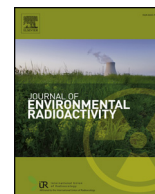


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Cesium desorption behavior of weathered biotite in Fukushima considering the actual radioactive contamination level of soils



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ABSTRACT

For the better understanding of radioactive contamination in Fukushima Prefecture at present and in future, Cs desorption experiments have been conducted mainly using weathered biotite (WB) collected from Fukushima Prefecture and considering the actual contamination level ($\sim 10^{-10}$ wt%) of radiocesium in Fukushima Prefecture. In the experiments, ^{137}Cs sorbed to WB by immersing in ^{137}Cs solution for one day was mostly desorbed by solutions of 1 M NaNO_3 , 1 M LiNO_3 , 10^{-1} M HCl , and 10^{-1} M HNO_3 , although it was barely desorbed by 1 M KNO_3 , 1 M CsNO_3 , 1 M NH_4NO_3 , and natural seawater. X-ray diffraction analysis of WB after immersing in these solutions suggested that the collapse of the hydrated interlayers in WB suppressed the desorption of Cs. On the other hand, ^{137}Cs was barely desorbed from WB even by the treatments with solutions of NaNO_3 and LiNO_3 if the duration for the sorption was longer than approximately two weeks, as well as radioactive WB collected from actual contaminated soils in Fukushima Prefecture. This result implies that Cs sorbed in WB became more strongly fixed with time. Probably removal of radiocesium sorbed in weathered granitic soil at Fukushima Prefecture is difficult by any electrolyte solutions, as more than seven years have passed since the accident.

1. Introduction

The accident at Fukushima Dai-ichi Nuclear Power Plant on March 2011 caused the release of various radionuclides into the environment (Masson et al., 2011; Yoshida and Kanda, 2012). Of these, radiocesium, particularly ^{137}Cs , is currently the major source of the high air dose rate in Fukushima Prefecture due to its abundance and long half-life (30.2 years). It is thus important to understand correctly the dynamic state and/or fate of radiocesium in the natural environment. Regional dynamics of radiocesium have been traced by monitoring the air dose rate and numerical simulations (Chino et al., 2011; Yasunari et al., 2011; Yoshida and Takahashi, 2012; Morino et al., 2013). Although radiocesium released to the atmosphere was partly discharged into the ocean (Estournel et al., 2012; Tsumune et al., 2012), it was deposited onto the ground and strongly retained by clay minerals within the soil (Tanaka et al., 2012; Saito et al., 2014). However, in spite of the intense air dose rate, actual atomic concentration of radiocesium in contaminated soil is extremely low (Yoshida and Takahashi, 2012), which prevents the use

of microscopic analysis in elucidating the precise state of radiocesium within the soil.

It is considered that natural phenomena, such as rainfall and wind action, possibly transfer radiocesium-sorbing particles into rivers; these are then further carried to the ocean, in particular, during heavy rain events (Nagao et al., 2013; Minoura et al., 2014). Previous studies reported that an increase in salinity influences the behavior of elements sorbed onto particles (Li et al., 1984). Hence, it was suggested that radiocesium is desorbed from the particles in areas around the sea coast (Patel et al., 1978; Olsen et al., 1981). Since the nuclear accident in 2011, the concentration of radiocesium has been monitored within the Tohoku region in Japan. For instance, in the Abukuma River estuary (a large river in Fukushima Prefecture), an increase in the concentration of dissolved radiocesium has been reported (Sakaguchi et al., 2015; Kakehi et al., 2016). A study using contaminated sediments collected from the rivers around Fukushima Prefecture indicated that the desorption of radiocesium from soil particles is influenced by both the mineral composition and water flux from the river to coastal areas (Takata

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et al., 2015). In addition, it was suggested that competing ions in the environment affect the sorption of Cs to minerals (Staunton and Roubaud, 1997). It was proposed that at a low concentration of Cs ($< 1.0 \times 10^{-6}$ M), Cs sorption to minerals is unaffected by Na^+ or H^+ but reduced by a high concentration of K^+ (Fuller et al., 2014).

