Detection of uranium and chemical state analysis of individual radioactive microparticles emitted from the Fukushima nuclear accident using multiple synchrotron radiation X-ray analyses

The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident was the most catastrophic nuclear incident since the 1986 Chernobyl disaster, and has been rated at the maximum level of 7 on the International Nuclear Event Scale. Large amounts of radioactive materials were released into the environment during the accident [1,2]. Although more than three years have passed, radioactive materials emitted from the FDNPP can still be detected in the environment. However, little is known about the physical and chemical natures of radioactive materials released during the early stages of the accident. Spherical microparticles (~2 μm ϕ) containing radioactive Cs were found in aerosol samples collected on 14 and 15 March 2011 in Tsukuba, which is 172 km southwest of the FDNPP using a scanning electron microscope (SEM) with an energy dispersive X-ray spectrometer (EDS) [3]. These microparticles consisted of Fe, Zn, and Cs and were insoluble in water.

We have conducted a more detailed study of the nature of the Cs-bearing radioactive aerosol microparticles using advanced analytical techniques and a synchrotron radiation (SR)-X-ray microbeam at beamline **BL37XU** [4]. 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 used to carry out nondestructive identification and qualitative detection of trace amounts of heavy elements in individual microparticles. To evaluate the conditions under which these particles were formed, chemical state analysis of the transition elements in the particles was performed by applying X-ray absorption near-edge structure (XANES) analysis and to reveal the crystal structures of the particles, X-ray diffraction (XRD) analysis was conducted. Brilliant X-rays from an advanced SR light source at SPring-8 enabled us to use a combination of these three analytical techniques. We applied these analytical techniques to the Cs-bearing microparticles from the FDNPP accident to reveal their nature and to further understand the accident as well as the effects on the environment and human health. Three radioactive particles, designated as particles A, B, and C, were sampled from the aerosol filter and placed on a flat Kapton® tape with a plastic holder for SR X-ray analyses. All samples were spherical with diameters of ~2 μm. Here we report the analytical results of particle A as an example.

The SR-μ-XRF spectra of particle A and the carbon tape background are shown in Fig. 1. In addition to Fe, Zn, and Cs, which were previously reported [3], the following 11 heavy elements were also detected in the particle: Cr, Mn, Rb, Zr, Mo, Sn, Sb, Te, Ba, Pb, and U. Figure 2 shows the distribution of selected elements from the SR-μ-XRF imaging of particle A in a SEM image corresponding to the imaging area. In this particle, the two-dimensional distributions of characteristic elements, including U, correspond well to the particle shape in the SEM image and the Cs distributions identified by the SEM-EDS analysis. To obtain additional evidence for the presence of U in the microparticle, we conducted U-L_3 edge SR-μ-XANES analysis on particle A (Fig. 3(a)). A clear edge jump is observed at the energy of the U-L_3 edge, confirming the presence of U within the

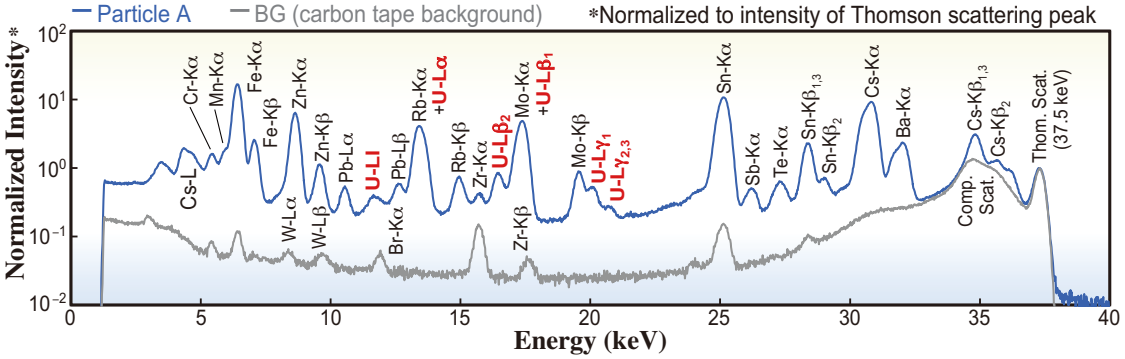

Fig. 1. Comparison of the SR-μ-XRF spectra obtained for particle A and the carbon tape background. Intensity of each spectrum is on a logarithmic scale.

