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Detection of Uranium and Chemical State Analysis of Individual Radioactive Microparticles Emitted from the Fukushima Nuclear Accident Using Multiple Synchrotron Radiation X-ray Analyses

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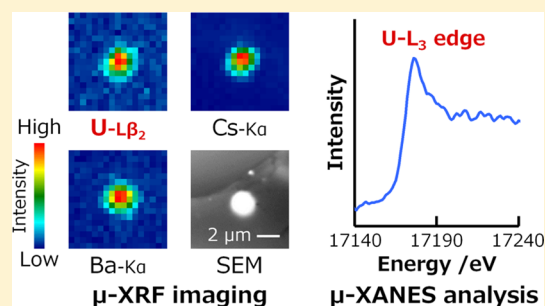
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S Supporting Information

ABSTRACT: Synchrotron radiation (SR) X-ray microbeam analyses revealed the detailed chemical nature of radioactive aerosol microparticles emitted during the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident, resulting in better understanding of what occurred in the plant during the early stages of the accident. Three spherical microparticles ($\sim 2\ \mu\text{m}$, diameter) containing radioactive Cs were found in aerosol samples collected on March 14th and 15th, 2011, in Tsukuba, 172 km southwest of the FDNPP. SR- μ -X-ray fluorescence analysis detected the following 10 heavy elements in all three particles: Fe, Zn, Rb, Zr, Mo, Sn, Sb, Te, Cs, and Ba. In addition, U was found for the first time in two of the particles, further confirmed by U L-edge X-ray absorption near-edge structure (XANES) spectra, implying that U fuel and its fission products were contained in these particles along with radioactive Cs. These results strongly suggest that the FDNPP was damaged sufficiently to emit U fuel and fission products outside the containment vessel as aerosol particles. SR- μ -XANES spectra of Fe, Zn, Mo, and Sn K-edges for the individual particles revealed that they were present at high oxidation states, i.e., Fe^{3+} , Zn^{2+} , Mo^{6+} , and Sn^{4+} in the glass matrix, confirmed by SR- μ -X-ray diffraction analysis. These radioactive materials in a glassy state may remain in the environment longer than those emitted as water-soluble radioactive Cs aerosol particles.



The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident is the largest nuclear incident since the 1986 Chernobyl disaster and has been rated at the maximum level of 7 on the International Nuclear Event Scale.¹ Large amounts of radioactive materials were released into the environment during the accident.^{2–4} Although more than 3 years have passed since the accident, the radioactive materials emitted from the FDNPP have been detectable in the environment. However, little is known about the physical and chemical natures of radioactive materials released during the early stages of the accident.^{5–7}

Adachi et al.⁵ found spherical microparticles containing radioactive Cs in aerosol samples collected on March 14th and 15th, 2011, in Tsukuba, 172 km southwest of the FDNPP and about 60 km northeast of central Tokyo. They revealed that these microparticles consisted of Fe, Zn, and Cs and were insoluble in water. Additionally, they calculated deposition area of these particles based on the size and hygroscopicity of the particles and concluded that these particles mainly fell to the ground through dry deposition. Such knowledge of the radioactive materials from the accident is important to understand potential environmental and human health impacts, an assessment of the accident sequence, and methods for decontamination of the radioactive pollution.

In this study, we conducted a more detailed study of the nature of the Cs-bearing radioactive aerosol microparticles by means of advanced analytical techniques using a synchrotron radiation (SR)-X-ray microbeam. In the previous study,⁵ a scanning electron microscope (SEM) with an energy dispersive X-ray spectrometer (EDS) was used for chemical characterization of the particles. In this study, X-ray fluorescence (XRF) analysis using a high-energy SR-X-ray microbeam, which is much more sensitive to heavy elements than SEM-EDS analysis, was introduced to carry out nondestructive identification and qualitative detection of trace amounts of heavy elements in individual microparticles. Although chemical analyses such as a laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) may have a better sensitivity than SR-XRF, it is difficult to analyze single microparticle sample. Moreover, chemical state and crystal structure information could not be obtained with LA-ICPMS.

To evaluate the conditions under which these particles were formed, chemical state analysis of the transition elements in the

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particles was carried out by applying X-ray absorption near-edge structure (XANES) analysis. X-ray diffraction (XRD) analysis was also conducted to reveal the crystal structures of the particles. Brilliant X-rays from an advanced SR light source at SPring-8 enabled us to use a combination of these three analytical techniques. The SR-X-ray microbeam was particularly suitable to obtain detailed information from individual microparticles.^{8,9} This study aims to apply these analytical techniques to the Cs-bearing microparticles from the FDNPP accident and to reveal their nature to further understand the accident as well as their effects on the environment and human health.

