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Editor's Choice

XRD and HRTEM Evidence for Fixation of Cesium Ions in Vermiculite Clay

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X-ray diffraction and high-resolution transmission electron microscopy showed that cesium ions (Cs^+'s) in a vermiculite clay formed a segregated monoionic layer in the interlayer spaces. Each ion was fixed simultaneously at the centers of hexagonal rings in the upper and lower silicate tetrahedral sheets. No Cs^+ was eluted even when Cs^+–vermiculite was kept at 80 °C for 48 h in the presence of a large excess of $Al(NO_3)_3$ or $[Co(NH_3)_6]Cl_3$.

^{137}Cs is a major radioactive component of high-level nuclear wastes. After the accident in the nuclear power plants at Fukushima last March, it has been widely dispersed in the northern Kanto district of Japan and is thought to be mostly fixed in soils.[1] Accordingly the removal of Cs^+ from soils is an urgent problem for lowering the radioactivity level in that area.

As is well known, Cs^+ is selectively and strongly adsorbed by the phyllosilicate fraction of soils.[2,3] A number of works have been reported on the interactions of Cs^+ with clays and its environmental fate.[4–7] Some of the conceptual models are presented to explain the high affinity of Cs^+ toward clays such as a frayed edge-planar site.[8–10] No evidence, however, has been presented so far concerning its fixed state at an atomic scale. The understanding of the detailed structure of immobilized Cs^+ can be a first step to develop methods of purifying radioactively contaminated soils.

We applied X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) to study the interaction of Cs^+ with a clay. The results gave insight for understanding its extremely high stability.

As a phyllosilicate clay, magnesium vermiculite (product from Transvaal, South Africa: denoted as Mg-Verm)[11] was used (Supporting Information; SI).[21] Its physical and chemical properties have been reported elsewhere.[12] Actually it is the interstratification of almost the same amount of the vermiculite layer with hydrated Mg^{2+} and K^+-mica layer with K^+ at the interlayer spaces, as shown below. This mineral was recently used as an adsorbate to remove Cs^+ in sea water.[13] 1.0 g of Mg-Verm was suspended in 5.0 mL of aqueous solution containing 18, 45, or 100 mmol L^{-1} $CsNO_3$ (denoted as samples (I), (II), and (III), respectively). The suspensions were stirred for 48 h at room temperature. After they were filtrated off, the clay particles were dried and subjected to XRD, FT-IR, and HRTEM. The filtrates were analyzed by ICP measurements. The specimens for HRTEM were prepared according to the method described in our previous work.[14] Clay samples were embedded in epoxy resin, applying pressure so that the (001) planes of the clay fragments were oriented. Then they were sliced perpendicular to the (001) planes, polished mechanically, and thinned to electron transparency by argon ion-milling. Finally the samples were carbon-coated before they were examined by TEM. HRTEM observation was performed at 200 kV using a JEOL JEM-2010UHR electron microscope (Cs: 0.5 mm) with a LaB_6 filament.

Table 1. Metal ions present in the filtrates for Cs^+-Verm, samples (I), (II), and (III) as determined by ICP measurements[a]

	Adsorbed Cs^+ /10^{-5} mol g^{-1}	Eluted Mg^{2+} /10^{-5} mol g^{-1}	Eluted K^+ /10^{-5} mol g^{-1}	Eluted Ca^{2+} /10^{-5} mol g^{-1}
Mg-Verm	0	0.28	0.23	0.18
Sample (I)	9.0	3.20	0.38	0.47
Sample (II)	21.6	10.9	0.73	1.12
Sample (III)	42.0	19.8	1.68	2.04

[a]Maximum errors: 2×10^{-6} mol g^{-1} (Cs^+) and 1×10^{-7} mol g^{-1} (other ions).

