Identification of Multiple Cs^+ Adsorption Sites in a Hydroxyl Interlayered Vermiculite-like Layered Silicate through ^{133}Cs MAS NMR Analysis

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^{133}Cs magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy revealed two Cs sites in Cs-adsorbed aluminium altered phlogopite (Cs Al-Phl), but only one site for Cs-adsorbed magnesium altered phlogopite (Cs Mg-Phl). Cesium ions in hydroxyl interlayered vermiculite-like layered silicate reside at sites in both mica zones and in interlayer wedge zones of Al-Phl. It is likely that chemical exchange of Cs^+ ions occurs between these two zones.

The accident at the Fukushima-Daiichi nuclear power plant in March 2011 released a significant amount of radionuclides, including cesium radioisotopes ^{134}Cs and ^{137}Cs. The highest contamination level of the radioactive cesium in soils and sediments in Fukushima was reported to be several tens to hundreds of kBq/kg.[1,2] These levels correspond to concentrations of 10^{-12} to 10^{-10} mol/kg of ^{134}Cs or ^{137}Cs. Even now, radioactive cesium at low concentrations is the major source of radiation in the Fukushima area because Cs is strongly adsorbed into the interlayer spaces of soil clays. After the accident, many researchers suggested that clay minerals, especially vermiculite-like minerals, are important for sorption and retention of Cs in the soil.[3-6]

Natural vermiculite formed by weathering of biotite or phlogopite (Phl) has an interstratified structure consisting of anhydrous layers containing potassium ions and hydrous layers containing magnesium ions. Previous studies have determined that artificially modified phlogopites by topotactic reactions showed controllable adsorption capabilities.[5] In particular, phlogopite samples altered with hydrated ions such as Na^+, Mg^{2+}, and Ca^{2+}, denoted by Na-Phl, Mg-Phl, and Ca-Phl, exhibited the same high Cs^+-adsorption capacity and Langmuir type adsorption as natural vermiculite. Thus, artificially modified phlogopites saturated with hydrated ions have the potential for increasing the Cs adsorption capacity.

On the other hand, studies have shown that phlogopite altered with hydrated Al^{3+}, (Al-Phl), formed hydroxyl interlayered vermiculite (HIV)-like structures, which exhibited wedge zones with partially enlarged interlayer spacings, typical of natural vermiculite. The Al^{3+} in these Al-Phl structures underwent minimal replacement with Cs^+ ions, but the Al-Phl exhibited high partition coefficients (K_d) at lower Cs concentrations, indicating significant selectivity for Cs.[5,7] When remnant mica transforms to vermiculite, the wedges in the silicate interlayers are splayed. These vermiculite interlayer wedges have been considered equivalent to those frayed edges of less thoroughly weathered mica particles, and should be similarly selective for large-ion alkali metals such as Cs^+ (Figure 1). Because sorption and retention of cesium radioisotopes in soil is such a catastrophic problem in Japan, it is important to understand the diverse mechanisms by which hydroxylated aluminium in the interlayers may trigger adsorption of Cs^+ ions.

In this study, we investigated the local structure of Cs Mg-Phl and Cs Al-Phl using ^{133}Cs magic angle spinning nuclear magnetic resonance (MAS NMR) measurements. Solid-state NMR spectroscopy is a powerful method for elucidating the local structure of measured ions in solids.[8-12] Among a number of Cs-adsorbed clays, it is reported that Cs-adsorbed vermiculite and a weathered synthetic F-rich phlogopite differ from others in ^{133}Cs MAS NMR results due to the dehydrated Cs^+ ions in interlayer sites.[8-10]