EXPERIMENTAL SECTION

Sample Collection. From March 14th at 21:10 to March 15th at 9:10 (JST), aerosol particles containing radioactive materials were collected at the Meteorological Research Institute (Tsukuba, Japan; 36.05° N, 140.13° E) using a high-volume aerosol sampler (HV-1000F, 1000 m³/24 h; Sibata Scientific Technology Ltd.) on a quartz fiber filter (QR100; Advantec). The detailed sampling procedures were described elsewhere.⁵ An imaging plate (IP; GE Measurement and Control, CR×25P computed radiography scanner) and micro-manipulator (AP-xy-01; Micro Support Corp.) were used to detect and separate the radioactive particles from the filter. Approximately 100 small dots, each of which suggests the presence of radioactive material, appeared on the IP image of the filter (Figure 1a). In the previous study,⁵ the particle number concentration was estimated to be around 10 radioactive particles/m³. Three radioactive particles, designated particles A, B, and C, were sampled from the filter and placed on glass substrates. Particles A and C in this study are the same as the particle nos. 3 and 2, respectively, in the previous study.⁵ They were subjected to the SEM-EDS analysis and gamma-ray spectrometry (see details of the measurements in the Supporting Information). After these analyses, the radioactive particles on the carbon tape fragment were removed and placed on a flat Kapton tape with a plastic holder for the SR X-ray analyses.

Synchrotron Radiation X-ray Analyses. The SR experiments were carried out at the BL37XU,^{8,9} a hard X-ray undulator beamline at SPring-8, at Japan Synchrotron Radiation Research Institute (JASRI). We used two beamtimes: beamtime A for measurements with a high-energy X-ray beam (17.1–37.5 keV) and beamtime B for those with a low-energy X-ray beam (7.0–15.0 keV). The sample was placed on an automatic XY stage. Monochromatic X-rays were obtained with a Si(111) double crystal monochromator, and the X-ray microbeam was produced by focusing Kirkpatrick–Baez mirrors. The area of the X-ray microbeam in beamtime A was 1.0 μm (V) \times 1.2 μm (H), while that of beamtime B was 0.6 μm (V) \times 0.8 μm (H). Using these X-ray microbeams, we applied three X-ray analytical techniques, SR- μ -XRF, SR- μ -XANES, and SR- μ -XRD. The intensity of the incident X-ray (I_0 intensity) was continuously monitored using an ionization chamber located before the focusing mirror. The SR- μ -XRF analysis, including two-dimensional imaging analysis, was carried out using 37.5 keV X-rays and a Si (Li) detector in beamtime A. The SR- μ -XRF spectrum was measured for 1000 s in live time per sample. The intensity of each spectrum was normalized to that of the Thomson scattering peak. To visualize the distributions of the elements in each particle, SR- μ -XRF imaging analysis of the particle was conducted with a step size of 0.5 μm (V) \times 0.5

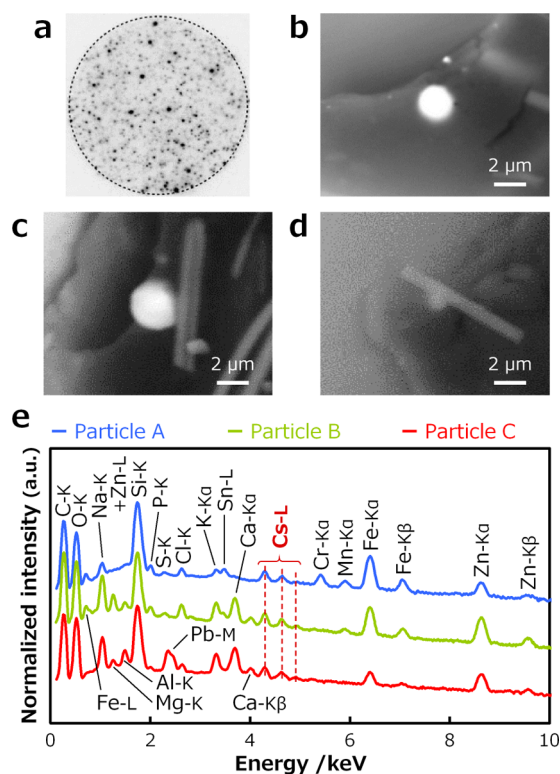


Figure 1. Characterization of radioactive aerosol particles prior to SR experiments. (a) IP autoradiography of the aerosol filter collected in Tsukuba after the FDNPP accident.⁵ Black dots indicate the presence of radioactive materials. (b–d) SEM images of (b) particle A (2.0 μm diameter), (c) particle B (2.8 μm diameter), and (d) particle C (1.4 μm diameter). (e) Comparison of the EDS spectra of the three particles. The intensity of each spectrum is displayed on a logarithmic scale and shifted in a longitudinal direction. A rodlike extraneous fouling over particle C (d) is a fragment of quartz fiber filter attached to the carbon tape.