Table 1 shows the results of the ICP analyses of the filtrates. For all of the samples, Mg^{2+} ions were eluted on the adsorption of Cs^+ at the molar ratio of ca. Mg:Cs = 1:2. It implied that Cs^+ was adsorbed on vermiculite through the ion-exchange mechanism. Since the amount of eluted K^+ was less than one-tenth of that of Cs^+, the ion-exchanging of Cs^+ took place selectively with Mg^{2+} but not with K^+ under the above treatment. According to the adsorption isotherm obtained by a separate experiment, the maximum adsorbed amount of Cs^+ was 0.61 mmol g^{-1} for this clay (Supporting Information).[21] Therefore, the loading level of Cs^+ ions was calculated to be 15%, 35%, and 70% for samples (I), (II), and (III), respectively.

Figure 1 shows the XRD patterns from Mg-Verm, samples (I), (II), and (III). For Mg-Verm, there were three peaks in the low-angle region. The weak but sharp peak at $2\theta = 6.2°$ (1.4 nm) probably corresponds to packets of vermiculite layers. The intense broad band at $2\theta = 7.4°$ (1.2 nm) is interpreted as the interstratification of the vermiculite layer (1.4 nm) and K^+-mica layer (1.01 nm). Finally the peak observed at $2\theta = 3.6°$ (2.4 nm) indicates packets with regular 1:1 interstratification of the vermiculite layer and K^+-mica layer, which is called hydrobiotite (see the TEM results below). The sharp peak at $2\theta = 6.2°$ immediately disappeared on the adsorption of Cs^+. The peak at $2\theta = 3.6°$ gradually decreased from sample (I) and completely disappeared in sample (III). When bare Cs^+ replaces selectively hydrated Mg^{2+}, the basal spacing should be 1.06 nm, considering Cs^+-mica (nanpingite)[15] and the difference of ion diameters between Cs^+ (0.38 nm) and K^+ (0.32 nm).[16] The disappearance of the 1.4 and 2.4 nm peaks is explained by transition from vermiculite layers to Cs^+-substituting layers with ion exchange between hydrated Mg^{2+} and Cs^+. However, this

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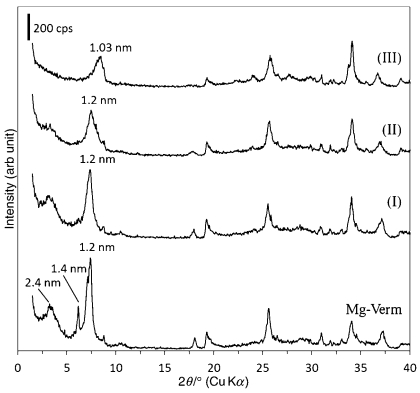

Figure 1. The XRD patterns of magnesium vermiculite (Mg-Verm: lowest) and the samples loaded with various amounts of Cs^+ ions (samples (I), (II), and (III) from the bottom to the top).

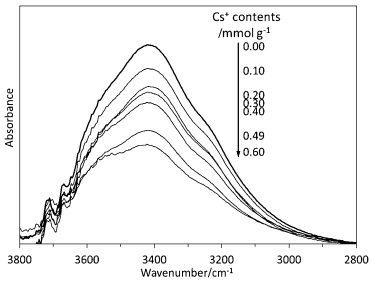

Figure 2. FT-IR spectra of magnesium vermiculite (Mg-Verm: heavy line) and the samples with different amounts of Cs^+. Each absorbance was normalized at 996 cm^{-1} assigned to Si–O stretching vibration.

reaction may generate a new peak corresponding to ca. 2.07 nm from regular 1:1 interstratifications of the Cs^+- and K^+-mica layers, but such a peak was not observed. The interpretation for this result is that X-ray scattering powers of K^+-mica layer and Cs^+-substituting layer are similar, owing to partial occupancy of the interlayer sites by Cs^+. A simple calculation indicates that the occupancy should be 0.1–0.5 in order not to form a peak for the regular interstratifications. The peak at 8.6° (1.03 nm) for sample (III) is just between 1.06 nm for Cs^+-substituting layer and 1.01 nm for K^+-mica layer.

Figure 2 shows the IR spectra of Mg-Verm by changing the loading level of Cs^+ ions. The broad peak around 3400 cm^{-1} was assigned to O–H stretches in water molecules partly adsorbed on clays and partly hydrating cations in the interlayer spaces.[17] The intensity of the peak decreased on increasing the loaded amount of Cs^+. It was saturated at nearly half of the initial absorbance on approximately 100% loading of Cs^+ ions. The remaining absorbance was due to adsorbed water molecules. This result suggested that Cs^+ was exchanged as a dehydrated state in clays. The conclusions were in accord with the XRD results.

