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message

Radioactive particles released from Unit 1 due to the Fukushima Daiichi Nuclear Power Plant accident Elucidation of chemical properties using synchrotron microbeam X-ray analysis

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Due to the Fukushima Daiichi Nuclear Power Plant accident in March 2011, highly radioactive particles were isolated at seven points from the soil in the northwest area of
Distortion
the nuclear power plant, where radioactive materials from Unit 1 are believed to have flown into the area. Many of the separated particles were around 100 ÿm in size and had distorted shapes, and their physical properties were clearly different from the spherical particles (Cs balls) with a diameter of several ÿm that were said to have been released from Unit 2. Ta. Fluorescence analysis of these particles using synchrotron microbeam X-rays at the large synchrotron radiation facility SPring-8
We applied nondestructive X-ray analysis, near-X-ray absorption edge structure analysis, and X-ray diffraction analysis to elucidate the detailed chemical properties. Particles derived from Unit 1 contain a richer variety of heavy metals than Cs balls, and in particular, elements such as Sr and Ba, which are highly volatile in a reducing atmosphere, were characteristically detected, and there was a clear non-uniform distribution of elements within the particles. I could see the sex. The main body of the particle was silicate glass like the Cs ball, but it contained a crystalline material of several ÿm in size, in which some metal elements such as Fe were concentrated. These particles are thought to have been released into the atmosphere between March 12 and 13, indicating that there is a connection between the nuclear fuel and the containment vessel.
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This suggests that melting was progressing at a fairly early stage. Furthermore, it has been demonstrated that information on the chemical composition of the radioactive substance itself can serve as a new index in place of the radioactivity ratio when estimating the source of release.

1 Introduction

Fukushima occurred as a result of the Great East Japan Earthquake on March 11, 2011. Due to the Daiichi Nuclear Power Plant (FDNPP) accident, a large amount of radioactive material was released into the environment and spread mainly in eastern Japan1)-3) . case To summarize the early events, first, on the evening of the 11th, the No. 1 unit
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Nuclear fuel melting begins, and the zirconium in the fuel cladding and cooling water reacted at high temperatures, and the hydrogen gas generated caused the first hydrogen explosion at 3:36 p.m. on the 12th2) . The next day, on the 13th, Unit 3 The nuclear fuel also melted, and a hydrogen gas explosion occurred around 11:30 on the 14th. Ta. Unit 2 lost its cooling function on the 14th, but Units 1 and 3 No such hydrogen gas explosion occurred. However, pressure vessels and It is believed that the pressure suppression pool was severely damaged, resulting in the release of a large amount of radioactive material into the environment3) . released in this way Today, more than six years after the accident, the radioactive materials However, topics related to the accident, such as decommissioning and contaminated soil, are interrupted. Invisible "radioactivity" that took root due to the accident Concerns about the Ru. Therefore, from the time of the accident to the present, we have seen how they are present in the environment. It is important to understand whether there has been a transition or change in the contaminated area. is extremely important for the future of

Generally, when detecting radioactive substances in environmental samples, Rather than analyzing the radionuclide itself, A method of analyzing radiation such as gamma *rays* is used. In particular, regarding radioactive Cs, there are two types of radionuclides with different production processes. (134 Cs and ^{137} The radioactivity ratio of Cs) is an effective index for estimating the source. It will be done. Regarding radioactive materials derived from the Fukushima Daiichi nuclear power plant accident, 137 Cs radioactivity ratio was approximately 1 in It is known that the value of the 134 Cs/ March 2011 after attenuation correction, but Komori et al . The value is approximately 0.9 for those derived from Units 2 and 3, and approximately 0.9 for those derived from Units 2 and 3. 1.0, indicating that detailed estimation of the source is possible. In addition to this value, Sato et al.5) used the 110mAg/137Cs radioactivity ratio as an index to classify contaminated soil collected in the northwest area of the Fukushima Daiichi Nuclear Power Plant into three groups.

Similar. However, evaluation based on radioactivity analysis Values are useful for verifying the risk of radiation exposure and estimating the source. Although it is effective, it affects physical and chemical properties and environmental dynamics. Linked to direct understanding of radioactive substances themselves, including carriers It's hard to put on. In addition, radioactive substances generally contained in environmental samples are Although it is a very small amount, it has become clear that more than 6 years have passed since the accident. present ^{134} The radioactive concentration of Cs (half-life: 2.07 years) was at the time of the accident.

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This has decreased to less than one-eighth, making it difficult to detect using gamma rays.

On the other hand, there has been an increase in research cases in recent years in which the radioactive materials themselves derived from the accident were analyzed and their properties clarified. Niimura et al.6) is an image of soil and plants contaminated with radioactive materials. autoradiography and We performed elution experiments and clarified the dynamic behavior of radioactive Cs. moreover Adachi et al.7) conducted a more direct analysis and found that One form of the emitted radioactive material was clarified. In this study, Atmospheric aerosol collected immediately after the accident in Tsukuba City, Ibaraki Prefecture? Spherical particles several micrometers in diameter containing radioactive Cs (commonly known as Cs balls) was separated and analyzed on a particle-by-particle basis. Starting from this research, many studies8)-11) on Cs balls were conducted, and the nuclear fuel U and its fission products were investigated. (FPs: Fission Products) and reactor constituent materials are mixed. It is clear that they are particles of silicate glass with a high oxidation number. became. The presence and chemical properties of such radioactive particles are This information is extremely important in understanding the events inside the reactor at the time of the disaster. the Cs ball ratios reported so far are approximately 1.0,7)8) and based on the 134 Cs/137 Cs Radioactivity. All of circumstances at the time of the accident. Well, at this point, Cs balls are being released from Unit 2 of the Fukushima Daiichi Nuclear Power Plant. It is thought that it was done.