μm (H) with an integration time of 4.0 s/point. The XRF intensities for each measured point were normalized to the I_0 intensity.

The SR- μ -XANES spectra of the particles and the reference samples were measured in fluorescence mode for the following absorption edges: the Fe–K edge (7 111 eV), Zn–K edge (9 661 eV), U–L₃ edge (17 171 eV), Mo–K edge (20 000 eV), and Sn–K edge (29 200 eV). The absorption edge energies used were based on experimental values in Deslattes et al.¹⁰

In the SR- μ -XRD analysis, the X-ray diffraction patterns of the samples were measured with a Debye–Scherrer optical system using a two-dimensional detector (CMOS flat panel) placed 200 mm behind the sample in beamtime B. Si powder (NIST SRM640c) was also measured as a reference material. The energy of the incident X-ray was set to 15.0 keV with an exposure time of 440 ms and an integration of 100 times/sample. Details of the SR measurements are given in the Supporting Information.

RESULTS AND DISCUSSION

Scanning Electron Microscope and Gamma-Ray Spectra Analyses of Radioactive Aerosol Microparticles. Figure 1b–d shows SEM images of the three microparticles analyzed in the SR experiments. They are spherical with diameters of ~ 2 μm . EDS spectra of the three particles are shown in Figure 1e. There were no apparent differences among

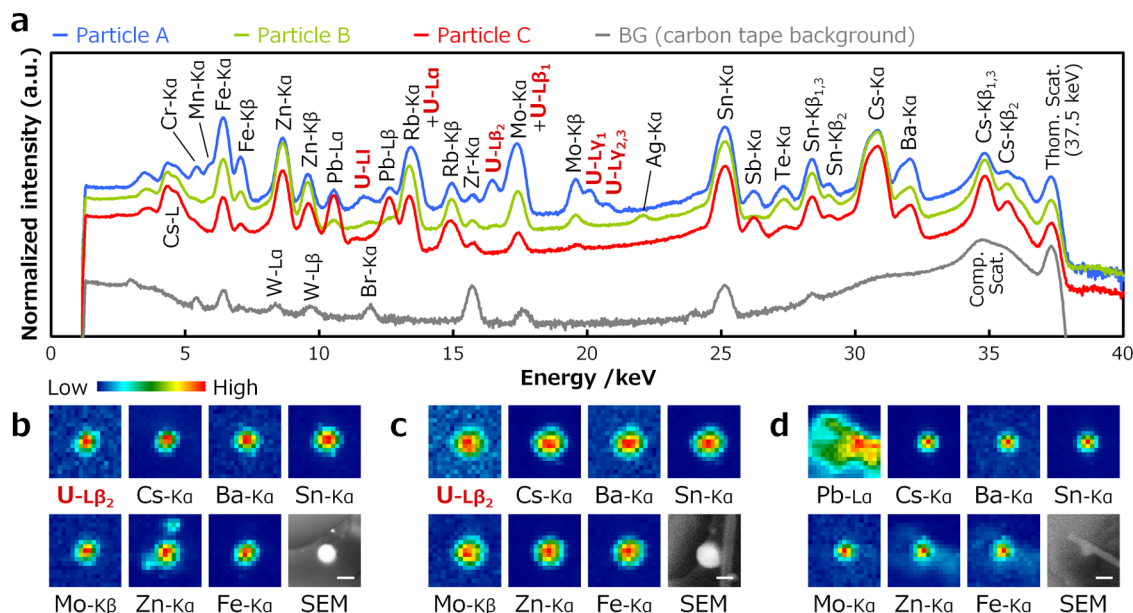


Figure 2. Results of SR- μ -XRF analyses. (a) Comparison of the SR- μ -XRF spectra obtained for particles A, B, and C and the carbon tape background. The intensity of each spectrum was displayed on a logarithmic scale and shifted in a longitudinal direction. (b–d) Distributions of representative elements extracted from the SR- μ -XRF images of (b) particle A, (c) particle B, and (d) particle C with enlarged SEM image corresponding to the imaging area (scale bar: 2 μ m).

