Here we report the results of multiple analytical techniques on sub-mm particulate material derived from Unit 1 of the Fukushima Daiichi Nuclear Power Plant to provide a better understanding of the events that occurred and the environmental legacy. Through combined x-ray fluorescence and absorption contrast micro-focused x-ray tomography, entrapped U particulate are observed to exist around the exterior circumference of the highly porous Si-based particle. Further synchrotron radiation analysis of a number of these entrapped particles shows them to exist as UO$_2$—identical to reactor fuel, with confirmation of their nuclear origin shown via mass spectrometry analysis. While unlikely to represent an environmental or health hazard, such assertions would likely change should break-up of the Si-containing bulk particle occur. However, more important to the long-term decommissioning of the reactors at the FDNPP (and environmental clean-up), is the knowledge that core integrity of reactor Unit 1 was compromised with nuclear material existing outside of the reactors primary containment.
A

ir-fall material derived from the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident has formerly been isolated and analyzed from localities across Japan, extending hundreds of kilometers away from the facility1–4. In contrast to the smaller and highly spherical fallout particles observed at greater distances from the accident site, larger particulates extracted from bulk sediment material sourced from close to the facility with a complex exterior form5,6, here we reveal new insight into the accident conditions.

Following the March 2011 accident and radioactive release core inventory modeling using the ORIGEN source-code7 attributed specific radioceesium (Cs*) activity and atomic (isotope) ratios to each of the sites of three operational reactor Units (1, 2, and 3) and spent fuel storage ponds (1, 2, 3, and 4)8. These characteristic ratios arise due to the contrasting half-lives of the fission product isotopes—137Cs (t1/2 = 30.17 years) and 134Cs (t1/2 = 2.065 years)9, and also as a consequence of the differing levels of burn-up of the fuel at each of these localities. Nishihara et al.8 attributed a 134Cs/137Cs activity ratio >1.0 to material derived from reactor Units 2 and 3 (1.08 and 1.04, respectively) and values <1.0 (0.94) to that from reactor Unit 1. Resulting from the decay of the shorter-lived 134Cs, activity values from the spent fuel ponds, in contrast, were <1.0 (Unit 1: 0.54, Unit 2: 0.64, Unit 3: 0.74, and the most heavily loaded, Unit 4: 0.68).

Unlike the major north-west trending fallout plume (the source of the majority of the land-ward contamination) that has been shown to exhibit the characteristic Cs* signature of reactor Unit 210–12, the Unit 1 release is of limited spatial extent. This contrasts with having not been released following the large-scale reactor building hydrogen explosions observed at Units 1 and 13, but a believed breach in the structural integrity of the primary containment vessel (PCV) on the 15 March 2011 (following extensive, later inspections)13–15.

Alongside wide-area mapping and monitoring studies, single-particle analysis has confirmed that the individual fine-scale radioactive material sourced from the region to the north-west of the plant also exhibited a Cs* ratio attributable to the FDNPP Unit 1. Owing to its widespread environmental dispersion, this particulate has been the subject of the majority of the Fukushima nuclear forensics studies undertaken thus far. Defined in the initial scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) particulate analysis of Adachi et al.2 as Ca-balls, these highly spherical and Si-based particles were collected by high-volume aerosol sampling in Tsukuba, 170 km SW of FDNPP. Kogure et al.17, conduce these Cs-balls to be formed by atmospheric condensation (around solid nucleation sites), however, attempts to reproduce such glassy particles has proved unsuccessful, which led the authors to suggest that the micro-particles were formed in highly specific conditions in the nuclear reactor environment. Subsequent synchrotron analysis of the same particulate by Abe et al.1, revealed the occurrence of U, in the center of a numbers of these particles—each of which averaged 2.1 μm in diameter. Further studies have extended the analysis of such micron-scale, reactor Unit 2-derived particulate through the application of destructive techniques, including transmission electron microscopy (TEM) following focused ion beam (FIB) sectioning to examine the interior structure and composition of the samples4,17,18.

