

Chapter 1

Nuclear Magnetic Resonance Study of Cs Adsorption onto Clay Minerals

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Abstract The release of radioactive cesium into the environment in the aftermath of disasters such as the Fukushima Daiichi disaster poses a great health risk, particularly since cesium easily spreads in nature. In this context, we perform solid-state nuclear magnetic resonance (NMR) experiments to study Cs^+ ions adsorbed by clay minerals to analyze their local structure. The NMR spectra show two kinds of peaks corresponding to the clays (illite and kaolinite) after immersion in CsCl aqueous solution; the peak at -30 ppm is assigned to Cs^+ on the clay surface while that at -100 ppm is assigned to Cs^+ in the silicate sheet in the clay crystal. This result is consistent with the fact that Cs^+ with smaller coordination number yields a small field shift in the NMR spectra. Moreover, after immersion in KCl aqueous solution, these peaks disappear in the NMR spectra, thereby indicating that our assignment is reasonable. This is because Cs^+ on the clay surface and in the silicate sheet is easily subject to ion exchange by K^+ . We believe that our findings will contribute to a better understanding of the pathway through which Cs transfers from the soil to plants and also to the recovery of the agriculture in Fukushima.

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1.1 Introduction

The occurrence of the Tohoku earthquake on March 11, 2011, led to the meltdown of the Fukushima Daiichi Nuclear Power Station in Japan. The accident released several kinds of radioactive elements such as ^{90}Sr , ^{134}Cs , ^{137}Cs , and ^{131}I into the environment. Human exposure to ^{137}Cs is a health risk because of its long half-life [1]. The element ^{137}Cs is mostly stabilized in the soil while small quantities are absorbed by plants such as rice [2]. In this manner, ^{137}Cs seeps into the food chain, leading to its internal exposure in humans and animals. In order to avoid internal exposure, it is important to understand the mechanism underlying its transfer from the soil to plants. Recently, it has been reported that the Cs transfer coefficient exhibits variation even for plants grown in soils with similar levels of radioactivity [3, 4]. Moreover, artificially added ^{137}Cs can be more easily absorbed by plants than stable Cs in the soil [5]. Thus, we have considered that one of the reasons for this phenomenon is the varied ways in which Cs (i.e., different Cs states) is adsorbed onto clay minerals in the soils.

The clay minerals that stabilize Cs include 1:1-type layer silicates and 2:1-type layer silicates [6]. These silicates stabilize Cs on the surface and silicate sheets because of their negative charges. In particular, in the case of 2:1-type layer silicates, Cs is strongly adsorbed at frayed edge sites (FESs) [7–10]. In this context, it is necessary to understand the stabilization mechanism to analyze the structure of Cs in the clay surface, silicate sheet, and FESs.

The concentration of Cs in the environment is of the order of parts per billion (ppb) or parts per trillion (ppt). Thus, very fine measurement techniques are required to measure such minute quantities and obtain their structural information. The technique of X-ray absorption fine structure (XAFS) spectroscopy is suitable for such measurements [11, 12]. However, the technique of XAFS requires synchrotron radiation, and hence, the method cannot be used in the laboratory. Therefore, another complementary method is required.

In this context, solid-state nuclear magnetic resonance (NMR) has been used to analyze the local structure of Cs in crystals and conventional glasses [13]. As regards the NMR spectra of cesium silicate crystals, Cs^+ ions with large coordination numbers (CNs) such as $\text{Cs}_6\text{Si}_{10}\text{O}_{23}$ exhibit a large field shift while those with smaller CNs ($\text{Cs}_2\text{Si}_2\text{O}_5$) exhibit a small field shift. In addition, the same relationship also holds for Cs present in mixed alkali silicate glasses. This relationship can be used to study the local structure of Cs in clay minerals. Moreover, solid-state NMR of clay minerals can be utilized to distinguish Cs on the surface and within silicate sheets [14–17]. In this study, we discuss the structure of Cs adsorbed onto two kinds of clay minerals (kaolinite as 1:1-type layer silicates and illite as 1:2-type layer silicates) by using solid state NMR together with XAFS spectroscopy.

1.2 Experimental

1.2.1 Sample Preparation

Kaolinite (Wako Chemicals), illite (G-O networks), $^{133}\text{CsCl}$ (Wako Chemicals), KCl (Wako Chemicals), and ultrapure water (Wako Chemicals) were used as received in our experiments. First, 5 g of illite was immersed in 50 mL of 0.01 M CsCl aqueous solution over time periods of 1 day, 1 month, 6 months, and 2 years. After immersion, the illite samples were separated by centrifugation. Next, 50 mL of ultrapure water was added to each illite sample followed by centrifugal separation. This washing process was performed twice. After washing, the illites were dried overnight at 40 °C. We referred to the various samples as illite_1d, illite_1m, illite_6m, and illite_2y depending on their immersion periods of 1 day, 1 month, 6 months, and 2 years, respectively. For comparison purposes, kaolinite was also immersed in 50 mL of 0.01 M CsCl aqueous solution over 1 day, 1 month, and 6 months. The kaolinites were also washed using the abovementioned washing process. Following the nomenclature used for the illite samples, we named the kaolinite samples as kaolinite_1d, kaolinite_1m, and kaolinite_6m.

