentration was as high as ~2.8 wt% (Nishihara et al., 2012) and occupied 32 of the 548 fuel assemblies in the unit 3 (Nuclear Emergency Response Headquarters, Government of Japan, 2011) leading to the serious concerns of radiotoxicity. The relationship between Pu isotopes clearly indicates that the Pu is not derived from MOX.

Table 3 shows that the $^{238}\text{U}$ ion count ranges from 835 to 975 (cps/nA) (Fig. 5a, Table 3). The isotope ratio is nearly identical to that calculated for the irradiated fuel of units 2 or 3 based on the burnup using ORIGEN2 code; ~0.019 (Nishihara et al., 2012). In our previous study (Imoto et al., 2017), the $^{235}\text{U}^{239}\text{U}$Pu isotope ratio of the analyzed CsMPs was determined to be ~0.029 with low $^{238}\text{U}$ counts; 11 cps/nA. These ratios plotted between that of non-irradiated fuel (0.039) and irradiated fuel (~0.019), which was ascribed to volatilization of a partially oxidized U oxide matrix can vary within the volume of SIMS microanalysis spots in AQC1-spot2, and 0.0059, which are between the different CsMPs.

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>AQC1-spot1</th>
<th>AQC1-spot2</th>
<th>OTZ</th>
<th>AQC2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection non-oxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{235}\text{U}$ (cps)</td>
<td>3.22 (±0.22)</td>
<td>3.78 (±0.32)</td>
<td>1.73 (±0.26)</td>
<td>3.84 (±1.08)</td>
</tr>
<tr>
<td>$^{239}\text{U}$ (cps)</td>
<td>0.69 (±0.14)</td>
<td>0.87 (±0.05)</td>
<td>0.41 (±0.13)</td>
<td>0.67 (±0.35)</td>
</tr>
<tr>
<td>$^{232}\text{U}$ (cps)</td>
<td>167 (±11)</td>
<td>195 (±16)</td>
<td>70 (±14)</td>
<td>192 (±48)</td>
</tr>
<tr>
<td>$^{235}\text{Pu}$ (cps)</td>
<td>0.81 (±0.1)</td>
<td>0.96 (±0.08)</td>
<td>0.49 (±0.15)</td>
<td>1.78 (±0.68)</td>
</tr>
<tr>
<td>Primary beam intensity (nA)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

| Detection oxide |            |            |     |      |
| $^{235}\text{U}^{239}\text{U}$ (cps) | 43.89 (±1.37) | 47.89 (±1.39) | 7.77 (±0.73) |
| $^{235}\text{U}^{239}\text{U}$ (cps) | 2268 (±63) | 2470 (±59) | 400 (±37) |
| $^{235}\text{Pu}^{238}\text{U}$ (cps) | 10.89 (±0.56) | 12.05 (±0.36) | 4.18 (±0.34) |
| $^{235}\text{Pu}^{238}\text{U}$ (cps) | 3.80 (±0.186) | 4.145 (±0.152) | 1.140 (±0.620) |
| $^{235}\text{Pu}^{238}\text{U}$ (cps) | 1.290 (±0.227) | 0.935 (±0.129) | 0.380 (±0.080) |
| Primary beam intensity (nA) | 0.2 | 0.2 | 0.2 | 0.2 |

