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Research paper

Identification of the actual cesium-adsorbing materials in the contaminated Fukushima soil

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ABSTRACT

Since the accident at the Fukushima nuclear plant in 2011, a number of studies have been carried out to clarify the adsorption state of radioactive cesium (Cs) in the contaminated soil. However, analyses of the individual radioactive particles in the actual soil are still elementary, particularly due to the extremely-low concentration of Cs. In this study, a micro-manipulator and focused ion beam (FIB) were combined with imaging plate (IP) autoradiography to explore the distribution of Cs in radioactive particles, and to identify the actual Cs-adsorbing materials. Consequently, direct observations of the radioactive sections indicated that weathered biotite and aluminous smectite adsorbed the Cs in the actual contaminated soil. In a platy-shaped weathered biotite, the radioactive Cs was distributed almost homogeneously. Moreover, the weathered biotite was inferred to have adsorbed the Cs in preference to the neighboring materials, such as the smectite and organic matter.

1. Introduction

At the present time, among the radioactive nuclides released by the accident at the Fukushima Daiichi-nuclear power plant in March 2011, cesium (Cs) that was mainly trapped at the soil surface still retains radioactivity because of its long-half life. The treatment of the contaminated soil is predicted to be problematic for a long time to come. Thus, it is necessary to understand the precise dynamic state of the Cs in the soil. However, particularly due to the extremely-low level concentration of Cs in the soil ($\sim 10^{-10}$), it is quite difficult to determine the Cs-adsorbing material and to get a detailed picture of the distribution of radioactivity.

Many laboratory experiments have shown that micas and vermiculite adsorb Cs with very high selectivity (Sawhney, 1972; Francis and Brinkley, 1976; Evans et al., 1983; Komarneni and Roy, 1988; Comans et al., 1991; Poinssot et al., 1999; Zachara et al., 2002). By collapsing of the layers, dehydrated Cs ions are rigidly fixed at the interlayer sites and hardly replaced by the other cations (Brouwer et al., 1983; McKinley et al., 2004; Nakao et al., 2008; Kogure et al., 2012; Kikuchi et al., 2015). Some researchers suggested that the Cs retention ability of soils is controlled by these minerals (Maes et al., 1999a, 1999b; Delvaux et al., 2000; Nakao et al., 2014). Among other clay minerals, smectite, which is an abundant clay mineral in Fukushima (Sano et al., 2010; Fujii et al., 2015), adsorbs Cs with relatively high selectivity although the retention ability is strongly influenced by its layer charge, grain size, etc. (Staunton and Roubaud, 1997; Degryse et al., 2004; Missana et al., 2014; Fukushi et al., 2014). The other clay minerals such as kaolinite are generally assumed to have limited retention ability for Cs (Cornell, 1993; Ejeckam and Sherriff, 2005).

Recently, the effect of the Cs concentration on the retention ability was investigated in clay minerals (Missana et al., 2014; Fuller et al., 2014). Several studies suggested that other clay minerals than micas and vermiculite increase the adsorption ability of Cs under the low concentration level (Kozai et al., 2012; Ohnuki and Kozai, 2013). However, the concentration level in these studies was still higher than that in the actual contaminated soil, and the investigation of the actual soil which has a complex phase system is still quite elementary. The imaging plate (IP) autoradiography technique which is capable of detecting radiation has been applied in previous research to identify radioactive particles in actual contaminated soil (McKinley et al., 2001; Mukai et al., 2014). But, since its spatial resolution is severely limited to around a few hundred micrometers at best, the detailed distributions of the Cs in the particles have not been discussed. In this study, to overcome

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this limitation, a micro-manipulator and focused ion beam (FIB) have been combined with IP autoradiography. By this method, the distribution of Cs in radioactive particles of actual contaminated soil was examined and identification of the Cs-adsorbing materials was attempted.

2. Materials and methods

The sample used in this study was a litter soil sample collected from fallen leaves on the ground in a forest near the boundary between Iitate village and Namie town in Fukushima, Japan. The details of the sample and the identification procedure of the radioactive particles were described in Mukai et al. (2014). In Mukai et al. (2014), the radioactive particles were classified into three types: (1) weathered biotite, (2) organic-rich particle and (3) aggregate of fine minerals. The distributions of the Cs in the three types of particles were explored. The weathered biotite and the organic-rich particles were placed on carbon conductive tape and divided into two-four sections by FIB (Hitachi FB-2100). Each divided section was relocated at intervals of more than 1 mm by a micro-manipulator (Quick Pro, Micro Support Co., Ltd.) and then their radioactivity was examined with an IP (BAS IP MS, Fuji Film). These procedures were repeatedly conducted. On the other hand, the aggregates of fine minerals were individually placed on an IP (FDL-UR-V, Fuji Film) with micro-grid patterns on the surface formed by laser ablation, using a YVO_4 laser maker to specify the location of the radioactivity. On the IP, each aggregate was crushed into several fragments with a micro-knife (MK-D, Micro Support Co., Ltd.) and the fragments were spread with ethanol. The imaging plates were kept in the dark for about several days and scanned with an IP reader (FLA-7000, Fuji Film). Lastly, the divided pieces of the organic-rich particles and the crushed fragments of the aggregates were subdivided and fixed onto transmission electron microscopy (TEM) grids for further electron microscopic analyses with the FIB micro-sampling system.

The particles, the pieces and the fragments were coated with carbon and analyzed using scanning electron microscopy (SEM, Hitach-S4500). In the SEM, back-scattered electron (BSE) observations and measurements of energy-dispersive X-ray spectrometer (EDS) with an ultrathin window (Kevex Sigma) were conducted with an accelerating voltage of 15 kV. The subdivided pieces and fragments fixed onto the grids were thinned for TEM analyses by FIB sputtering. The TEM analyses were performed on a JEOL JEM-2010UHR operated at 200 kV. For a divided piece of the weathered biotite, synchrotron X-ray diffraction measurement was made at the beam-line (BL22XU) of SPring-8. The accelerating voltage was 15 kV and the diffraction pattern was recorded on an IP.