Detailed chemical properties at the single particle level as described above are reported. Only the Cs ball is affected by the tsunami. Regarding Unit 1, which was affected by a large amount of water and caused a hydrogen gas explosion, the Therefore, it is unclear what kind of radioactive material was released. Ru. Therefore, in this study, we investigated radioactive particles thought to have originated from Unit 1. The purpose of this study was to analyze the particles at the single particle level and elucidate their physical and chemical properties. Among the contaminated soil collected in the northwest area of the nuclear power plant by Sato et al.5) , which was estimated to contain radioactive materials originating from Unit 1 based on the 134 Cs/137 Cs radioactivity ratio We isolated highly radioactive particles. It is thought to have originated from this Unit 1. There are physical and chemical properties between the particles and the Cs balls from Unit 2. If a difference is found, the generation and production of radioactive materials at Unit 1 and Unit 2 will be It is now possible to chemically consider the differences in the process leading to release. radioactivity Estimating a new emission source to replace the 134 Cs/137 Cs ratio. Furthermore, the chemical properties of radioactive materials can be used as a constant indicator Be expected. On the other hand, radioactive materials derived from these accidents is a document that records the initial situation of the accident, and is also a multifaceted document. Due to the necessity of analysis, it is desirable to destroy the sample during analysis. Not. Therefore, in this study, we focused on complex X-ray analysis8) using microbeam X-rays at the large synchrotron radiation facility SPring-8. Synchrotron radiation microbeam X-ray fluorescence analysis (SR-ÿ-XRF) was used to analyze the chemical composition of particles and the structure near the X-ray absorption edge. We aim to non-destructively elucidate the chemical properties of radioactive particles by analyzing the chemical state of elements in particles using (SR-ÿ-XANES) and the crystal structure of particles using powder X-ray diffraction analysis (SR-ÿ-XRD). Ta.

2 experiments

2.1 Analytical samples and separation method Analytical samples were collected from Namie Town, Futaba District, Fukushima Prefecture according to the classification of Sato et al.5) Soil samples collected in the “red group” area (R-area) of These are 7 radioactive particles (Particles 1 to 7) separated from Particles. Soil samples from this group were found by Sato et al.5) to contain radioactive materials originating from Fukushima Daiichi Nuclear Power Plant Unit 1, based on the 134 Cs/137 Cs radioactivity ratio. 134 Cs/137 Cs radioactivity ratio. In addition, it was It has been pointed out that also indicated that radioactive material originating from Unit 2 or Unit 3 had come from . We also separated 10 radioactive particles from soil samples5) from the Green Group area (G-area) where they were harvested, and analyzed their physical properties and properties. It was used for comparison of chemical composition. We compared the radioactive particles isolated from these soil samples with the analysis results of Cs balls from a previous study8). Ta. These Cs balls were released from the night of March 14, 2011 until the next morning. Atmospheric aerosol and It was collected by

The separation method was based on previous research 7) 8), and the University of Tsukuba isotope It was conducted at the Environmental Dynamics Research Center. First, place the soil sample on the IP. Spread it out, expose it closely, and radiate it using autoradiography. Visualize the distribution of radioactive particles and determine the range where highly radioactive particles exist was separated. This separation operation is repeated several times to obtain one particle level. I narrowed it down to Bell. Kapton tape on acrylic board (Teraoka Seisakusho 650S #25) was prepared, and this One radioactive particle was attached to the adhesive surface and used as a measurement sample.

2•2 Analysis methods

2.2.1 *Ge* semiconductor detector (SEIKO EG&G) was used to measure the *gamma*- ray spectrum of each sample on a particle-by-particle basis. obtained ^{134}Cs and ^{137} Radioactivity of Cs Regarding concentration, attenuation correction was applied as of March 11, 2011. went. The cumulative time is ^{134} Net count of Cs (central energy 604 keV) can be integrated over 30,000 times. Even more careful A low-vacuum scanning electron microscope (SEM: Morphological observation using Tachihi Technologies SU 3500) and the same Composition analysis was performed using an energy dispersive X-ray detector (EDS: Horiba X-max, effective element area 50 mm2) connected to the device. went. No pretreatment such as vapor deposition is performed during SEM-EDS measurement. won.

2.2.2 Synchrotron radiation X-ray analysis Synchrotron radiation X-ray analysis was performed at SPring-8's spectroscopic analysis beamline BL37XU12) . This bee In the mu line, the hard X-ray region generated by the undulator is Synchrotron radiation can be focused down to approximately 1 ÿm in length and width using a Kirkpatrick-Baez (KB) mirror focusing element, making it possible to perform multiple X-ray analyzes using a monochromatic X-ray microbeam as a probe. can be done. The sample is fixed to the XY stage along with the acrylic holder.

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Table 1 Decay-corrected activity (as of March 2011) of ^{134}Cs and ^{137}Cs in radioactive particles 1-7 separated from soil collected at R-area located at the area northwest of the FDNPP

	Particle 1	Particle 2	Particle 3	Particle 4	Particle 5	Particle 6	Particle 7
^{134}Cs (Bq)	101±0.47 42.0±0.47 35.0±0.2 109±0.03			30.2±0.2	42.8±1.7	66.6±2.7	35.8±1.4
^{137}Cs (Bq)	45.1±0.03 38.7±0.1 0.93			33.3±0.1	46.3±1.9	71.3±2.9	38.8±1.6
134 Cs/137 Cs	0.93		0.90	0.91	0.92	0.93	0.92

It has been established. Measurement conditions were based on previous research8) . used in this study The energy of the incident X-rays varies from 7.0 keV to 37.5 keV. Due to the wide area, measurements can be made for both high energy (17.1 to 37.5 keV) and low energy. 2 beam times for energy (7.0-15.0 keV) I went there. In high-energy measurements, the incident X-ray The beam size was 1.0 ÿm horizontally x 1.2 ÿm vertically at the sample position, and SR-ÿ-XRF and SR-ÿ-XANES were performed using a Canberra Si(Li) semiconductor detector installed at a scattering angle of 90°. The beam size during low-energy measurements was 0.6 ÿm in width x 0.8 ÿm in height, and a silicon drift detector (manufactured by Röntec) was installed at a scattering angle of 90°.

In addition to SR-ÿ-XRF and SR-ÿ-XANES using Xflash 2000), SR-ÿ-XRD using a two-dimensional detector was performed. All measurements were performed non-destructively and under atmospheric conditions. In addition, high energy measurement The difference in the types of semiconductor detectors for low-energy and low-energy measurements is that Considering the difference in detection sensitivity for the target energy region This is because the more suitable one was selected.

2.2.3 Analysis of chemical composition and elemental distribution using SR-ÿ-XRF

SR-ÿ-XRF uses monochromatic synchrotron radiation X-rays of 37.5 keV, 15.0 keV, and 7.0 keV as excitation light to analyze each particle. The chemical composition was analyzed. The spectrum was integrated for 300 seconds per sample, and the Thomson Normalized by scattering intensity. Also background (BG) As a result, measurements were also taken on the underlying Kapton tape. Ta. In order to quantitatively consider the detected elements, Glass certified reference materials containing various elements (SRM made by NIST) 611, SRM 613) was crushed and analyzed in the same way, and the main components detected were The sensitivity coefficient is calculated for each element, and the content source is calculated for each particle. The raw semi-quantitative value was calculated. The sensitivity coefficient here is This refers to the value obtained by dividing the normalized intensity of each element obtained in the analysis of SRM611 and 613 by the certified value. means the excitation efficiency of Furthermore, we performed XRF imaging by scanning the sample horizontally and vertically on an XY stage to visualize the distribution of each element. The step width for imaging was 3.0 ÿm horizontally and 3.0 ÿm vertically, and the integration time per point was 2.0 seconds. The energy of excited X-rays during imaging is basically 37.5 keV, and when measuring the Cs-Kÿ distribution, it was set to 36.5 keV to remove the influence of Ba-Kÿ rays, and when measuring low energy, the particle element was set to 36.5 keV. When understanding the distribution, we set it to 15.0 keV, and when measuring the distribution of Cr-Kÿ and Mn-Kÿ rays , we set it to 7.0 keV to eliminate the influence of Fe-Kÿ rays.