Figure 3a shows the HRTEM image of Mg-Verm. In most of the layers, their spacing changes alternatively. Our previous work[18] reported that hydrated Mg^{2+} at the interlayer spaces in vermiculite or hydrobiotite is removed with water molecules in the vacuum environment of ion-milling or TEM, accompanying the collapse of the spaces. This results in the basal spacing of ca.

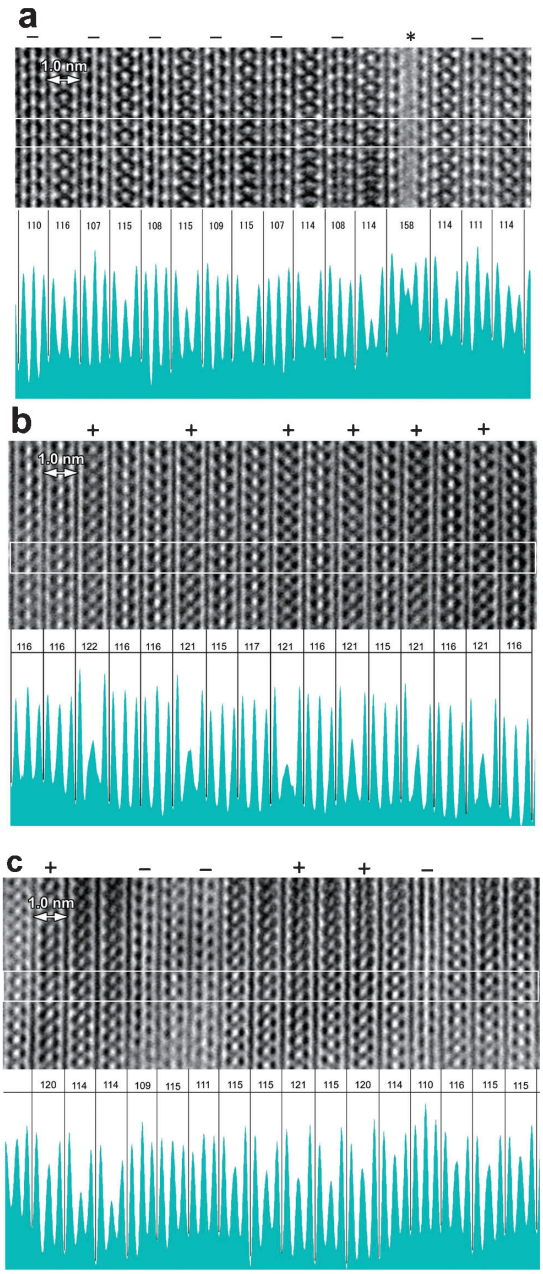

Figure 3. HRTEM images of (a) magnesium vermiculite (Mg-Verm) before loading Cs^+, (b) sample (III) (70% Cs^+ loading), and (c) sample (I) (15% Cs^+ loading). The lower is the profile of the image contrast across the layer stacking (the horizontal direction), obtained by integrating the pixel contrast inside the white rectangle along the layers (the vertical direction). The three digit figure indicates the number of the pixels for the spacing of each layer. The characters "–" and "+" indicate the collapsed vermiculite layers and Cs^+-substituting layers, respectively. The rests are considered K^+-mica layers. The asterisked interlayer in (a) may be a microcleavage or an uncollapsed one by some reason.