the three spectra, consistent with the previous results⁵ indicating that their major components were Fe, Zn, and Cs. Some of the peaks for light elements (e.g., Si and Ca) may have originated from both the glass substrate and the particle itself. Gamma-ray spectra of the three particles detected both ^{134}Cs and ^{137}Cs in each particle with activity ratios of ~ 1 (decay corrected as of March 2011). The decay-corrected activities for ^{134}Cs and ^{137}Cs were $1.20 (\pm 0.05)$ Bq and $1.29 (\pm 0.02)$ Bq for particle A, $1.49 (\pm 0.06)$ Bq and $1.49 (\pm 0.03)$ Bq for particle B, and $1.07 (\pm 0.05)$ Bq and $1.10 (\pm 0.02)$ Bq for particle C, respectively. In the previous study,⁵ it is pointed out that the activity ratios between ^{134}Cs and ^{137}Cs of the radioactive materials released by the FDNPP accident were ~ 1 . It is thus confirmed that these three particles are radioactive ones derived from the FDNPP accident.⁵

Detailed Chemical Composition Analysis. The SR- μ -XRF spectra of the three particles and the carbon tape background are shown in Figure 2a. In addition to Fe, Zn, and Cs, all of which were previously reported,⁵ the following eight heavy elements were detected in all three particles: Rb, Zr, Mo, Sn, Sb, Te, Ba, and Pb. Several unique elements were also detected from specific particles, i.e., Mn and Cr in particle A and Ag in particle B.

In addition to these elements, U–L lines in the SR- μ -XRF spectra appeared in particles A and B. To address potential interferences from elemental contamination such as W, which could be due to contamination from the micromanipulator needles during the particle separation procedure, we used SR- μ -XRF imaging analysis and visualized the elemental distributions within each particle. Figure 2b–d shows the distributions of selected elements from the SR- μ -XRF imaging of the three particles with enlarged SEM images corresponding to the imaging area (additional SR- μ -XRF images are shown in Figure S1 in Supporting Information). In particles A and B, the two-dimensional distributions of characteristic elements, including U corresponded well to the particle shapes in the SEM images and the Cs distributions identified by the SEM-EDS analysis.

In these images, we found homogeneous distributions of most elements in the particles except that of Pb in particle C (Figure 2d). Although strong peaks for Pb–L lines were detected in the spectrum of particle C, the Pb distribution was distinctly different from those of the other elements and the SEM image of the particle, indicating that the Pb did not originate from the particle components.

Verification of the Presence of Uranium. In order to obtain additional evidence for the presence of U in the microparticles, we conducted U–L₃ edge SR- μ -XANES analysis (Figure 3a). While no absorption edge for U was observed for particle C, clear edge jumps were observed for both particles A and B at the energy of the U–L₃ edge, confirming the presence of U within the aerosol microparticles in the environment. This result implies that elements other than radioactive Cs were emitted along with Cs from the reactor into the atmosphere.

Chemical State and Crystal Structure. SR- μ -XANES spectra of the Fe, Mo, and Sn K-edges for these three particles are shown in Figure 3b–d (see Figure S2 in Supporting Information for Zn K-edge). Peak positions and the shapes of the pre-edges between the particles and the reference materials agreed well, indicating that these elements occurred as Fe^{3+} , Mo^{6+} , Sn^{4+} , and Zn^{2+} . In addition, features of the SR- μ -XANES spectra of the three particles corresponded to those of the glass references.

SR- μ -XRD patterns of the three particles and Si powder as a reference material (see Figure S3 in Supporting Information) showed that the particles had no diffraction peak while the Si powder showed clear Debye–Scherrer rings. This result suggests that the particles are amorphous, glassy materials. These observations together with their spherule shapes implied that they experienced melting at a high temperature and rapid cooling as aerosol under oxidative conditions.

Relevant Element Sources around the Reactors. We explored the possible sources of the 14 elements (Cr, Mn, Fe, Zn, Rb, Zr, Mo, Ag, Sn, Sb, Te, Cs, Ba, and U) found within the microparticles by the SR- μ -XRF analysis. The reactors of the