Hydrothermal treatment of phlogopite was conducted according to a procedure detailed in a previous publication,[5] and Cs-adsorbed Mg-Phl and Al-Phl were also obtained. The chemical compositions of Mg-Phl and Al-Phl were $(K_{0.52}Mg_{0.17}Na_{0.01}Ca_{0.01})(Mg_{2.6}Fe_{0.45}Ti_{0.01})(Al_{0.91}Si_{3.06})O_{10}(F_{0.11},OH_{1.89})$ and $(K_{0.59}Na_{0.01}Al_{0.14})(Mg_{2.54}Fe_{0.43}Ti_{0.01})(Al_{0.91}Si_{3.07})O_{10}(F_{0.11},OH_{1.89})$, and their cation exchange capacity (CEC, the amounts of the interlayer cations including K^+ ions) estimated by the IPC data are 213 and 234 meq/100g, respectively. The uptakes of Cs^+ were determined using aqueous solutions containing 7.5 mmol L^{-1} CsCl (equivalent to 1000 ppm Cs, which is equal to ca. 35% CEC). The adsorption amount of Cs into Al-Phl was 0.099 mmol/g (Table S1). Moreover, in order to clarify the Cs^+ absorption stability of the material, it was important that Cs^+ ions bound in Al-Phl were removed through ion-exchange with Mg^{2+} ions. The desorption treatments described in the work by Morimoto et al.[13] were applied to the samples.

^{133}Cs MAS NMR measurements were made with a JEOL ECA800 spectrometer of 18.8T. The Larmor

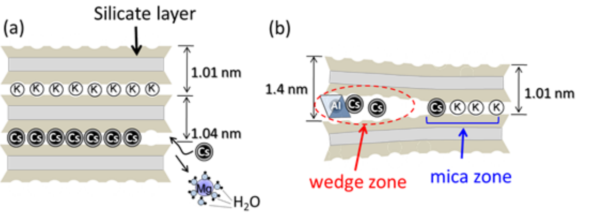

Figure 1. Conceptual view in cross-section of interlayers: (a) Cs^+-adsorption into Mg-Phl and (b) Cs^+-adsorption into the hydroxylated interlayers (wedge zone and mica zone) of Al-Phl.

frequency for ^{133}Cs corresponds to 105 MHz, using a 3.2 mm diameter single-tune MAS probe operated at room humidity and temperature. The spinning rate of the rotor was set to ca. 20 kHz. Spectra were obtained using a single-pulse experiment with a typical pulse width of 0.5 μs, which corresponds to the ca. π/8 rf tip pulse angle of the liquid standard. The π/2 pulse length was 2.3 μs. Chemical shifts were referenced to 1.0 M aqueous solutions of CsCl. Each scan was accumulated at a repetition time of 0.5 s. For Cs Al-Phl, the nutation experiment[8] at a repetition time of 0.1 s was executed at room humidity and temperature, as was the spin-lattice relaxation time, T_1, measurement by saturation recovery method[14] of ^{133}Cs.

Figure 2 shows XRD patterns obtained for the Mg-Phl and the Al-Phl, following exposure to the Cs^+ solution. In the case of Mg-Phl (Figure 2a), the peaks of 2.4, 1.42 and 1.19 nm essentially disappeared after treatment with Cs^+ solutions at 1000 ppm (representing an aqueous 7.5 mmol L^{-1} CsCl solution). The disappearance of those peaks for Mg-Phl can be explained by the transition from vermiculite-like layers (which are hydrated layers) to Cs^+-substituted layers with ion exchange between hydrated Mg^{2+} and dehydrated Cs^+. This is consistent with the previous sorption experiment, which showed an approximately equivalent relationship between the quantities of adsorbed Cs^+ ions and desorbed Mg^{2+} ions. In contrast, the XRD patterns of the Al-Phl samples exhibit a reduction in the intensity of the 1.41 nm peak, with no other major changes (Figure 2b). This suggests that interlayer aluminium ions partially transfer to hydroxyl-Al interlayers during hydrothermal treatment and cannot be easily exchanged with Cs^+ ions.

Figure 3 shows the spectra of ^{133}Cs MAS NMR measurements for Cs Mg-Phl, Cs Al-Phl, and Cs-desorbed Al-Phl. Only one simple broad peak with large spinning sidebands was observed for Cs Mg-Phl at 41 ppm (Figure 3a). In contrast, the broad peak for Cs Al-Phl (Figure 3b) at 43ppm is joined by a shoulder peak at 1 ppm, and large spinning sidebands are also observed. Next, to clarify the adsorption site of Cs, the sample was treated with 3M $MgNO_3$ solution to initiate desorption. For Cs-desorbed Al-Phl, a more pronounced split at 53 and -15 ppm was observed, along with equally reduced signals compared to Cs Al-Phl (Figure 3c).