Here we focus on the much larger diameter (>100 μm) and considerably more angular particulates collected much closer to the FDNPP5,16, which possess a lower 134Cs/137Cs activity ratio of <1.0 and are therefore ascribed the radioactive release from reactor Unit 1 (occurring earlier on the 12 March 2011, associated with the reactor-building hydrogen explosion13–15). The contamination (and particulate) was deposited within a plume to the north–north-west/north of the Fukushima site—trending towards the nearby city of Minamisoma—consistent with the prevailing wind conditions and directions at the time of the release19,20. In addition to the contrasting release mechanisms, the main 60 km long (Unit 2) contamination plume was the result of wet deposition caused by coincident rainfall events—whereas the plume from Unit 1 was deposited under dry conditions21,22. Corroboration of the spatially contrasting 134Cs/137Cs activity ratios around the FDNPP has been detailed in the work of Nishizawa et al.11.

The larger particulates have received sparse attention compared to the Unit 2 particulate, perhaps, because it has been found closer to the FDNPP site (<5 km), where people will not return to reside for a considerable period of time23. This Unit 1 material was first identified and isolated by Satou16 who identified a mean particle diameter >100 μm and a lower activity (Bq) per particle volume (μm³) (1.0 × 105 × [volume]0.39) than Unit 2-derived material (2.0 × 1016 × [volume]1.40)24. Initial synchrotron characterization of this material, comparing its composition to the smaller Cs-balls was undertaken by Ono et al.9. Within this work, on a small 75 μm × 75 μm spherical portion of an elongate sub-mm particle, a highly heterogeneous (including Mo, Fe, Ni, Cd, Sn, and Cr) distribution of elemental constituents was identified alongside the existence of U in addition to other elements concentrated around its surface. Additional analysis of Unit 1 particulate suggests that the bulk of the sub-mm particle results from the melting and amalgamation of fibrous (Si-based) Rockwool™ thermal insulation material under the intense heat following the loss of coolant incident (LOCI)24.

This work seeks to determine if these inclusions (that have same length-scale as the U particulate contained within the highly spherical Unit 2 particulate1), are of actinide composition and if so, whether they can be unequivocally sourced to Unit 1 at the FDNPP. The means of attributing the U to specific FDNPP reactors relies on contrasting 235U-enrichment levels contained in the different reactors fuel assemblies. While reactor Units 2 and 3 contained fuel with 3.8 wt% 235U (greater than the 0.7 wt% 235U of natural U), the fuel of Unit 1 was constituted by 235U concentrations of between 3.4 and 3.6 wt%25.

Results

Fluorescence tomography. Rendering of the U signal derived from synchrotron radiation micro-x-ray fluorescence (SR-μ-XRF) applied to a series of 2.5 μm thickness slices obtained following the synchrotron radiation micro-x-ray tomography (SR-μ-XRT) analysis are shown in Fig. 1. As a result of the earlier compositional analysis performed on this material, the locations of Fe-rich and cement fragments contained within this material are also shown. From these two-dimensional reconstructions, the U particulate is observed to be near-exclusively associated with the exterior circumference of the particle—occurring at depths averaging 10 μm into the highly porous Si-based matrix. While the U particulate appears to possess a highly rounded form (owing to the 5.0 μm diameter round beam profile and resulting 2.5 μm step size of the XRF measurements) the size and spherical shape is likely to represent an exaggeration of its true size and a greater degree of rounding than its true form.

We note that one U particulate is found not on the particulates exterior, but rather within the sub-mm CF-01 sample. This particle (highlighted in Fig. 1g—22.5 μm thickness section) is conversely enclosed by several spherical voids (that together constitute 24% of the particle’s total internal pore volume), in addition to being closely associated with the highlighted Fe and cement composition fragments. Following the earlier examination of this ejecta material, such a high-energy release scenario is believed to have embedded these reactor-sourced structural
fragments (such as steel and cement) into the surface of this Si-based insulation material. The incorporation of these fragments into this softened material resulted in the U particulate, formerly located around its surface, becoming pushed deeper into the particle towards its center. The existence of the larger number of more peripheral U particles (located only several microns under the bulk particles surface) can be attributed to the softened state of the Si-based matrix combined with the considerable gas (volatile) over-pressure that existed around the reactor’s PCV environment. These conditions served to force the actinide composition material into the particle, having been generated by the earlier U volatilization/particle formation that followed the integrity compromise and extensive melting of the Unit 1 reactor core13,14.