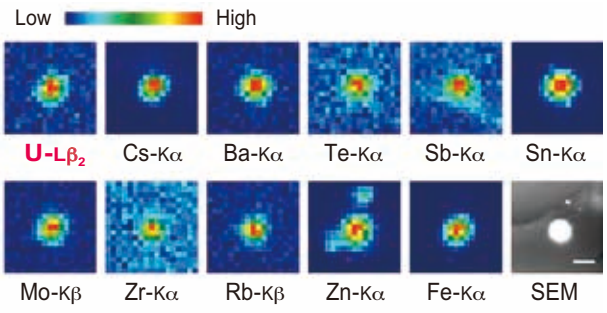

Fig. 2. Distributions of representative elements extracted from the SR-μ-XRF images of particle A with an enlarged SEM image corresponding to the imaging area (scale bar: 2 μm).

particle in the environment. This result implies that in addition to Cs from reactor, elements related with nuclear fuel were also emitted into the atmosphere.

The SR-μ-XANES spectra of the Fe, Mo and Sn for the particle are shown in Fig. 3(b-d), respectively. The peak positions and the shapes of the pre-edges for particle A and the reference materials are consistent, indicating that these elements occur as Fe^{3+}, Mo^{6+}, and Sn^{4+} in the glass matrix. In addition, SR-μ-XRD pattern of particle A shows that the particle does not exhibit a diffraction peak, suggesting that the particle is an amorphous, glassy material. These characteristics imply that the microparticle may 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.

We then explored the possible sources of the 13 elements (Cr, Mn, Fe, Zn, Rb, Zr, Mo, Sn, Sb, Te, Cs, Ba, and U) found within the microparticles by SR-μ-XRF analysis. The nuclear fission reaction of U may produce 8 of the elements (Rb, Zr, Mo, Sn, Sb, Te, Cs, and Ba) as fission products (FPs). A Zr–Sn alloy was used for fuel cladding within the reactors. Stainless steel, which commonly consists of Fe, Cr, and Mn, was used in the vessel structure. Zn was added to the primary cooling water in the FDNPP for corrosion control to reduce ^{60}Co. Therefore, we conclude that the U fuel, FPs, and components of the reactors are very likely the sources of the elements identified within the radioactive microparticle. Because these elements likely originated from multiple sources, we assume that they melted together during the accident and eventually formed spherical microparticles.

Clarifying the nature of these microparticles should assist in understanding what occurred in the reactors during the early stages of the accident. Accurate simulations of the distribution and deposition of radioactive materials depend on the physical and chemical natures of the materials of interest. Our results should help improve models simulating how the radioactive materials were formed and 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, will be important to further understand the mechanisms of particle formation and emissions as well as their potential human health and environmental impacts.

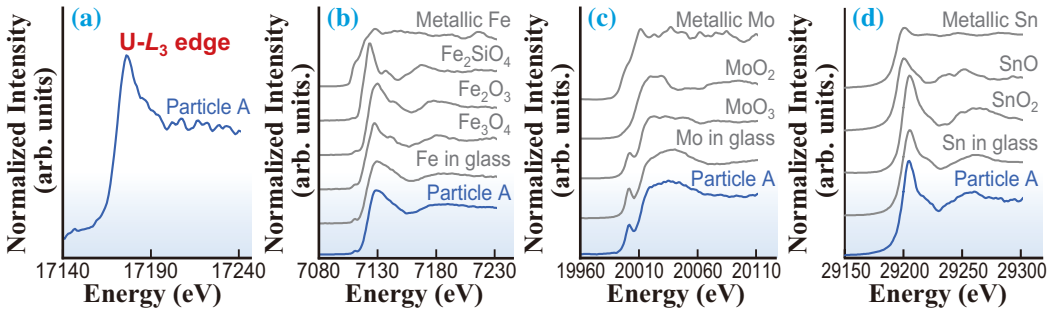

Fig. 3. Results of SR-μ-XANES analyses. **(a)** U-L_3 edge SR-μ-XANES spectrum of particle A, demonstrating the presence of U in the particle. Comparisons of the **(b)** Fe-*K* edge, **(c)** Mo-*K* edge, and **(d)** Sn-*K* edge SR-μ-XANES spectra of particle A and the reference materials.

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