3. Results and discussion

3.1. Weathered biotite

At first, the distribution of the Cs was investigated in a radioactive weathered biotite, named “WB1” (Fig. 1a). EDS measurements for the WB1 showed peaks of O, Mg, Al, Si, K, Ti and Fe. The WB1 was divided into four pieces (WB1A–D) using FIB, and the radioactivity of each piece was examined with the IP (Fig. 1b). The scanned IP indicated that all the divided pieces had radioactivity, though the intensities of their radiation had some variation. On these pieces, further analyses were conducted. The piece “WB1B” was subdivided again into four small pieces (WB1Ba–Bd) and their radioactivity was examined in an analogous way (Fig. 1c). The result of the IP autoradiography showed that all the small pieces still had radioactivity although their radiation intensities were weakened.

The intensity of the small piece “WB1Bc” inside of the particle was almost the same as that of the other small pieces. The other piece “WB1D” was subdivided into two pieces with elongated shapes (WB1Da and Db) and they were found to be radioactive (Fig. 1d). Then, the side facet of the radioactive small piece “WB1Da” was turned up by the micro-manipulator. The WB1Da was subdivided again into two small pieces (WB1Da1 and Da2) along the cleavage direction and the radiation was examined. The result of the IP autoradiography showed that the two small pieces constituting the upper and the lower parts of the WB1 were both radioactive. These results in Fig. 1 definitely indicated that the radioactive Cs was distributed almost homogeneously in the WB1.

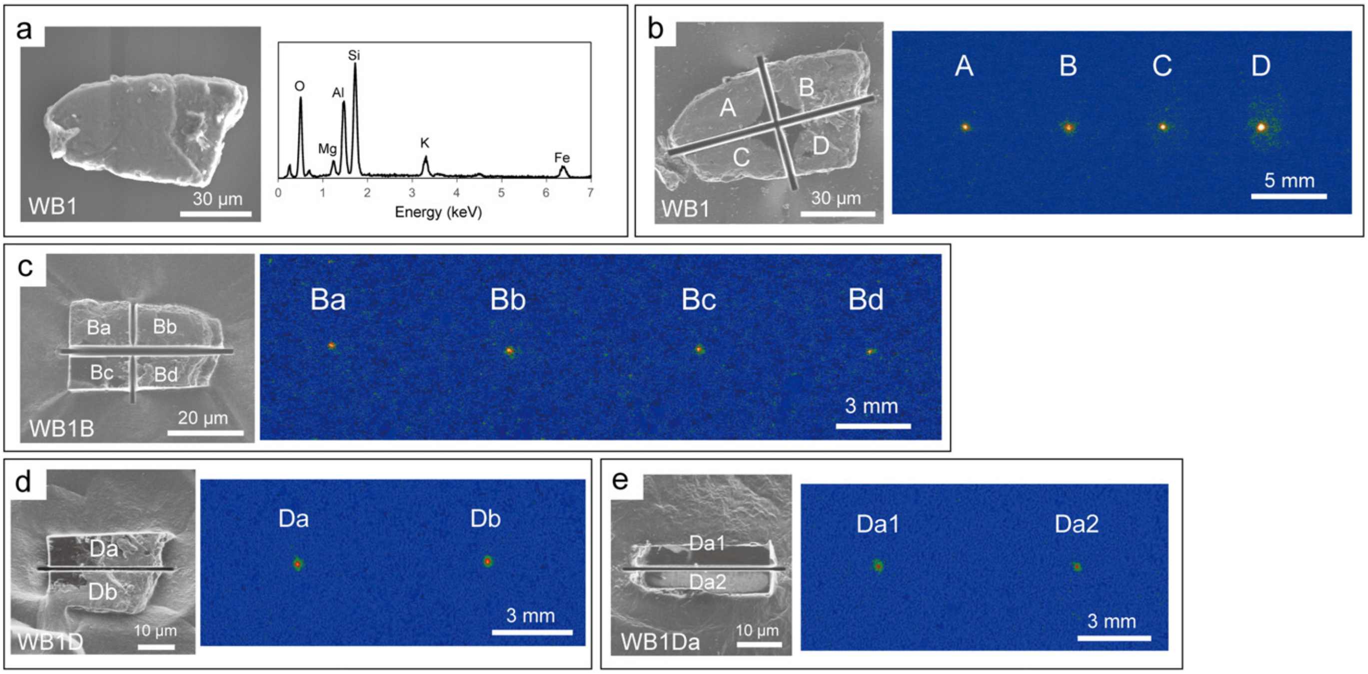

Fig. 1. Exploring cesium (Cs) distribution in a weathered biotite, named “WB1”. (a) SEM image and EDS spectrum of the WB1. The platy shape of the particle and the EDS spectrum represent weathered biotite. (b) Scanning ion microscopy (SIM) image of the WB1 divided into four pieces by FIB, and read-out imaging plate (IP) image from the divided pieces. Each of the divided pieces (WB1A–D) was relocated by micro-manipulator. (c) SIM image of the WB1B divided into small four pieces (WB1Ba–Bd), and read-out IP image from the small pieces. (d) SIM image of the WB1D divided into two pieces (WB1Da and Db), and read-out IP image from the two pieces. (e) SIM image of the WB1Da subdivided into two small pieces (WB1Da1 and Da2), and read-out IP image of the small pieces. The side facet of the WB1Da was turned up and divided along the cleavage plane.