X-ray absorption near edge structure. The results of the analysis performed on two of these inclusions are presented in Fig. 2. The x-ray absorption near-edge structure (XANES) spectra of the particles are characterized by a broad white line that peaks at 17,176–17,177 eV, before smoothly decreasing to a minimum at 17,200 eV. This shape has been previously attributed to the U(IV) oxidation state in uranium oxides and glasses, whereas more oxidized forms, such as U(V) and U(VI), are characterized by an increasingly asymmetric shape, with an additional shoulder growing around 17,185–17,195 eV26–28.

Beam damage, characterized by the reduction of the white line intensity within tens of seconds, has previously been reported for U-containing glasses by Halse29. However, these modifications are not accompanied by further changes of the XANES shape relating to a change in the oxidation state upon exposure to the incident x-ray beam. Here, spectra remain unchanged after 15 min of continued beam exposure and data collection—therefore discounting any beam-induced oxidation of the particles. While it is possible to obtain XANES data from the U-containing particles, local structure information derived from the succeeding EXAFS region of the spectra is not amenable in this instance, this likely the result of the large size of the incident x-ray beam (2 μm x 2 μm) in comparison to that of the enclosed U particulate, the subject of analysis.

Fig. 1 Combined X-ray tomography and fluorescence cross-sections: sequential longitudinal slices (upwards from the horizontal mid-plane) through the SR-μ-XRT reconstruction, overlain with U composition data (shown in red, and additionally circled in 22.5 μm section) as determined via SR-μ-XRF mapping. The location of Fe (orange) and cement (blue) composition regions are highlighted. The values shown represent the thickness of the tomograph.
These results confirm the identical structure of the particulate contained within the CF-01 sample to that of standard UO₂ nuclear fuel. While highly suggestive of the high melting-point fuel material used extensively in nuclear reactors around the world, U in the (IV) state is also found in numerous naturally occurring primary and secondary uranium ore minerals—with one of the most commonly encountered being that of uraninite (UO₂). With the Si-based particle’s precursor Rockwool™ insulation material (derived from a basaltic precursor material) typified by a low U content of 0.2 ppm, and owing also to the spatially heterogeneous (circumferential) distribution of the U particulate, an anthropogenic provenance is most likely. It is therefore also through the application of SIMS to derive true isotopic ratios that a natural occurrence can be entirely excluded.

**Secondary ion mass spectrometry.** With SR-μ-XANES analysis showing the U to exist in the U(IV) oxidation state (as UO₂) and, therefore, the composition of either nuclear fuel or naturally occurring mineral material, the isotopic results provided by SIMS analysis serves as the critical indicator in ascribing it definitively to a reactor source—and to Unit 1 at the FDNPP. The result of SIMS compositional mapping over the vertical cut face produced by ion beam depth profiling is shown in Fig. 3. From this image, a micron-scale particle at 238 amu (marked in red) is observed on the vertical face of the milled region, as expected following earlier XRF elemental mapping and ion beam sample preparation. Also apparent is a discrete region of ca. 10 μm diameter at the base of the trench, with a mass of 137 amu—attributed to the fission product 137Cs.

The mass spectra (between 231 and 241 amu) of this U particle is shown in Fig. 4. From this, the discernible peaks are at 238 and 235 amu. The ratio of integral peaks gives an atomic ratio (235U/238U) of 0.0354 ± 0.0015 (3.54 ± 0.15 wt% ²³⁵U). This elevated ²³⁵U concentration above the globally averaged natural abundance of 0.72% clearly identifies this material as being anthropogenic. The absence of other masses (e.g. 234, 236, 239, and 240 amu) within the spectra (Fig. 4) could be attributed to the lack of fuel burn-up of this component of fuel material, and therefore transmutation of the parent isotopes that would result in the ingrowth of these additional mass species (N.B. the burn-up of the fuel in reactor Unit 1 averaged a considerable 39.5 to 45 GWD/t). The poor mass-sensitivity of SIMS at these higher mass-units could equally be invoked to represent the detection of only these two masses (²³⁵U and ²³⁸U), and not the lower concentrations of the other actinide species that may exist. With
higher-sensitivity instrumentation, mass peaks at both 234 and 236 amu would be expected—lending additional support to the materials reactor provenance.