Abalom et al. (1995, 1999) suggested that the bioavailability and environmental mobility of radiocesium decline with time elapsed after deposition in the soil. This is known as the “aging effect”, and this phenomenon was observed in various plants and contaminated soil in the studies of the accident at the Chernobyl Nuclear Power Plant in 1986 (Rigol et al., 1999; Roig et al., 2007). Experimental studies also reported that the soil-to-plant transfer factor and extractability by NH_4^+ gradually declines after the deposition of Cs (Evans et al., 1983; Takeda et al., 2013). In addition, it was suggested that the rate of the decline is dependent on the soil type (Takeda et al., 2013). Furthermore, a Cs sorption/desorption experiment using illite has suggested that sorbed Cs slowly migrates into unexchangeable sites (Comans et al., 1991).

Several studies suggested that micaceous minerals sorb Cs with high selectivity (Sawhney, 1970, 1972; Francis and Brinkley, 1976; Evans et al., 1983; Komarneni and Roy, 1988; Zachara et al., 2002). The Cs sorption behavior of micaceous minerals follows a Freundlich isotherm and such minerals contain several types of Cs sorption sites (Staunton and Roubaud, 1997). At low concentrations, the frayed edge sites (FES) that form around the edge of the micaceous minerals due to weathering, are suggested to dominantly sorb Cs with a high affinity. FES are predominantly accessible by cations with a low hydration energy, such as Cs^+ , K^+ , and NH_4^+ (Sawhney, 1970, 1972). In addition, it was proposed that the wedge-like interlayer zones between the mica and Al-hydroxyl interlayered vermiculite (HIV) are sites with a similar high-affinity (Goto et al., 2014; Zaunbrecher et al., 2015). These sites are formed in the partial transformation of mica to HIV by weathering (Harris et al., 1992; Maes et al., 1999).

Although particular attention was focused on illite as a Cs-sorbent (Brouwer et al., 1983; Comans et al., 1991; Comans and Hockley, 1992; Staunton and Roubaud, 1997; Zachara et al., 2002; Fuller et al., 2015), analyses of actual contaminated soils in Fukushima Prefecture indicated that weathered biotite (WB), or partially vermiculitized biotite, is a dominant mineral species forming radioactive soil particles (Mukai et al., 2014, 2016a). A study of contaminated sediments at the Hanford site in eastern Washington, USA, also reported that minerals similar to WB are responsible for retaining radiocesium (McKinley et al., 2001). In addition, weathered micaceous minerals are also known to sorb Cs efficiently (Komarneni and Roy, 1988). A sorption experiment with very low ^{137}Cs concentrations which considered the actual contaminated level in Fukushima Prefecture, indicated that WB is superior in sorbing Cs to other clay minerals coexisting in the solution (Mukai et al., 2016b). As weathered granitic soil with abundant WB is common in the Fukushima Prefecture (Endo and Kimiya, 1987; Kamei et al., 2003), these studies suggest that WB plays a crucial role in determining the behavior of radiocesium in the environment.

In this study, we have conducted a desorption experiments of Cs from weathered biotite (WB). Compared to previous studies (Morimoto et al., 2012; Tamura et al., 2015; Yin et al., 2016, 2017), we used actual WB collected from the contaminated area in Fukushima Prefecture, and radiocesium concentration comparable to that in the radioactive WB particles in Fukushima Prefecture. We believe that such differences are important because Cs desorption behavior must be strongly influenced by the types of the sorption sites in minerals, which can differ among the micaceous minerals and depend on the amount of sorbed Cs (e.g. Cornell, 1993). This work can be expected to provide data intimately associated to the actual sorption state of radiocesium in Fukushima Prefecture.