2.2.4 Analysis of chemical state by SR-ÿ-XANES Among the elements detected by SR-ÿ-XRF, four elements are Mn, Fe, Zn, and Mo. SR-ÿ-XANES, a fluorescence method, was performed at the K absorption edge to investigate the chemical state inside the particles. These elements reflect chemical states A similar analysis was conducted in a previous study8) for the three elements Fe, Zn, and Mo.

Regarding Mn, it is thought that it originates from Unit 1, which is the subject of this study. Because it was characteristically detected as a radioactive particle, it was selected as a measurement element. It was selected based on the following. The energy step width is 1 eV, and the absorption edge The range of 100 eV before and after was measured. Measurement time per point was set for 2 to 6 seconds depending on the detected intensity. Metals, oxides, glass, etc. of each element were prepared as reference materials. The glass was synthesized by adding oxides of each metal to soda-lime glass made from the reagents Na_2CO_3, $CaCO_3$, and SiO_2 , and firing it in an oxidizing atmosphere in an electric furnace. In principle, each measurement

Elements that were found to be concentrated near the center of the particle Regarding this, we also measured its concentrated portion.

2.2.5 Crystal structure analysis using SR-ÿ-XRD A CMOS flat panel sensor was installed 200 mm behind the sample position. The crystal structure of the sample was then analyzed using SR-ÿ-XRD using the transmission Debye-Scherrer method. The energy of the incident X-ray is 15.0 keV. We made it monochromatic and accumulated 100 measurements with an exposure time of 440 milliseconds. The measurement location is the same as SR-ÿ-XANES. In addition, Si powder (NIST SRM 640c) was measured under the same conditions as a reference material, and the diffraction pattern was Ensure that there is no deviation in the lattice spacing (d value) calculated from the turns. I confirmed that.

3 Results and discussion

3.1 Radioactivity and physical properties of particles

7 radioactive particles isolated from soil samples in R-area. ^{134}Cs and ^{137} Each radioactivity concentration of Cs, and The 134 Cs/137 Cs radioactivity ratio is 1. According to previous research4), this value is approximately 0.9, which is summarized in Table the same as that of Fukushima Daiichi Nuclear Power Plant Unit 1. This corresponds to radioactive substances released by Okay predicted that the soil would contain radioactive Based on the 134 Cs/137 Cs radioactivity ratio, it was materials derived from the soil. Even if the radioactive particles actually separated were analyzed individually, The radioactivity ratio that can be determined to be the origin was shown.

Among these seven particles, four representative particles (Particles 1 to 4)

The SEM images are shown in Fig. 1a-d. According to previous research7) , the Cs balls originating from Unit 2 were all spherical particles with a diameter of several ÿm. In contrast, the shape of the radioactive particles originating from Unit 1 is They varied in size and ranged in size from 50 to 250 ÿm, which was clearly larger than the Cs ball. Regarding this clear difference in physical properties, Differences in the origin of the sample itself, i.e., whether it was isolated from soil or not This is due to the difference in whether it was collected as air aerosol or not. There is a possibility that Therefore, Figures 1e and f show SEM images of radioactive particles separated from soil samples in the G-area. Based on this from Unit 2 134 Cs/137 Cs radioactivity ratio, it was determined that the soil or 3 contained radioactive materials, but in reality These particles isolated from the soil (Fig. 1e, f) are similar to the Cs balls from Unit 2 that were discovered in the atmospheric aerosol. It had the physical properties of This means that particles originating from Unit 1 The difference in physical properties between the Cs ball and the soil It is important to note that this is not due solely to the difference in whether the I'm tasting it. However, in R-area and G-area, Fukushima Daiichi Nuclear Power Plant Since the distances from the We cannot deny the possibility that it flew into the R-area. Originated from Unit 1 The number of cases in which radioactive particles that can be determined to be found in the environment will increase. It is hoped that these points will become clearer.

The Cs balls believed to have originated from Unit 2 contain radioactive Cs on the order of 1 Bq per particle7),8) . In contrast, the particles derived from Unit 1 analyzed this time contain radioactive Cs on the order of 10 to 100 Bq per particle (see Table 1), and the radioactivity of each particle is If you look at it in detail, the latter is clearly higher. But long When comparing the specific radioactivity considering the particle size, it is found that The Cs balls containing 1 Bq level of radioactive Cs in a few micrometers have a higher specific radioactivity than the particles derived from Unit 1, which have a relatively large particle size. I can say yes.

Among the 7 particles said to have originated from Unit 1, Particles 1 to 4 are examples. The SEM-EDS spectrum of is shown in Fig. 2a. The EDS spectrum is expressed logarithmically on the vertical axis. not shown here All particles originating from Unit 1, including small particles, have Si and O as their main components. It became clear that About particles 1 and 2 The results of mapping Si-K lines by EDS are shown in Fig. 2b, c. The distribution of Si in both particles corresponds to the SEM image shown in Fig. 1, indicating that Si is contained throughout the particles.

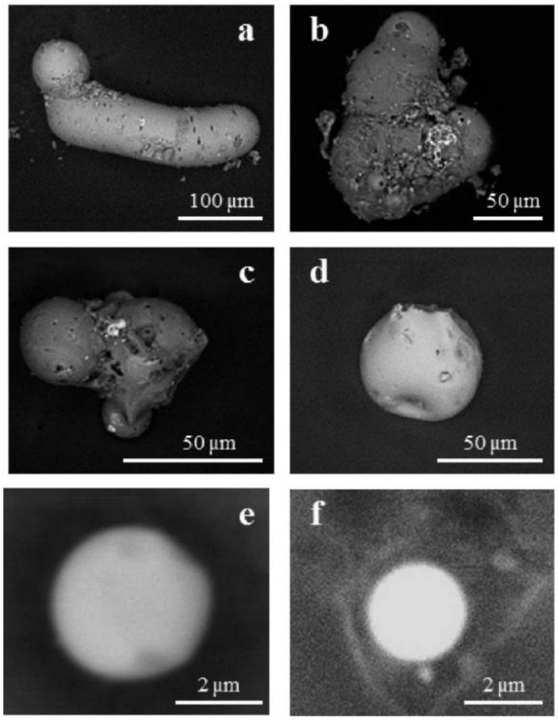

Fig. 1 SEM images of radioactive particles separated from soil samples collected at the area northwest of the FDNPP

(a) Particle 1, (b) Particle 2, (c) Particle 3, (d) Particle 4 separated from soil collected at R-area. (e, f) Radioactive particles separated from soil collected at G-area.