While the Cs (137 amu) region is characteristically rounded in its form, the U fragment is significantly more angular. This angularity supports the theory that a loss of structural integrity occurred in the fuel assemblies following their extensive melting in the LOCI and an ensuing fragmentation/particle generation. This gas was resultantly incorporated into the partially molten Si-based material in the diffuse manner observed. The gas was then volatilized and could be identified utilizing the methods described in this work, this study has chosen to focus solely on source attribution using combined U and Cs analysis. Future work will utilize other advanced synchrotron-based x-ray analysis techniques alongside advanced multi-technique evaluation on U-containing material sourced from the reactor building hydrogen explosion that occurred in Unit 1 of the FDNPP. The combined use of these techniques allows for the detailed study of the materials and their evolution over time, providing insights into the conditions that took place during the accident.

Source attribution. With the likely anthropogenic provenance of the U particulate inclusions shown through combined SR-μ-XANES and SIMS analysis, a comparison of the \( ^{235}U \) content of this U particle (CF-01) is shown alongside the published values for reactor Units 1, 2 and 3 (alongside that of natural U) in Fig. 6. Having been attributed in earlier works to reactor Unit 1 through its \( ^{134}Cs/^{137}Cs \) activity ratio, the atomic ratio \( ^{235}U/^{238}U \) content in this single U particle further supports this provenancing. In contrast to reactor Units 2 and 3 which, as shown in Fig. 6, were operating with higher UO2 fuel enrichments of 3.8 wt% \( ^{235}U \), Unit 1 was operating with enrichments between 3.4 and 3.6 wt% \( ^{235}U \). The 3.54 ± 0.15 wt% \( ^{235}U \) (0.0354 ± 0.0015 \( ^{235}U/^{238}U \) atomic ratio) determined for the (CF-01) particle reported here is, therefore, consistent with the published core loading values for reactor Unit 1.

![Fig. 5 Cs and Ba mass spectra: SIMS mass spectra (positive bias) between 135 and 138 amu, derived from the Cs-rich region evidenced to exist within the CF-01 bulk particle (identified in Fig. 3)](image1.png)

![Fig. 6 Core inventory comparison: comparison of the \( ^{235}U \) wt% (±2σ) measured in this work via SIMS (CF-01) with operational wt% \( ^{235}U \) values published by the sites operator, TEPCO)](image2.png)
elements and isotopic ratios to further constrain the materials provenance and conditions/environment of formation.

Methods

Sample collection and preparation. Bulk (~100 g) exposed samples, identified to exhibit elevated levels of radioactivity when scanned using a hand-held Geiger–Müller instrument, were collected in October 2014 within the highly contaminated Restricted Zone and a site formerly attributed to have been contaminated by reactor Unit 111,12. This material was obtained from the ground (as dust samples) at 37.4379’N, 141.0222’E, 2.4 km NNE from the center of FDNPP. To extract the particles from the surrounding organic sediment, a multi-stage autoradiography, division, and extraction process was employed38. After removal, each of the sub-mm particles was placed onto a piece of adhesive Kapton® film. An initial quantification of each particle was then performed using SEM with associated energy-dispersive spectroscopy (EDS) and gamma-ray spectrometry performed using a high-volume detector, the results of which are discussed elsewhere34. Greater than 20 similar sub-mm particles were extracted from the sediment and found upon here representative of the average size/volume, with typical surface composition and internal structure6.

To enable SR analysis of this representative particle, it was further enclosed within additional layers of x-ray transparent Kapton® film for the multiple synchrotron-based techniques. A corner of the Kapton® envelope was glued onto a 1 cm aluminum support pin, which was then attached to a magnetic base for its transport. Synchrotron radiation analysis