In early studies, the release of Pu from the FDNPP was considered to occur through volatilization and the amount of Pu released was estimated relative to that of Cs. This was based on the assumption that Pu isotopes and $^{137}\text{Cs}$ were released from the reactors following the same general fate in the meltdown environment (Zheng et al., 2013). Schwantes et al. (2012) proposed that the relative amount of released Pu was proportional to its volatility, which in turn is correlated with...
its Gibbs free energy of formation at 1000 K (Schwantes et al., 2012). However, experimental studies have revealed that the volatility of Pu is lower than that of U (Pontillon et al., 2010; Pontillon and Ducros, 2010), and the amount of Pu released through volatilization has been considered to be negligible in the FDNPP (Grambow and Poinssot, 2012). In addition, ambiguity remained for the wide range of Pu radioactivity in bulk soil samples (Sakaguchi et al., 2014; Yamamoto et al., 2014). This is partly ascribed to the difference in the form of the released Cs; soluble Cs and CsMPs, which formed through different processes and timing (Furuki et al., 2017). The distribution of Pu is not identical to that of Cs. Rather, the scattered occurrence of trace Pu in the surrounding environments reported in the previous studies (Sakaguchi et al., 2014; Yamamoto et al., 2014) is attributed to the Pu transport in the form of microparticles as inferred in the previous study (Kirchner et al., 2012; Zheng et al., 2012). As shown in the micro XRF maps in Fig. 3, Zr occurrence is heterogeneous, indicating that the UO2 in the CsMP was not subject to the homogenization or volatilization and that the fuel fragment itself was captured by the CsMP and released to the environment through the same mechanisms reported previously (Ochiai et al., 2012). This is the direct evidence of Pu release along with fuel fragments that has never been reported for the FDNPP. In general, the particulate occurrence of Pu affects the mobility, bioavailability, transportation, and dose conversion factors, depending on the physicochemical properties (Salbu and Lind, 2016). As shown in previous studies, the scattered distribution of Pu derived from the FDNPP was observed in the large area at ~50 km of radial distance affected by radioactive Cs released from units 2 and/or 3 (Sakaguchi et al., 2014; Yamamoto et al., 2014), while CsMPs were ubiquitously distributed in the area (Ikehara et al., 2018). This suggests that even though fuel fragments were found to be associated with CsMPs in the present study, not all CsMPs contained the fragments when they were released and transported over large distances. In addition, it is highly probable that other fuel fragments were also released directly without association with CsMPs during the explosive events; however, the size must be small enough to allow them to be transported over long distances. Although the discovery of a particulate form of Pu released from the FDNPP may raise the potential risk of Pu uptake, even at large distances from the FDNPP, the Pu radioactivity in bulk samples does not exceed the range of radioactivity from global fallout from the testing of nuclear weapons (MEXT and GSI, 2012; Zheng et al., 2013). Such a low concentration of Pu may not have significant health effects (Taylor, 1995); however, the actual interaction mechanism can be more complicated depending on the occurrence of fuel fragments in CsMPs; either attaching onto the surface or encapsulated by the CsMP. The present study highlights that the fuel fragments containing Pu were released from the reactors to the surrounding environment associated with micron-scale CsMPs. These fuel fragments provide partial but direct information on the processes that the nuclear fuels experienced during the meltdowns, as well as on the current status of debris. Notably, other fissionogenic radionuclides, such as Sr are also associated with the fuel fragment, which is also consistent with the very low-volatility of Sr (Pontillon and Ducros, 2010). These results also suggest that the concentrations of Pu isotopes in the fuel composition of the debris can be reasonably estimated by using a code such as ORIGEN. Currently, the radiation doses are still too high to access inside the reactors; ~11 and ~80 Sv/h within primary containment vessels (PCVs) of units 1 and 2 in 2017, respectively (Tokyo Electric Power Company Holdings, 2017, 2018). Direct characterization of fuel