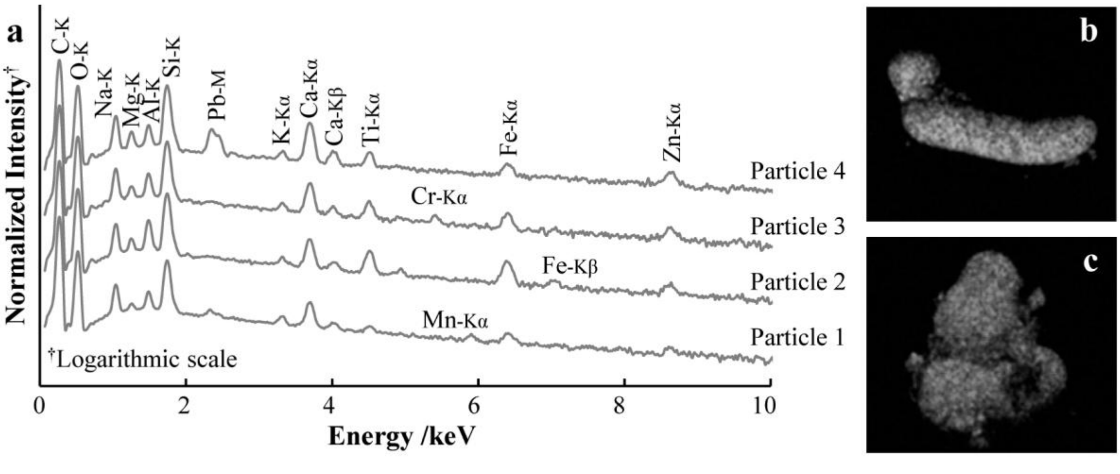

Fig. 2 (a) Comparison of SEM-EDS spectra of the four particles emitted from the FDNPP Reactor 1. Results of SEM-EDS elemental mapping of the Si-K line of (b) Particle 1 and (c) Particle 2

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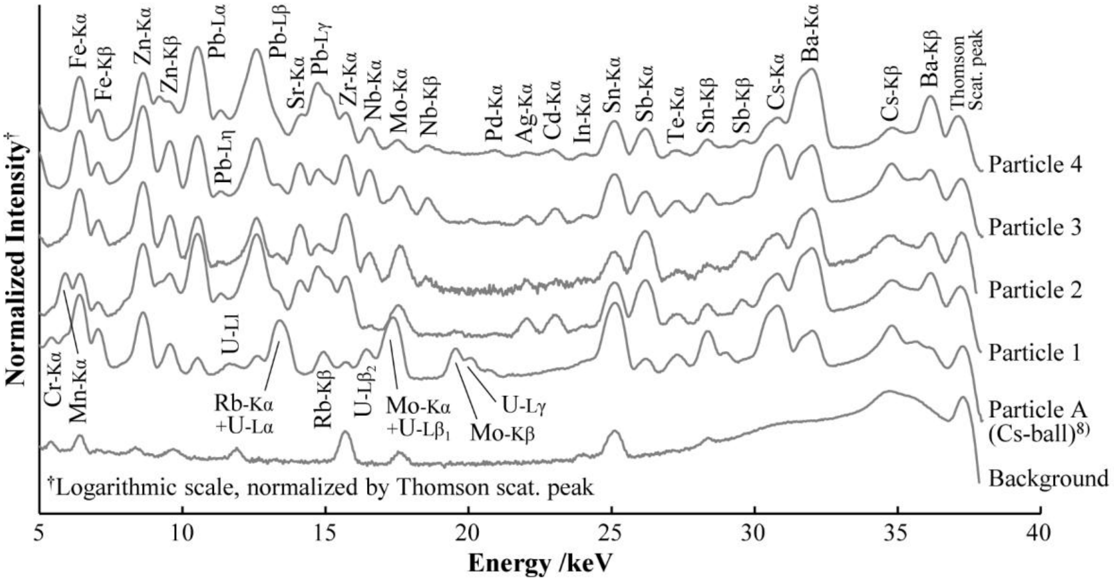

Fig. 3 Comparison of the SR-ÿ-XRF spectra (excited by 37.5 keV X-rays) of bulk parts of the four radioactive particles emitted from the FDNPP Reactor 1, Particle A (Cs-ball) emitted from the FDNPP reactor 2 and the background part of particles 8) .

Table 2 Comparison of 21 elements detected by SR-ÿ-XRF in radioactive particles emitted from the FDNPP reactor 1 and Cs-balls emitted from the FDNPP reactor 2 (ÿ, detected in common; ÿ, detected from some particles; ×, not detected)

	Cr	Mn	Fe	Ni	Zn	Rb	Sr	Zr	Nb	Mo	Pd	Ag	Cd	In	Sn	Sb	Te	Cs	Ba	Pb	U
Particles from reactor 1	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ
Cs-balls	ÿ	ÿ	ÿ	×	ÿ	ÿ	×	ÿ	×	ÿ	×	ÿ	×	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ	ÿ

I understand. These results are similar to those for Cs ball 9) to 11) .

It was confirmed that particles derived from carbon dioxide are also substances whose main components are Si and O.

It shows. In addition, Fe and Zn were also detected in the EDS spectrum, which also have characteristics similar to those of Cs balls7) .

Ru. However, in the Cs ball, Cs-L also appears in the EDS spectrum.

However, in the particles originating from Unit 1, the EDS

In this analysis, no Cs-L line was detected. This difference is the particle

This is due to the concentration of Cs in

We will respond accordingly. This is due to the difference in the situation inside the reactor between Unit 1 and Unit 2.

Or, it is thought that it reflects the difference in the generation and release process of particles.

It will be done.

3.2 Elucidation of chemical composition and elemental distribution

As a result of SR-ÿ-XRF analysis of seven particles originating from Unit 1, the detected elements were qualitatively similar. Here we examine

Four representative particles (Particle

Taking 1 to 4) as an example, Figure 3 shows the SR-ÿ-XRF spectrum obtained with 37.5 keV excitation. These spectra are expressed logarithmically along the vertical axis. In addition, as described later, these particles

Although there is a local concentration of elements, the spectra shown here

All torques were obtained from the bulk portion. For comparison, we also analyzed the three-particle Cs ball analyzed in a previous study8).