2. Methods

2.1. Preparation of radiocesium-sorbing mineral samples

WB was collected from an outcrop of weathered granitic body in Ono-town, Fukushima Prefecture, Japan. Electron microprobe X-ray analysis determined the average chemical composition as $(\text{K}_{0.49}\text{Ca}_{0.03}\text{Na}_{0.01})(\text{Fe}_{0.02}^{2+}\text{Fe}_{0.85}^{3+}\text{Mg}_{0.83}\text{Al}_{0.60}\text{Ti}_{0.13}\text{Mn}_{0.01})(\text{Al}_{1.14}\text{Si}_{2.86})\text{O}_{10}(\text{OH})_{1.95}\text{F}_{0.04}\text{Cl}_{0.01}$. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio was determined by Mössbauer spectroscopy. Compared to the chemical composition of fresh biotite collected from Ono-town (Kikuchi et al., 2015), depletion of K and oxidation of Fe are distinct. Ferruginous smectite, SWa-1 (from source clay minerals of the Clay Mineral Society), was selected for experimental use as another mineral species because it sorbs Cs better than other clay minerals but not as effectively as WB (Mukai et al., 2016b).

Based on the method of Mukai et al. (2016b) the samples of WB and SWa-1 sorbing ^{137}Cs were prepared and their radioactivity was examined. The minerals were firstly crushed and sieved to 25–53 μm in size. For each sample, considering the variability, four particles were placed at 2 mm intervals on acrylic substrate with Kapton double stick tape using vacuum tweezers attached to a micro-manipulator (Quick Pro, Micro Support Co., Ltd.). The solutions of ^{137}Cs (3.7 MBq mL^{-1} nominal, Eckert & Ziegler Isotope Products, California, USA) was diluted to 50 Bq mL^{-1} (1.1×10^{-11} M) for WB and 125 Bq mL^{-1} (2.8×10^{-11} M) for SWa-1 using reverse osmosis water, and 50 μl of solution was dropped onto the substrates. The samples were immersed in solutions of ^{137}Cs for 24 h, 168 h, 336 h, or 672 h as a normal condition. During the immersions, the acrylic substrates on which the mineral particles were placed were enclosed in a styrol box to avoid desiccation.

Radioactive WB particles, which sorbed radiocesium through the accident, were collected from contaminated soil sampled more than two years after the accident (in 2013) in the field at Iitate village, located 30 km northwest of the Fukushima Dai-ichi Nuclear Power Plant, as described in Mukai et al. (2014).

Acrylic substrates containing these radioactive mineral particles were intimately contacted to IPs (BAS-MS, Fuji Film) for 24 h. IPs were scanned with an IP reader (FLA-7000, Fuji Film), and the radioactivity of each mineral particle was then estimated from the intensity of the IP signal calibrated using “standard” WB particles from Fukushima Prefecture, whose radioactivity was measured using a germanium γ -ray spectrometer.

2.2. Radiocesium desorption experiments

Solutions for desorption experiments of prepared radioactive samples were summarized in Table 1. Natural seawater and related electrolyte solutions were prepared for desorption experiments. In consideration of the salt concentration of natural seawater, the related electrolyte solutions were 4.7×10^{-1} M NaCl, 4.7×10^{-1} M NaCl + 3.5×10^{-2} M MgCl_2 + 1.8×10^{-2} M MgSO_4 , 4.7×10^{-1} M NaCl + 10^{-2} M CaSO_4 , and 4.7×10^{-1} M NaCl + 10^{-2} M KCl. To investigate the effect of K^+ , the radioactive mineral samples were treated with mixed solutions of 10^{-5} M to 1 M KCl + 1 M NaCl, and radioactive samples were also reacted with solutions of 10^{-5} M to 1 M KCl and 10^{-5} M to 1 M NaCl.

The volume of solutions prepared for desorption experiments was commonly 50 μl . The samples were reacted with the electrolyte solutions and natural seawater for 1 h, 24 h, or 168 h. During the reactions, the samples were enclosed in a styrol box. After each ^{137}Cs sorption/desorption treatment, solutions were gently flushed with reverse osmosis water, and substrates dried at ambient conditions. Changes in radioactivity of mineral particles were estimated using IP autoradiography prior to and following desorption treatments. An example of the procedure used in obtaining measurements of ^{137}Cs desorption

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