---

**Fig. 5.** Uranium and Pu isotopic signature of CsMPs released from units 2 or 3 at FDNPP. (a) 235U/238U isotopic ratio of the CsMPs as a function of ion counts (cps/nA) as compared with the values of irradiated and non-irradiated fuels installed in the FDNPP at the time of meltdowns (horizontal lines), which were calculated based on the burnup using the ORIGEN code (Nishihara et al., 2012). For comparison, 235U/238U of the volatilized U in the CsMPs (Imoto et al., 2017) is also plotted. (b) The ratios of 238Pu/238U and 239Pu/238U on four spots of analysis for the three CsMPs. Only the non-oxide form is included for OTZ because of the limited volume of the sample. (c) 239Pu/238U and 239PuO/238UO ion counts of the AQC1 and AQC2 compared with the ratios of bulk soils and litter samples (Zheng et al., 2012), calculated inventory using ORIGEN2 (Nishihara et al., 2012), ORIGEN ARP (Kirchner et al., 2012; Schwantes et al., 2012), and CASMO5 (Yamamoto et al., 2018), the MOX fuels only installed in the FDNPP unit 3 (ORIGEN2 calculation displayed as dashed lines) (Nishihara et al., 2012), and global fallout (Kelley et al., 1999). Error bars exist within the symbols unless otherwise noted.
fragments that were released to the environment (or collected from preliminary investigations inside the reactors using robots) is of crucial importance for understanding the properties of the debris prior to its removal in the course of decommissioning, which is expected to require several decades.

CRediT authorship contribution statement


Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors are grateful to Dr. Watanabe for her assistance on SEM analyses at the Center of Advanced Instrumental Analysis, Kyushu University. This study was partially supported by JST Initiatives for Strategic Energy Basic and Generic Strategic Research and by a Grant-in-Aid for Scientific Research (KAKENHI) from the Japan Society for the Promotion of Science (16K12585, 16H04634, JP26257402). S.U. is also supported by The Mitsubishi Foundation/Research Grants in the Natural Sciences, Environmental Radioactivity Research Network Center (F-19-03), and by ESPEC Foundation for Global Environment Research and Technology (Charitable Trust) (ESPEC Prize for the Encouragement of Environmental Studies). G.T.W.L. and W.R.B acknowledge UK NERC funding (NE/M014088/1). The Diamond Light Source (NT21121-1) and the Swiss Light Source (20181008) are thanked for analysis time, and Connaught Falls (University of Manchester) is thanked for assisting with the SR-μXRF and XANES analysis. R.C.E. was partially supported by the U.S. Department of Energy, National Nuclear Security Administration, Office of Defense Nuclear Nonproliferation Research and Development under Contract No. DE-AC02-76SF00515. The findings and conclusions by the authors of this paper do not necessarily state or reflect those of the JST.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.140539.

References

Abe, Y., Iizawa, Y., Terada, Y., Adachi, K., Igashiri, Y., Nakai, I., 2014. Detection of uranium moval in the course of decommissioning, which is expected to require preliminary investigations inside the reactors using robots) is of crucial importance for understanding the properties of the debris prior to its removal in the course of decommissioning, which is expected to require several decades.

CRediT authorship contribution statement


Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors are grateful to Dr. Watanabe for her assistance on SEM analyses at the Center of Advanced Instrumental Analysis, Kyushu University. This study was partially supported by JST Initiatives for Strategic Energy Basic and Generic Strategic Research and by a Grant-in-Aid for Scientific Research (KAKENHI) from the Japan Society for the Promotion of Science (16K12585, 16H04634, JP26257402). S.U. is also supported by The Mitsubishi Foundation/Research Grants in the Natural Sciences, Environmental Radioactivity Research Network Center (F-19-03), and by ESPEC Foundation for Global Environment Research and Technology (Charitable Trust) (ESPEC Prize for the Encouragement of Environmental Studies). G.T.W.L. and W.R.B acknowledge UK NERC funding (NE/M014088/1). The Diamond Light Source (NT21121-1) and the Swiss Light Source (20181008) are thanked for analysis time, and Connaught Falls (University of Manchester) is thanked for assisting with the SR-μXRF and XANES analysis. R.C.E. was partially supported by the U.S. Department of Energy, National Nuclear Security Administration, Office of Defense Nuclear Nonproliferation Research and Development under Contract No. DE-AC02-76SF00515. The findings and conclusions by the authors of this paper do not necessarily state or reflect those of the JST.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.140539.

References


Choppin, G., Hohart, D.E., 2019. Discovery of the transuranium elements inspired rear-