The spectrum of Particle A and the underlying Kapton part

The spectrum of is also shown. From Fig. 3, various elements were detected in the particles derived from Unit 1 in addition to Cs, which was detected by gamma-ray spectrum measurements (Table 1).

Combining the results with 15.0 keV and 7.0 keV excitation, a series of

The 21 elements detected by SR-ÿ-XRF in particles and Cs balls8) derived from Unit 1 are summarized in Table 2, and the chemical composition is qualitatively determined.

Compared to. As can be seen from Fig. 3, the particles derived from Unit 1 contain elements such as Sr and Ba that become highly volatile in a reducing atmosphere11).

In contrast, Cs balls are volatile in an oxidizing atmosphere.

Many Rb with high values were detected. In addition, overall No. 1

Particles derived from the machine contain more types of elements, and there are compositional differences.

was found. Next, we

visualized the distribution of each element within the particles using SR-ÿ-XRF imaging. For example, at the end of Particle 1

On the other hand, sufficient strength was obtained to discuss the elemental distribution, and

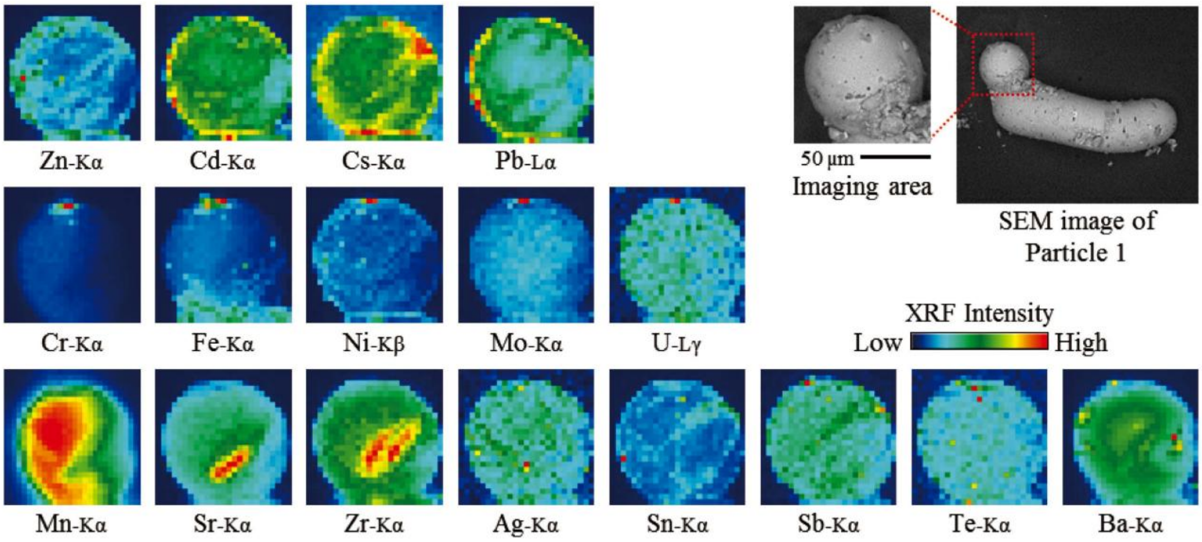

Fig. 4 Distributions of 17 representative elements in Particle 1 obtained by SR-ÿ-XRF imaging with SEM images corresponding to the imaging area

For the 17 elements that did not have significant peak overlap with other elements, Figure 4 shows the imaging results. Regarding the element distribution in Cs balls, although it has been pointed out that there is a concentration of some elements on the nm order within the particles9), SR-ÿ-XRF imaging, which is the same as in this study, shows that there is a significant concentration of elements within the particles . No significant compositional maldistribution was observed8) , suggesting that the composition is relatively uniform. Ru. On the other hand, in the particles derived from Unit 1, the original It became clear that the elements were unevenly distributed (see Fig. 4). Within the analyzed range, the four elements Zn, Cd, Cs, and Pb are The distribution is relatively similar, and the strength is high at the outer edge of the particle. Therefore, it is thought that it exists in large quantities on the surface. Cs to the ball However, it has been pointed out that Cs may exist in large amounts on the particle surface9),10) , making the relationship interesting. Furthermore, Cr, Fe, Ni, It became clear that Mo was concentrated in a region several ÿm at the end of the particle, and the U and L lines were also detected from this point. Mn was distributed throughout the particles, but other elements were It showed a unique distribution, and concentrated points of several micrometers were also observed for some elements.

Next , we estimated the origins of the 21 elements (Table 2) detected in radioactive particles from Unit 1 by SR-ÿ-XRF based on previous research on Cs balls8). U comes from nuclear fuel It is thought that 14 kinds of heavy elements (Rb, Sr, Zr, Nb, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba) are elements contained in FPs of nuclear fuel. However, regarding Zr and Sn It is also possible that this is derived from the Zr-Sn alloy of the fuel cladding. Ru. In addition, in relation to the Ag detected by SR-ÿ-XRF here, the soil in R-area containing radioactive materials derived from Unit 1 110mAg has been detected5) . Pb is thought to originate from the Pb plate inside the containment vessel, and metallic Pb has an extremely low melting point of 327.5°C. Therefore, it is expected that it would have melted easily. Cr, Mn, Fe, Ni, Regarding Zn, it is thought that it originates from the constituent materials of the nuclear reactor. I can see it. In particular, Cr, Fe, and Ni are contained in general stainless steel. SUS316 and SUS316L with Mo added have high durability. It has excellent corrosivity and is also used in the Fukushima Daiichi Nuclear Power Plant Unit 1 reactor. It is highly likely that As mentioned earlier, these four elements are located at the same point. Stainless steel containing Mo is the source of this concentration point. It is assumed that this is closely related to the development of Also, Mn, Ni and Mo There is also a possibility that it originates from the Mo-Mn-Ni steel of the pressure vessel. Regarding Zn, in previous research8) However, it may be included in the above constituent materials or as a plating. It is also possible that it was used. In addition to these elements In addition, in the EDS spectrum (Fig. 2a), Si is the main component and various elements from C to Ca are detected, indicating that they are used as insulation materials or is presumed to be derived from concrete, but there are no concrete To determine the origin, it is necessary to identify the material actually used in the reactor. A direct comparison is essential.