In order to remove the Cs adsorbed onto illite, 1 g of the sample illites_2y was immersed in 50 mL of 0.01 KCl aqueous solution for 2 h and 2 days. These illites were also washed as per the abovementioned washing process. These “re-ion-exchanged” samples were referred to as illite_2y_KCl2h and illite_2y_KCl2d.

Further, pristine samples of illite and kaolinite were also analyzed. Table 1.1 lists all the analyzed samples along with the corresponding experimental conditions.

Table 1.1 Sample notations of clay minerals used in this study

Notation	Period of immersion in CsCl(aq)	Period of immersion in KCl(aq) after immersion in CsCl(aq)
illite_pristine	–	–
illite_1d	1 day	–
illite_6m	6 months	–
illite_2y	2 years	–
illite_2y_KCl2h	2 years	2 h
illite_2y_KCl2d	2 years	2 days
kaolinite_pristine	–	–
kaolinite_1d	1 day	–
kaolinite_6m	6 months	–

1.3 Structure Analyses

The crystal structures were analyzed by powder X-ray diffraction (XRD) (RINT 2100, RIGAKU). We used a Cu X-ray source that was operated at 40 kV and 40 mA via the conventional $2\theta/\theta$ method. The diffractions were acquired at intervals of 0.02° . The extended X-ray absorption fine structure (EXAFS) spectra were obtained at the cesium K-absorption edge via the fluorescence method (BL14B2, SPring-8). The cumulated number of measurements was 40. The XAFS spectra were analyzed by using ATHENA [18].

The solid-state ^{133}Cs NMR spectra of all the samples were acquired using a Chemagnetics CMX400 spectrometer utilizing a commercial probe (4 mm). The rotation speed was set to 10 kHz with an accuracy ± 10 Hz. At an external field of 9.4 T, the resonance frequency was set to about 103.7 MHz. For each measurement, the widths of the 90° pulses were set to 2.2 μs . The spectra were obtained with a cycle time of 10 s. The chemical shift reference was 1 mol/L CsCl aqueous solution, whose chemical shifts were set to 0 ppm.

1.4 Results

Figure 1.1 shows the XRD patterns of the illite_pristine, illite_6m, kaolinite_pristine, and kaolinite_6m samples. In the case of illite, the peak around 27° shows a shift to a higher angle after immersion in CsCl, thereby indicating a decrease in the lattice constant. On the other hand, for kaolinite, the peak around 27° shifts to a lower angle, which indicates an increase in the lattice constant.

Figure 1.2 shows k^2 -weighted K-edge EXAFS spectra for the illite_2y and illite_2y_KCl2h samples. As previously reported for the radial distribution functions (RDFs), the first, second, and third peaks can be assigned to Cs–O, Cs–Si, and Cs–Cs, respectively [19, 20]. However, we have not obtained the RDF in the present stage. We can just note that there is a little change in EXAFS spectra for the illite_2y and illite_2y_KCl2h samples.

Figure 1.3 shows the ^{133}Cs NMR spectra of the illite and kaolinite samples after immersion in CsCl solution. The NMR spectra for all the illites exhibit peaks at around -30 and -100 ppm. On the other hand, the NMR spectra for kaolinite_1d and _1m exhibit only one peak at around -30 ppm. The kaolinite_6m sample (which was immersed for a longer time) exhibits a clear peak at around -30 ppm and a small peak at around -100 ppm.

The effect of re-ion-exchanging by K^+ on the NMR spectra was also studied (Fig. 1.4). The NMR peak for illite_2y_KCl2d vanished, although the peak at around -30 ppm was still observed for illite_2y_KCl2h.