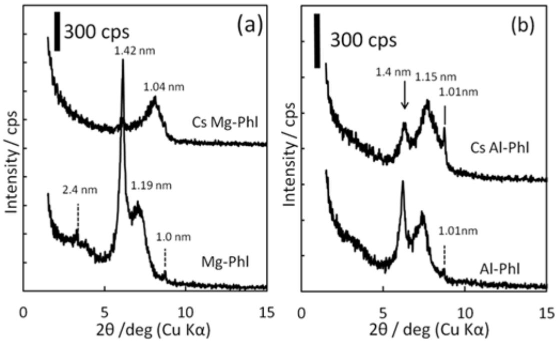

Figure 2. XRD patterns of (a) Mg-Phl and (b) Al-Phl before (bottom) and after (top) treatment with aqueous solutions containing 7.5 mmol L^{-1} CsCl.

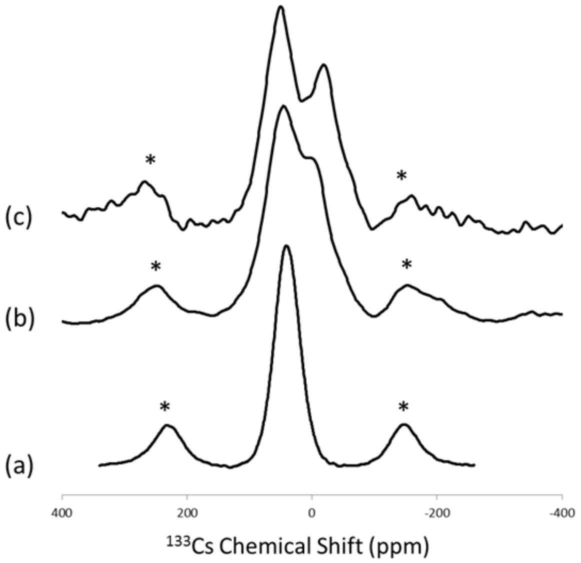

Figure 3. ^{133}Cs MAS NMR spectra of (a) Cs Mg-Phl, (b) Cs Al-Phl, and (c) Cs-desorbed Al-Phl. Here, the scans were accumulated 10,000, 300,000, and 300,000 times, respectively. Spinning sidebands are marked by asterisks *.

For Cs Mg-Phl, the observation of just one peak is reasonable because of the simple layer structure. This broad peak with large spinning sidebands suggests that the adsorbed anhydrous Cs^+ ions were firmly fixed with basal O atoms in the interlayer, (possibly 9-fold coordination), similar to vermiculite and weathered synthetic F-rich phlogopite.[8-10] There is a slight change in the position of the peak at 41 ppm for Cs Mg-Phl compared to the peaks of both vermiculite at 55.1 or 60 ppm and weathered synthetic F-rich phlogopite at 43.1 ppm. However, these differences in peak positions are plausible since the ^{133}Cs chemical shift is very sensitive to small changes in local environment because of the many electrons in Cs^+ ions.[9] The main peak at 43 ppm for Cs Al-Phl and the additional shoulder peak at 1 ppm most likely is due to Cs^+ ions in the mica zones and the wedge zones, respectively. The reduced double peaks of Cs-desorbed Al-Phl are also likely due to Cs^+ ions reduction.