3.3 Elucidation of chemical state and crystal structure

The SR-ÿ-XANES spectra of the Mn-K absorption edge of Particles 1 to 3 are shown in Figure 5a along with the reference material. mentioned earlier As with SR-ÿ-XRF, similar spectra were obtained for the seven particles analyzed this time, so here we will use three particles as an example. Showing the results. 3 The spectrum of the particle is near the center of the particle. This is what was obtained, and in order to see the chemical state of the particle body, A bulk part with no element concentrations is selected. shown here The spectrum of particles originating from Unit 1, including the four particles that are not All have similar shapes and are smooth with no fine structure. Since the spectrum was very strong, it was found that ions were present in the glass. This is considered to be a state that exists. Also, reference materials with different oxidation numbers Compare the energy of the illuminated substance and the white line of the spectrum

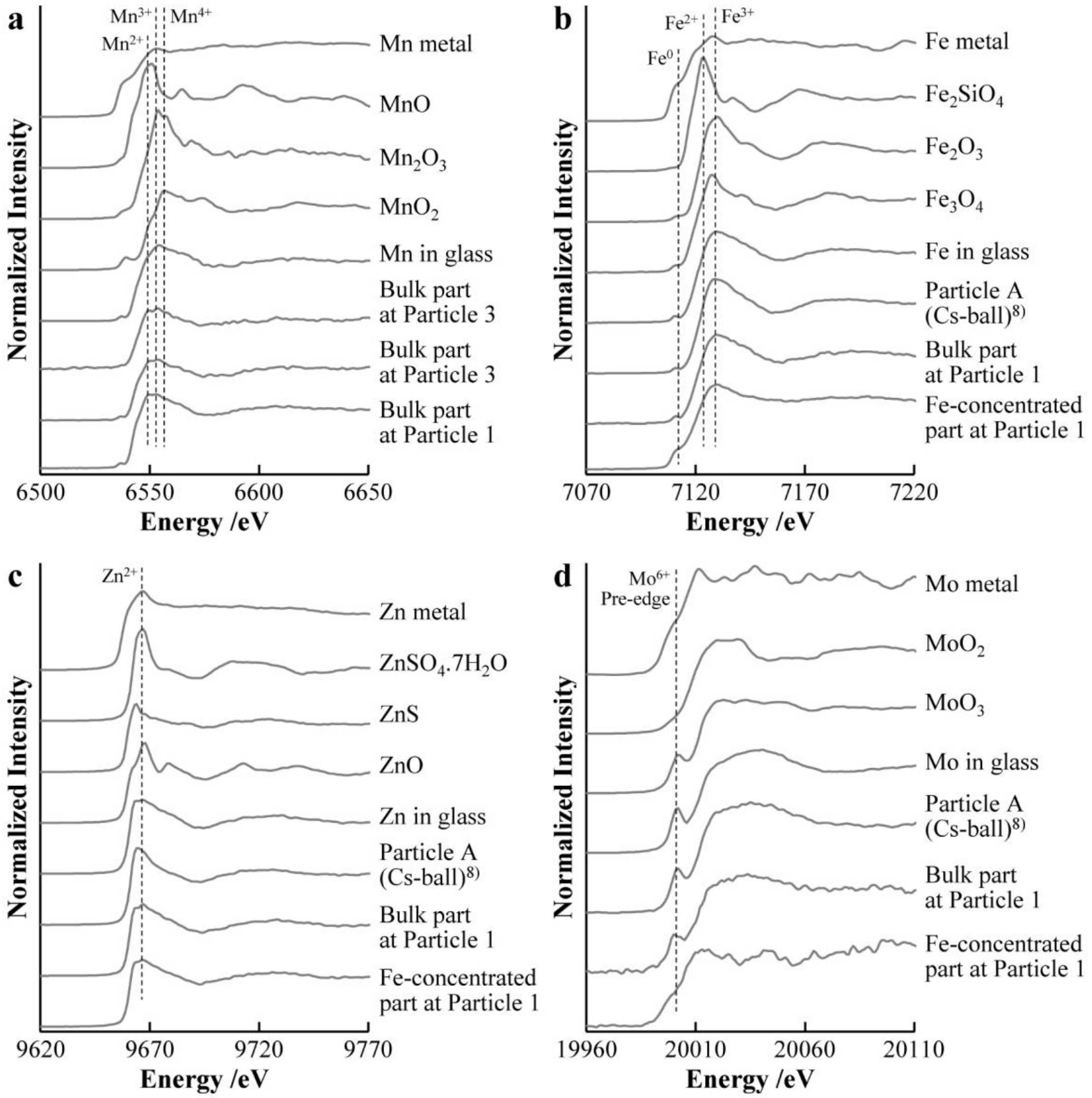

Fig. 5 Results of SR-ÿ-XANES analyses Comparison of the

(a) Mn-K edge, (b) Fe-K edge, (c) Zn-K edge and (d) Mo-K edge SR-ÿ-XANES spectra of the radioactive particles and the reference materials.

As a result, it corresponds to Mn^{2+} and Mn^{3+}, and has a relatively low acidity. It was shown that it exists in numerical terms.

Next, focusing on Particle 1, we investigated the concentration of Fe, Zn, and Mo in two locations: the main part of the particle and the concentration point of Fe etc. seen in Fig. 4. The K-edge SR-ÿ-XANES spectra are shown in Fig. 5b-d. In addition, for comparison, Particle A of the Cs ball and each Spectra of reference materials for the elements are also shown. First, Particle 1 Regarding the particle main part, all three elements, Fe, Zn, and Mo, are The shape matched the spectrum when it existed in the lath. In particular, looking at the results of the Mo-K absorption edge (Fig. 5d), a pre-edge peak characteristic of Mo^{6+} was detected, indicating that it is in a high oxidation number state. It is thought that it exists. Regarding Fe, judging from the energy of the white line in the spectrum, it is thought that Fe^{3+} is the main element. These three elements are highly The result of glassy state due to oxidation number is similar to that of Cs balls in previous research8). It was similar to that of Furthermore, in the main body of Particle 1, SR-ÿ-XRD was then performed, but no diffraction peaks were detected, supporting the SR-ÿ-XANES results that it was in a glassy state. Combined with the results of the SEM-EDS analysis mentioned above, similar to the Cs ball, The main component of particles derived from Unit 1 was also silicate glass. It is thought that Silicate glass has a relatively high stability in the environment. Unlike water-soluble radioactive substances, this particle There is a danger that the radionuclides contained in the particles will leach and diffuse into the environment. The risk is considered to be low. At the same time, this result shows that these emissions suggesting that radioactive particles have long-term effects in the environment. There is.