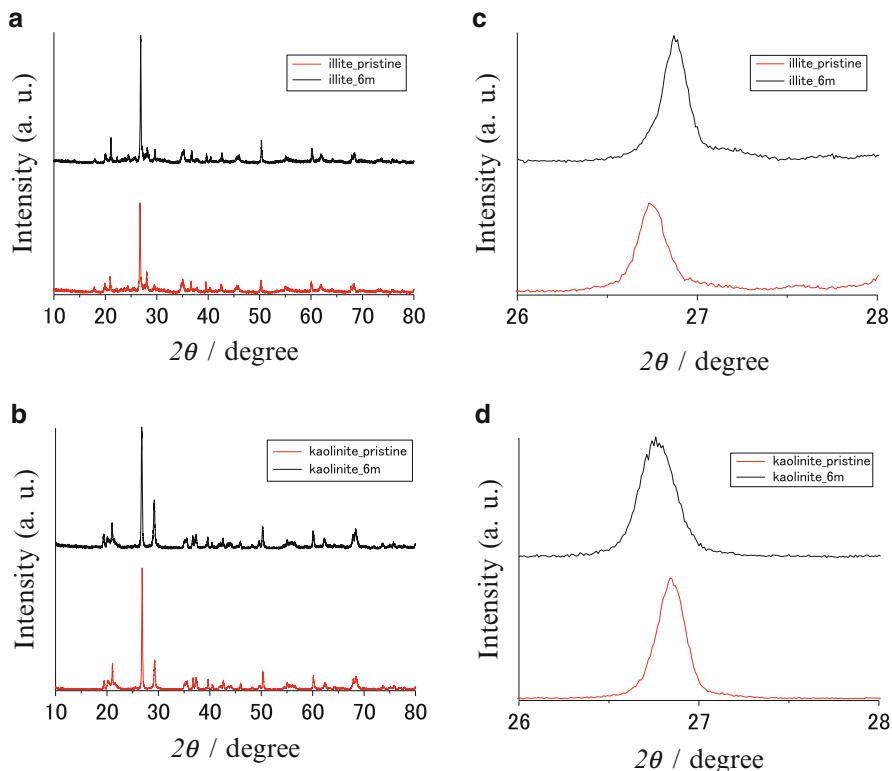


Fig. 1.1 XRD patterns of illite (a) as received and after immersion in KCl solution, (b) kaolinite as received and after immersion in KCl solution. Highest peaks around 27° assigned to (0 0 6) are also shown as (c) and (d)

1.5 Discussion

After sample immersion in CsCl solution, the lattice constant change for illite is different from that for kaolinite, as shown in Fig. 1.1; the lattice constant of illite decreases, while that of kaolinite increases. This is because hydrated K^+ in the silicate sheet is replaced by Cs^+ in illite; on the other hand, in the case of kaolinite, a proton is replaced by Cs^+ . Alteration in the k^2 -weighted K-edge EXAFS spectra for illite after immersion in CsCl solution as shown in Fig. 1.2 may support these observations.

As shown in Fig. 1.3, the NMR spectra of illite exhibit two peaks at -30 and -100 ppm, while those of kaolinite exhibit two peaks (one clear peak and one very small peak at -30 and -100 ppm, respectively). Kaolinite has a negative surface charge on the crystallite. Accordingly, the clear peak at -30 ppm can be assigned to the surface Cs^+ . In contrast, illite has a negative charge between silicate sheets. As a result, the peaks at -100 ppm can be assigned to Cs^+ in the silicate sheets.