0.95 nm, smaller than that (1.01 nm) of K^+-mica layers. Hence, the smaller spacing in Figure 3a (the pixel number of 107–111) is originally the vermiculite layers with hydrated Mg^{2+}. Besides,

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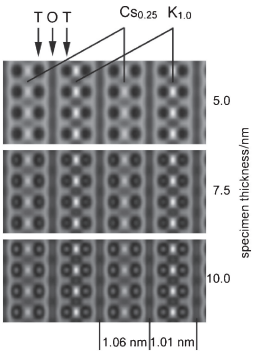

Figure 4. Multislice contrast simulation for the interstratifications of K^+-mica layers and Cs^+-substituting layers. The arrows with "T" and "O" indicate the position of the silicate tetrahedral sheet and magnesium octahedral sheet, respectively. In the simulation, the occupancy at the Cs^+ interlayer spaces is assumed 0.25, and the layer thickness 1.06 nm. TEM parameters for the simulation are: the acceleration voltage 200 kV, spherical aberration coefficient 0.5 mm, defocus value −35 nm.

the contrast at the interlayer spaces of the K^+-mica layer shows a row of dark spots which correspond to K^+ ions (Figure 4), whereas the interlayer space of collapsed vermiculite layers (indicated with "−") does not contain such dark spots. Moreover, the contrasts for the two tetrahedral sheets across the K^+ interlayer space do not shift, which means that K^+ ions locate at just the center of the facing hexagonal rings in the two tetrahedral sheets. To the contrary, the two tetrahedral sheets are displaced by $1/3b$ ($b = b$-axis length of the unit lattice of a layer) along a basal plane at some collapsed interlayer spaces, as reported for hydrobiotite[18] and talc.[19] This results in reducing the electrostatic repulsion of negatively charged oxygen atoms in the facing tetrahedral sheets. Such displacement is only possible when the interlayer regions are empty or occupied by relatively small cations.[20]

Figure 3b shows the HRTEM image of sample (III) (70% loading of Cs^+ ions). Again, two kinds of basal spacing are observed. However, a careful comparison with Figure 3a indicates that the smaller spacing corresponds to K^+-mica. The increase of the larger spacing (indicated with "+") is ca. 5%. Hence this spacing is considered to correspond to Cs^+-substituting layers. Their contrast is similar to that of K^+-mica layers. This means that Cs^+ ions locate at the same place as K^+, the center of the two hexagonal rings in both tetrahedral sheets, identically with Cs^+-micas (nanpingite). However, probably the occupancy is small from XRD results and image simulation in Figure 4, which almost reproduced the experimental contrast in Figure 3b.

Figure 3c shows the HRTEM image of sample (I) (15% loading of Cs^+ ions). The basal spacing takes three close but different values. If compared to Figures 3a and 3b, it is apparent that they are Cs^+-substituting layer, K^+-mica layer, and collapsed vermiculite layer with no interlayer materials. This means that Cs^+ substitution tends to form monoionic interlayers with a certain basal spacing, rather than some mixed-ionic interlayers with hydrated Mg^{2+} or K^+ showing intermediate basal spacing. This result gives an important insight for the stability of Cs^+ in vermiculite clay. Namely, Cs^+ ions tend to concentrate to some hydrated interlayer space rather than distribute homogeneously in all hydrated interlayer spaces and stabilize themselves by collapsing the space and being surrounded closely by basal oxygen atoms. Hence, the adsorption state of Cs^+ is almost the same, regardless of the total amount of Cs^+ loading. These situations are considered to be a main structural reason for the extremely high affinity of Cs^+ ions toward phyllosilicate clays.

In order to evaluate the stability of immobilized Cs^+, 5 mL of aqueous solution containing 0.6 mol L^{-1} $Al(NO_3)_3 \cdot 9H_2O$ or $[Co(NH_3)_6]Cl_3$ was mixed with 1.0 g of Cs^+-exchanged vermiculite (35% loading). Here these trivalent cations were chosen because the higher valent cations were expected to be more efficient in removing intercalated Cs^+. The suspensions were filtrated off after they were kept at 80 °C for 48 h. When the precipitates were analyzed by EDX, no Cs^+ was eluted to a solution within 2% of experimental error (SI[21]). The results indicated that intercalated Cs^+ was hardly removed by simple ion-exchanging with external cations. It is necessary to destruct the concerted binding by the upper and lower tetrahedral sheets to make Cs^+ free. One possibility would be to expand the interlayers by use of a large and highly charged cation or a bulky ligand strongly coordinating Cs^+.

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