Next, looking at the SR-ÿ-XANES spectrum obtained for the concentration point of Fe etc. in Particle 1 (see Fig. 4), we see that

Table 3 Lattice spacing (d-value/Å) of Fe-concentrated part on radioactive particles 1-7 detected by the SR-ÿ-XRD

Particle No.							ÿ-Fe2O3 14)
1	2	3	4	5	6	7	d/hkl
1.81	1.79	1.85				ÿ 1.841/024	
1.91							
2.10	2.11		2.03	2.09	2.09		
	2.22	2.22				ÿ 2.207/113	
	2.32	2.33				2.35 ÿ	
	2.53	2.53	2.60	2.51	2.53	2.519/110	
2.70	2.71	2.72				ÿ 2.700/104	
				2.95	2.95		
3.20							
3.34		3.35	3.35				
	3.70	3.70				ÿ 3.684/012	
4.20							

For Zn unrelated to concentration (Fig. 5c), there is no clear difference from the main part. Although not found, Fe (Fig. 5b) and Mo (Fig. 5d) Therefore, the spectral shape differs between the main part and the concentration point. became. Regarding Mo, there is a pre-edge peak characteristic of Mo6+. was not detected, and Fe was also found to be a compound or metal with a low oxidation number. It was shown that there is a possibility that the situation is About this concentration point When SR-ÿ-XRD was performed, it was not observed in the main body part. Many clear diffraction peaks were detected, indicating the presence of crystalline substances. It became clear. Similar local concentrations of Fe occurred in the other six particles. There are also diffraction peaks detected by SR-ÿ-XRD in both cases. It was served. 7 From the diffraction pattern obtained at the Fe concentration point of the particles The calculated *d* values are summarized in Table 3. Common between different particles Diffraction lines with *d* values have also been detected, or similar results have been detected. It is also possible that crystalline substances are contained in multiple particles. Special For those with *d* values of 3.7, 2.7, 2.5, 2.2, and 1.8 Å, ÿÿÿÿ-Fe2O3 14ÿ 012 plane (d=3.684 Å, relative intensity 30), 104 Surface (d=2.700 Å, phase intensity 100), 110 surface (d=2.519 Å, phase intensity 100) relative strength 70), 113 plane (d=2.207 Å, relative intensity 20), 024 plane (d=1.841 Å, relative intensity 40). In other words, within one particle, there is a bond on the order of several ÿm with the base of the glass. It is said that crystalline substances are mixed and the chemical state is non-uniform. Interesting results were shown.

At present, there is no sufficient phase identification for these crystalline substances. It is difficult to say that it was carried out, and as in Particle 1, Mo, U, etc. If it does not contain characteristic heavy elements, the Fe concentration point will be located in the soil. It is also possible that these are deposits from other people. Microscopic Raman spectroscopy Introduction of excellent methods for identifying minute substances, such as analytical methods, or Although it will be a broken analysis, only the crystal part will be picked up. By performing XRD using a Gandolfi camera, It is expected that the true nature of these crystalline substances will be elucidated. Ru.

3.4 Estimation of the situation inside the reactor at the time of the accident

As mentioned above, regarding radioactive particles thought to have originated from Unit 1, Therefore, the Cs balls that are believed to have originated from Unit 2 have different physical and chemical properties. It became clear that the patient had symptoms. Below, we will explain the differences in their properties. Based on and the particle generation and release process.

The important difference in chemical composition is, as mentioned earlier, that These particles are highly volatile in reducing atmospheres such as Sr and Ba. It is characterized by the fact that it contains the following elements. This is the particle generation stage This suggests that there was a difference in the atmosphere inside the reactor of Unit 1 and Unit 2. This is an important finding. Next, see the results of SR-ÿ-XANES and the result assuming a low oxidation number (Mn and Mo at the concentration point) and the results assuming a high oxidation number (Fe and Mo in the main body) Both were shown. The reduction reaction of the metal element occurs after particle formation. It is difficult to imagine that the particles from Unit 1 will continue to progress, so the particles originating from Unit 1 are likely to be in a reducing atmosphere. It was generated under an enclosed atmosphere and released into the atmosphere at a high temperature, resulting in It is thought that some elements were oxidized. Grains from Unit 1 Both the ball and the Cs ball are made of Si, Cr, Mn, Fe, and Zn. Because it contains many elements derived from the constituent materials of the furnace, both In these furnaces, the particles are generated not only around the fuel but also in the furnace. It can be seen that some of the material itself was also melted. In addition, until release The progress of melting, or what was used in Units 1 and 2. Differences in furnace materials are reflected in differences in the content of these elements. it is conceivable that.

Unlike atmospheric aerosols collected at a specific time, soil aerosols In the case of a sample, it does not have time resolution, so it was originally It is unclear when the particles were released from the Fukushima Daiichi nuclear power plant. I can't break it. However, the particles discovered this time that are believed to have originated from Unit 1 Regarding the child, the vent and hydrogen explosion occurred on March 12-13, 2011. The radioactive material released by the nuclear power plant was transported north from the nuclear power plant. Based on the results of Tsuruta et al.15) , these particles are 3 It is estimated that it was likely released between the 12th and 13th of May. child In this case, only one day after the earthquake occurred at 14:46 on the 11

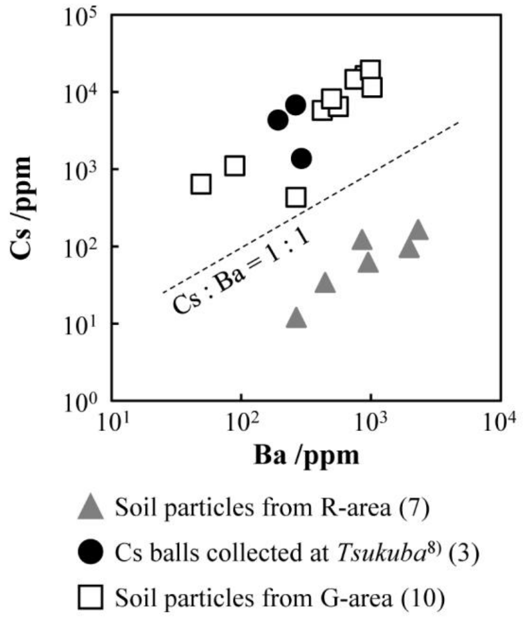

Fig. 6 Plot of semi-quantitative values of Cs and Ba in the radioactive particles separated from soil collected at R-area *(n* = 7), the Cs-balls collected at Tsukuba *(n* = 3) and the radioactive particles separated from soils collected at G-area *(n* = 10).