Secondary ion mass spectrometry. Having determined the locations at which U composition particulate was located inside the parent particle, isotopic analysis was performed using magnetic sector (MS) SIMS. The MS-SIMS system used in this study was a custom-built instrument utilizing a primary Ga+ ion beam to sputter the samples surface before filtering and measuring the resulting secondary ion species across the 0–300 amu mass range. However, as the U-containing particulate was observed to exist several sub-microns below the surface of the sample, FIB milling (using an FEI Helios Nanolab® 8600 dual FIB-SEM system) was conducted to expose the particle and produce a cut face ~80 × 80 μm. Prior to this preparation (and subsequent SIMS analysis), the particle was carefully removed from its Kapton® film envelope and placed onto a low elemental background electrically conductive carbon Spectro Tab (TED PELLA Inc.) before being sputter-coated (Edwards Vacuum ScaNox Six) with a 2 nm thick film of conductive Au. Progressively decreasing Ga+ ion beam cutting energies (reduced from 16 nA to 90 pA) were used to obtain a surface free from the artefacts of the milling process. With a flat surface produced on the highly textured CF-01 particle to a depth just above the location of the U composition particle, depth profiling was first used to locate the edge of the actinide fragment. A ×5000 magnification was used—producing a 40 × 40 μm trench (along a dwell-time of 2500 ms for each of the six mass units measured) to mill to a depth of 10 μm. A rapid-scan ion map (two rafter frames) was then performed on the cut vertical surface, where the U particle was observed to exist (using the same parameters as those employed for depth profiling) to exactly locate the contained particle. Finally, a spectrum over the U mass window (231–241 amu, with 0.05 amu steps and 5000 ms dwell-time) was performed to evaluate the specific isotopic composition of the U inclusion. This mass range was swept three times to enhance the signal quality and reduce spurious noise within the data.

Synchrotron radiation analysis. SR analysis of the particle was performed on the I13-1 (coherence imaging) and the I18 (micro-focus spectroscopy) beamlines at the Diamond Light Source (DLS; Harwell, UK)36. Both three-dimensional SR-µ-XRF and SR-µ-XAS of the particle were first performed on the I13-1 beamline, prior to SR-µ-XAS on the I18 beamline. With a distance of 250 μm between the insertion device (canted undulator) and the sample, the I13-1 beamline utilizes the highly coherent x-rays produced by the experimental optics, with an energy range of 4–23 keV (a maximum of 19 keV was used in this work) and typical flux of 1017 photons/s. Despite being located closer to the insertion device, the I18 beamline uses a similar optical setup to the longer I13-1 beamline—with a comparable energy range of 3–22 keV, tunable in 0.5 eV increments using a cryogenically cooled Si(111) monochromator.

Using the I13-1 beamline at the Diamond Light Source36, the particle was studied using both µ-XRF, and 3D µ-XRF. For the XRT acquisition, the sample was illuminated with a 19 keV collimated X-ray beam. The particle was rotated over a range of 180° in steps of 0.1°. The projections were acquired with an optical microscope coupled to a 26 μm-thick GGG:Eu scintillator. The total optical magnification of ×20 provided a pixel size of 0.45 μm. For the 3D XRF analysis, the X-ray beam was rastered through a 5 μm pinhole positioned upstream of the sample. At each angle of the 3D XRF, the sample was scanned with respect to the beam in a raster grid of 40 × 20 steps with a step size of 2.5 μm, giving a field of view of 100 μm × 50 μm. At each scan position, the X-ray fluorescence spectrum was acquired using a single channel silicon drift Vortex® X-ray detector placed in the plane of the sample, normal to the direction of propagation of the beam. The sample was rotated over a range of 180° in steps of 4.5°.

From the series of fluorescence projections, the three-dimensional volume for each particle was reconstructed using the ordered-subset penalized maximum-likelihood algorithm, with weighted linear and quadratic penalty algorithms in the Tomokit software51. An iterative algorithm to correct for the degree of sample self-absorption that occurred was also employed for the tomography results. The reconstructed overlay images were produced using ImageJ and Python software platforms.