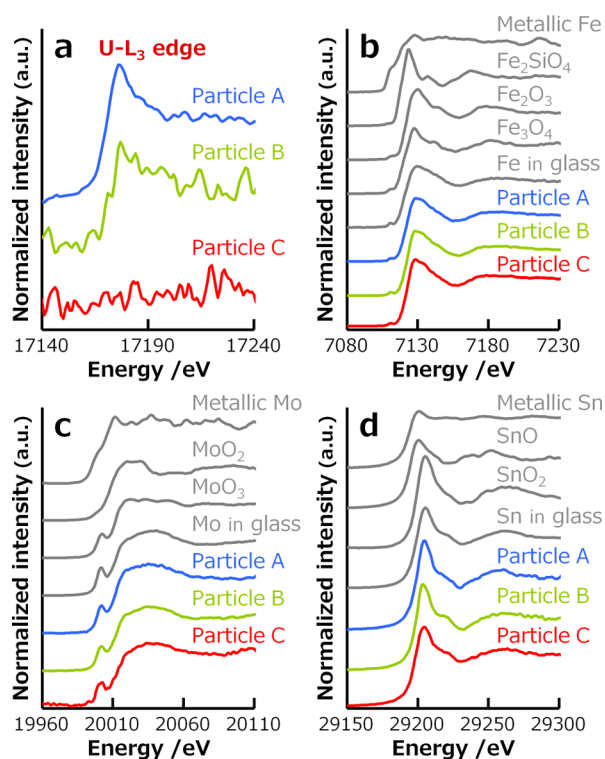


Figure 3. Results of SR- μ -XANES analyses. (a) Comparison of the U-L₃ edge SR- μ -XANES spectra of the three radioactive particles demonstrating the presence of U in particles A and B. (b–d) Comparisons of the (b) Fe-K edge, (c) Mo-K edge, and (d) Sn-K edge SR- μ -XANES spectra of the three particles and the reference materials.

FDNPP (see Figure S4 in Supporting Information) were boiling-water reactors (BWR),¹¹ and the fission fuels composed of U (only no. 3 reactor used mixed oxide fuel¹¹). As a result of the nuclear fission reaction of U, the fission products (FPs) could yield 9 elements (Rb, Zr, Mo, Ag, Sn, Sb, Te, Cs, and Ba)^{11–13} found in the particles. Zr–Sn alloy was used for fuel cladding within the reactors.¹⁴ Stainless steel, which commonly consists of Fe, Cr, and Mn, was used in the structure of the vessel. Zn had been added to the primary cooling water in the FDNPP¹⁵ for corrosion control to reduce ⁶⁰Co. On the other hand, given the possibility of a molten core as a result of the nuclear meltdown may react with a concrete base as suggested by the presence of Si in the particles, it should be noted that a percentage of some elements (e.g., Rb and Zn) may be originated from components of the concrete. Because of the lack of the access to the damaged reactors, we do not have direct evidence to identify the source of these elements. However, we conclude that U fuel, FPs, and components of the reactors are very likely the sources of the elements identified within the three radioactive microparticles, although further investigation will be needed to confirm their sources. We assume that, because these elements could have originated from multiple sources, they were melted together during the accident and eventually formed spherical microparticles.

Environmental Impacts of the Microparticles. If our hypothesis that some heavy elements in the particles were produced by nuclear fission reactions is correct, these particles likely contained additional short-lived radionuclides when they were released during the accident.^{11,12} Thus, the specific activity of these particles at the time of release may have been several

times higher than that presently associated with the radioactive Cs. In addition to the previous report that these particles are insoluble in water,⁵ our study revealed that they are glassy materials with highly oxidized states. These characteristics suggest that they could have a relatively long-term impact on the environment, i.e., continued release of soluble radioactive Cs into the environment as these insoluble glassy particles degrade. Similar radioactive particles have been detected in soils, plants, and mushrooms collected from the area surrounding the FDNPP as shown by IP autoradiography.⁷ Although there is no chemical and size information for the particles reported in other studies, it is probable that some radioactive particles found in these previous studies are the same as the microparticles characterized in our study.

CONCLUSIONS

The present study has provided better understanding the accident based on chemical information recorded in individual 2- μ m radioactive Cs-bearing particles emitted from the FDNPP accident using an SR-X-ray microbeam. The SR- μ -XRF analyses directly identified U and heavy elements, that may originate from the fuel, FPs and materials used in the FDNPP, contained in the aerosol particles together with radioactive Cs, although isotope ratios should be identified to conclude their exact sources. The SR- μ -XANES and XRD analyses showed that these particles were highly oxidized glassy materials. Clarifying the nature of these microparticles assists in understanding what occurred in the reactors during the early stages of the accident. Simulation of distribution and deposition of the radioactive materials depends on physical and chemical natures of materials of interest, and our results could improve models simulating how radioactive materials were formed and were distributed from the reactors into the environment during the accident. Further quantitative investigations of the chemical nature of the radioactive particles including quantification and chemical state analysis of U and FPs in the particles will be important to understand further mechanisms of particle formation and emissions, as well as their potential human health and environmental impacts.

ASSOCIATED CONTENT

Supporting Information

Additional material as described in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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