8)

Meanwhile, a melting reaction between the nuclear fuel and surrounding reactor materials progressed inside the Unit 1 reactor. That means that. As mentioned earlier, at the time of generation of these particles, Analysis results show that there was a reducing atmosphere inside the furnace. However, as of the 12th, the Unit 1 reactor was filled with hydrogen gas. This corresponds to the estimated situation inside the reactor. Also, The heterogeneity of the chemical composition and chemical state of these particles This is consistent with the assumption that the time from generation to release was short. Ru. The hydrogen explosion on the 12th occurred in the reactor building, not the core. Therefore, the production process of the radioactive particles involved a hydrogen explosion. It cannot be determined that they are directly related. However, this Considering that these particles are relatively large and have a distorted shape, Therefore, it is possible that hydrogen explosion was one of the main release processes. The risk of damage to the containment vessel and venting (reducing pressure inside the vessel) is high. Cs released from Unit 2 during steam release work) It is thought that the release process was different from that of the ball.

3.5 Classification of sources using chemical composition

As mentioned at the beginning, Units 1 and 2 to 3 of the Fukushima Daiichi Nuclear Power Plant ratio, it is difficult to detect 134 Although there is a difference in the 134 Cs/137 Cs radioactivity Cs because more than 6 years have passed since the radioactive accident. It is becoming. Therefore, radioactive materials derived from Unit 1 and 2-3 Chemical composition as a new criterion for identifying radioactive materials originating from reactors We propose a classification based on As mentioned above, Unit 1 The chemical composition of the radioactive materials derived from the source and the Cs balls derived from Unit 2 There is a difference in . Therefore, radioactive particles from Unit 1 in R-area 7 Cs ball particles, 10 radioactive particles isolated from soil in the G-area, and 3 Cs ball particles analyzed in a previous study8).

For the 15 elements detected by SR-ÿ-XRF (Table 2), the fluorescent X-ray intensities normalized by Thomson scattered radiation and the standard Calculate the semi-quantitative value using the sensitivity coefficient calculated from the substance. Ta. Among the semi-quantitative values obtained, plots are made for Ba and Cs. was created (Fig. 6). From this figure, it can be seen that there is a clear difference in composition between the particles derived from Unit 1 and the Cs balls. child Looking at the 10 particles isolated from the soil in G-area, we find that It had compositional characteristics similar to Cs balls. 2 for G-area ~As it has been pointed out that radioactive materials originating from Unit 3 may have come into the air5) , soil analysis results and particle analysis results have been confirmed. We responded without contradiction. At present, these numbers are semi-quantitative values. However, there is still room for verification and improvement regarding the quantitative accuracy of this method. Nono, if there is such a clear compositional difference, it is sufficient to classify it. It can be said that it is possible. Therefore, this study shows that chemical composition is effective as a new classification index for radioactive substances isolated from environmental samples in place of the 134 Cs/137 Cs radioactivity ratio. It has been proven that

4 Conclusion

This study focuses on radioactive particles released from Unit 1 of the Fukushima Daiichi Nuclear Power Plant. The chemical properties of the particles were elucidated by non-destructive synchrotron X-ray analysis, and 2 It was demonstrated that this ball is different from the Cs ball that is believed to have originated from the No. 1 The particles originating from Unit No. 1 are clearly larger and more distorted than the Cs balls. Many of them were shaped like Cs balls, but their specific radioactivity was lower than that of Cs balls. It was low. SR-ÿ-XRF revealed that the particles derived from Unit 1 contain more types of heavy metals than Cs balls, especially Sr and Ba. Contains elements that are highly volatile in reducing atmospheres such as It became clear that Also, elements are unevenly distributed within the particles. Some elements, including Cs, were abundant on the surface. On the other hand, it was also observed that some elements such as Fe and U were concentrated within a range of several ÿm. The main components of the particles are Si and O. SR-ÿ-XANES and SR-ÿ-XRD also showed that this particle was silicate glass. However, Fe etc.

At points where elements were concentrated, X-ray diffraction data revealed that oxides, etc. crystalline substances exist, and the chemical state within the particles is also uneven. Consistency was seen. These particles were collected on March 12-13, 2011. It is thought that hydrogen gas was released, or that a hydrogen gas explosion occurred on the 12th. It was suggested that this may have been the main cause of the release. This conclusion The result is that the fuel and surroundings are depleted at an extremely early stage in the Unit 1 reactor. This indicates that the components on the edges were melting. Furthermore, the chemical composition of radioactive particles can be used as an indicator for estimating the source of the emission. It was shown to be effective.

The chemical properties of radioactive particles isolated from these environments Understanding is not just about providing information to decipher the accident event. In addition, evaluation of the impact on the human body and the environment, and furthermore, This is an important finding that will lead to the development of efficient removal methods. Fortune As the dismantling work of the Shima Daiichi Nuclear Power Plant progresses, the direct contact between such particles and the material actually left in the furnace. It is hoped that this will enable more accurate comparisons.

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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

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Seven radioactive particles were separated from a soil sample collected at the Northwest region of the Fukushima Daiichi Nuclear Power Plant (FDNPP). It has been pointed out that the soil is contaminated by radioactive materials emitted from reactor 1 of the FDNPP by the accident that occurred in March, 2011. The physical characteristics of these radioactive particles with –100 ÿm in diameter and non-uniform shape are clearly different from those of spherical microparticles, known as Cesium-balls, thought to be emitted from the FDNPP reactor 2. Three kinds of synchrotron radiation-based X-ray analyses (X-ray fluorescence analysis, X-ray absorption near edge structure analysis and X-ray diffraction analysis) were nondestructively applied to radioactive particles using a micro-focused X-ray beam at the SPring-8 to investigate their detailed chemical properties. Various elements related to fission products of nuclear fuel and components of the reactor were detected from the particles emitted from the FDNPP reactor 1 with an obvious heterogeneous elemental distribution. In particular, the chemical compositional feature of these particles was characterized by several elements (Sr, Ba *etc.),* which were easily volatilized in a reducing atmosphere. Although a main component of the particles was identified as silicate glass similar to the Cesium-balls, some crystalline materials were also found in microscopic regions containing Fe and other metallic elements. We concluded that these radioactive particles were emitted from reactor 1 to the atmosphere during 12th to 13th March, 2011. Our results suggest the fact that the nuclear fuel and the reactor vessels around the fuel were melted together at a very early stage of the accident. In addition, it was demonstrated that chemical compositional information of individual radioactive materials can be a new indicator as an alternative to the radioactive ratio to estimate the source of emissions.

Keywords: Fukushima Daiichi Nuclear Accident; radioactive material; synchrotron radiation X-ray analysis; micro-XANES; radioactive microparticles.