For the I18 SR-µ-XANES analysis, an identical particle setup was used. Prior to the analysis, an initial two-dimensional SR-µ-XRF scan was made of the particle at 21 keV (full beam size flux at 10 keV = 1017 photons/s), with the sample similar rastered through the incident X-ray beam in 2 μm steps (resulting in a 2 μm spatial (pixel) resolution) to re-establish the positions of the high-density (U-containing) particles. Once these positions were located, SR-µ-XANES was performed. For this analysis, the stage position was maintained whilst the incident beam energy was varied—tuned by the monochromator over the U-238 edge (17,166 eV), at various energy steps (5 eV from 17,025 to 17,140 eV, 0.5 eV from 17,140 to 17,205 eV, 1 eV from 17,205 to 17,275 eV, 2 eV from 17,275 to 17,400 eV, and 2.5 eV in the final 2.5 eV steps from 17,400 to 17,510 eV). Three repetitions of each scan were made in each instance to improve the resulting signal-to-noise ratio in the data. The SR-µ-XANES data was analyzed using the Demeter (ATHENA/ARTEMIS) suite of software62—based on the open-source IFEFFIT code63. Calibration of the I18 monochromator (with an inherent stability of ±0.05 eV per day) and after the analysis was undertaken using a series of material standards with characteristic emission features. The material standard for the U-238 edge comparison was sourced from the International X-ray Absorption Society Database (Reference: atm-1c-glass reference I5 edge)64.

Data availability

The raw (unprocessed) data that supports the findings of this study are available from Mendeley Data, with the https://doi.org/10.17632/46db2h9kwr.1

Received: 27 June 2018 Accepted: 11 June 2019 Published online: 26 June 2019

References

1. Abe, Y. et al. Detection of uranium and chemical state analysis of individual radioactive microparticles emitted from the Fukushima nuclear accident using multiple synchrotron radiation X-ray analyses. Anal. Chem. 86, 8521–8525 (2014).
2. Adachi, K., Kajino, M., Zaizen, Y. & Igarashi, Y. Emission of spherical cesium-bearing particles from a early stage of the Fukushima nuclear accident. Sci. Rep. 3, 5 (2013).
3. Inoto, J. et al. Isotopic signature and nano-technology of cesium-rich micro-particles: release of uranium and fission products from the Fukushima Daiichi Nuclear Power Plant. Sci. Rep. 7, 12 (2017).
4. Yamaguchi, N. et al. Internal structure of cesium-bearing radioactive microparticles released from Fukushima nuclear power plant. Sci. Rep. 6, 1 (2016).
5. Inoto, J., Morita, M., Matsuo, Y., Griffiths, I., Richards, D. & Scott, T. Analysis of external surface irregularities on Fukushima-derived fallout particles. Front. Energy Res. 5, 9 (2017).
6. Ono, T. et al. Investigation of the chemical characteristics of individual radioactive microparticles emitted from reactor 1 by the Fukushima Daiichi Nuclear Power Plant accident by using multiple synchrotron radiation X-ray analyses. Bunsui Kagaku 66, 251–261 (2017).
7. Crawford, A. G. Origen2: a versatile computer code for calculating the nuclides compositions and characteristics of nuclear materials. Nucl. Technol. 62, 335–352 (1983).
8. Nishihara, K., Iwamoto, H. & Suyama, K. Estimation of Fuel Compositions in Fukushima-Daiichi Nuclear Power Plant. IAEA (Ibaraki) 2012–2018 (2012).
9. CRC Press, CRC Handbook of Chemistry and Physics—Table of Isotopes (CRC Press, Boca Raton, FL, 2015).
10. Zheng, J. et al. 135Cs/137Cs isotopic ratio as a new tracer of radioecosystem released from the Fukushima Nuclear Accident. Environ. Sci. Technol. 48, 5435–5438 (2014).
11. Nishizawa, Y., Yoshida, M., Sanada, Y. & Torii, T. Distribution of the 134Cs/137Cs ratio around the Fukushima Daiichi Nuclear Power Plant using an unmanned helicopter radiation monitoring system. J. Nucl. Sci. Technol. 53, 1–7 (2015).
12. Chino, M. et al. Utilization of 134Cs/137Cs in the environment to identify the reactor units that caused atmospheric releases during the Fukushima Daiichi Accident. Sci. Rep. 6, 1 (2016).
13. IAEA. Technical Vol. 1 of 5: Description and Context of the Accident. In The Fukushima Daiichi Accident 238 (IAEA, 2015). http://www-pub.iaea.org/MTCD/Publications/PDF/AdditionalVolumes/P1710/Pub1710-TV1-Web.pdf.
14. TEPCO. Fukushima Nuclear Accident Analysis Report 2012 (2012).