Frequently, a broad peak accompanied by a shoulder peak is caused by second order nuclear quadrupole perturbations in which the spin number, I, is more than ½, as in^{133}Cs (I=7/2). To clarify whether the double peaks of Cs Al-Phl corresponded to two sites, the nutation experiment was carried out (Figure 4)[8]. The π/2 length of 2.0 μs, which is similar to 2.3 μs for the liquid standard, is not related to the large quadrupole moment. Therefore, the split signals must be due to two different chemical environments.[8]

The shoulder peaks at 1 ppm for Cs Al-Phl and -15 ppm for Cs-desorbed Al-Phl can be explained by the rapid exchange of Cs^+ ions using the Stern-Gouy model. In the Stern layer, Cs^+ ions are relatively tightly bound to the basal oxygens and in the Gouy diffuse layer, Cs^+ ions are partially hydrated.[8-12] In hectorite, illite, and others, the signals from the Stern layer and Gouy layer merge into a single peak under conditions of fast chemical exchange.[8-12] Due to the wider space in the Al-Phl wedge

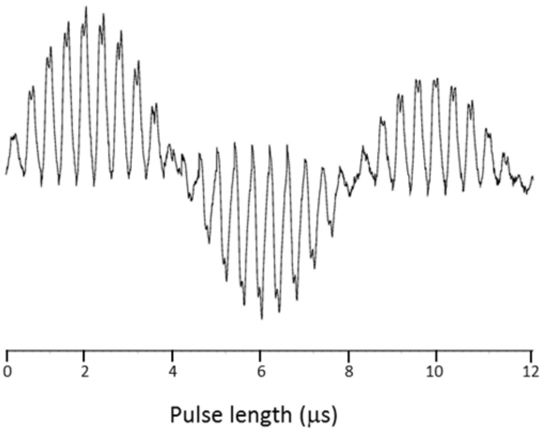

Figure 4. ^{133}Cs signal amplitude dependence of Cs Al-Phl on the tipping pulse length from 0.4 μs to 12 μs in the interval of 0.4 μs.

zones, which act as the Gouy diffuse layer, partial hydration of Cs^+ ions is possible.

The wider split in Cs-desorbed Al-Phl is probably caused by the relatively slow chemical exchange between the remaining Cs^+ ions in Cs-desorbed Al-Phl compared to the exchange that occurred in Cs-adsorbed Al-Phl.[15] ^{133}Cs-T_1 for two sites in Cs Al-Phl was measured and the results were found to be 15 ms at 43 ppm and 17 ms at 1 ppm (Figure S1). Since the apparent T_1 (T_1') values measured by the saturation recovery method at two sites were similar, it can be inferred that the same is true for the chemical exchange occurring in Cs Al-Phl.[16] Moreover, Cs^+ ion reductions in Cs-desorbed Al-Phl is likely a result of the chemical exchange process. To clarify, Figure 1 shows a conceptual view in cross-section of interlayers for Cs Mg-Phl and Cs Al-Phl. For the Mg-Phl, Cs^+ ions are located in the mica zones due to ion exchanges of hydrated Mg^{2+} (Figure 1a). On the other hand, the Al-Phl has wedge zones (Figure 1b) in addition to the mica zones.

For Cs adsorption in Al-Phl, the experimental data agrees with the Freundlich model, indicating surface heterogeneity of the adsorbent.[5] The experimental data fits the calculated regression model well, and the R^2 values of 0.97 indicates the goodness of the fit (Figure S2). When this sample was reacted with hydrated magnesium ions (Mg^{2+}) and desorption occurred, absorbed Cs^+ ions were released from the surface of the Al-Phl, corresponding to approximately half of the adsorption amount (Table S1). This experiment suggests that Cs^+ ions adsorb on two sides of the hydroxylated aluminium interlayers: the base side near hydrated $Al^{3+,}$ and the apex side near the mica zone of the acute isosceles triangle-like wedge zone.[7]

In conclusion, the hydroxyl interlayered vermiculite (HIV)-like structures formed when phlogopite is altered with hydrated Al^{3+} affect the adsorption of Cs^+ ions. Cesium ions in HIV type layered silicate reside at sites not only in mica zones but in interlayer wedge zones of Al-Phl. Moreover, ^{133}Cs NMR results indicate that Cs^+ ions are probably chemically exchanged between these two zones. Therefore, these results can prove useful in designing artificially altered phlogopites which are more suitable than natural vermiculite for Cs decontamination.

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