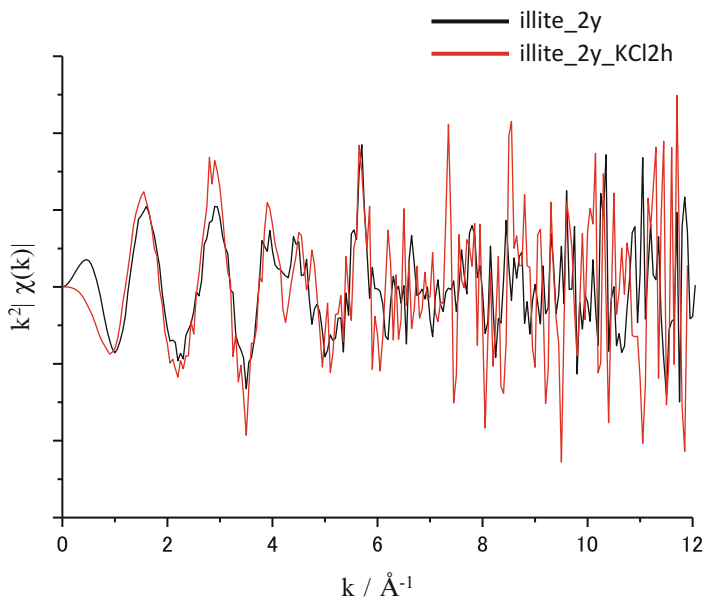


Fig. 1.2 k^2 -weighted K-edge EXAFS spectra for illite_2y and illite_2y_KCl2h

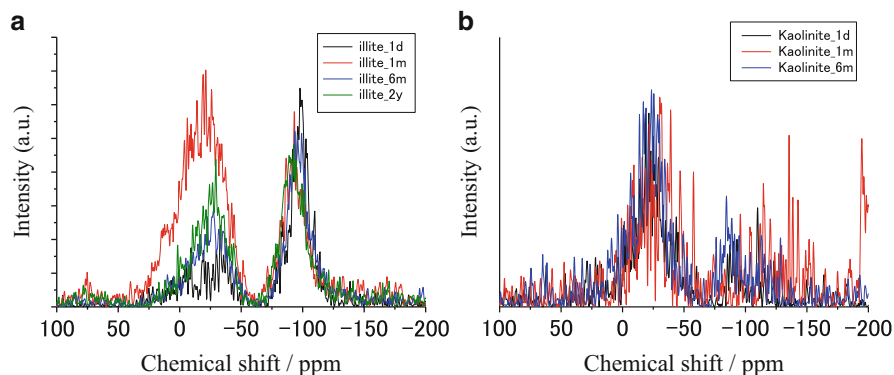


Fig. 1.3 NMR spectra of clays immersed in CsCl aqueous solution for several periods (a) illite, (b) kaolinite. The chemical shift reference is CsCl (aq)

These assignments agree well with the results of previous NMR experiments; Cs^+ with larger CN values exhibits a large field shift, while that with smaller CN values exhibits a small field shift [13]. In another NMR experiment, there also existed two kinds of peaks for illite immersed in CsCl [14]. These results also support our assignment.

After re-ion-exchange (using KCl) over a relatively long period (2 days) for illite (Fig. 1.4), no peak was observed in the NMR spectrum, thereby indicating that all

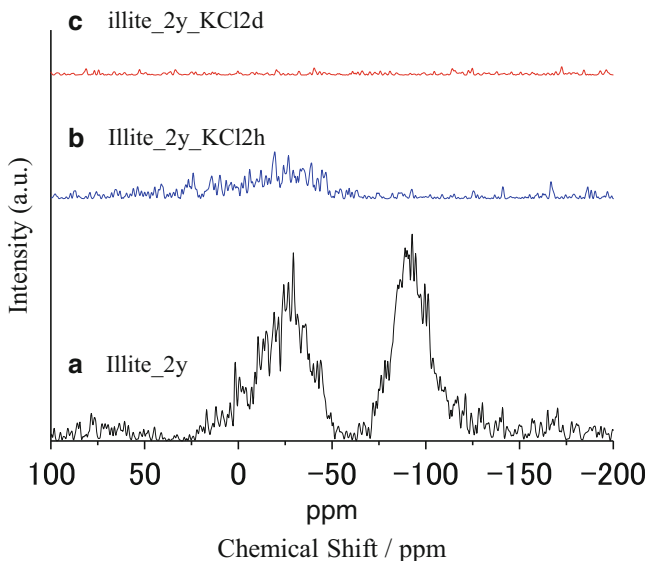


Fig. 1.4 NMR spectra of illite (a) immersion in CsCl solution for 2 years, (b) ion-exchanged illite by immersion in KCl for 2 h, (c) ion-exchanged illite by immersion in KCl for 2 days. The chemical shift reference is CsCl (aq)

the Cs^+ ions on the surface and in the silicate sheet had been replaced by K^+ . This result supports our assignment because Cs^+ on the clay surface and in the silicate sheet is easily ion-exchanged by K^+ [6]. This result also indicates that no FESs were observed in this experiment. One of the reasons for the absence of the FES signature is the low concentration of the total amount of Cs^+ . After re-ion-exchange for a short period of time (2 h), we observed only one peak at -30 ppm. This result can be attributed to the fact that Cs^+ in the silicate sheet is more easily replaced by K^+ than that on the surface.

In conclusion, solid-state ^{133}Cs NMR is useful for analyzing Cs^+ adsorbed onto clay minerals; this method can be used to distinguish Cs^+ sites in the clay minerals. In the near future, we plan to perform structure analysis of Cs^+ in soil in order to understand the mechanism of transfer of Cs from the soil to plants. We believe that this study will contribute to the recovery of agriculture in Fukushima in the near future.

1.6 Conclusions

We performed ^{133}Cs NMR experiments in conjunction with XRD and EXAFS to analyze the adsorption of Cs^+ onto clay minerals such as illite and kaolinite. Our NMR results indicate that the observed peaks at -30 and -100 ppm can be assigned

to Cs⁺ on the surface and in the silicate sheet, respectively. After re-ion-exchange by using aqueous KCl, the Cs⁺ ions were replaced by K⁺ ions. We believe that our findings will contribute to a better understanding of the mechanism of Cs transfers from the soil to plants. We plan to use the NMR method in our future studies on understanding of the mechanism of transfer of Cs⁺ from the soil to plants.

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