Localization of cesium on montmorillonite surface investigated by frequency modulation atomic force microscopy

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ABSTRACT

Cation exchange of clay mineral is typically analyzed without microscopic study of the clay surfaces. In order to reveal the distribution of exchangeable cations at the clay surface, we performed in situ atomic-scale observations of the surface changes in Na-rich montmorillonite due to exchange with Cs cations using frequency modulation atomic force microscopy (FM-AFM). Lines of protrusion were observed on the surface in aqueous CsCl solution. The amount of Cs of the montmorillonite particles analyzed by energy dispersive X-ray spectrometry was consistent with the ratio of the number of linear protrusions to all protrusions in the FM-AFM images. The results showed that the protrusions represent adsorbed Cs cations. The images indicated that Cs cations at the surface were immobile, and their occupancy remained constant at 10% of the cation sites at the surface with different immersion times in the CsCl solution. This suggests that the mobility and the number of Cs cations at the surface are controlled by the permanent charge of montmorillonite; however, the Cs distribution at the surface is independent of the charge distribution of the inner silicate layer. Our atomic-scale observations demonstrate that surface cations are distributed in different ways in montmorillonite and mica.

1. Introduction

Cations present at the surfaces and interfaces of clay minerals are exchangeable with other cations in solution to compensate the permanent negative charge of clay. Several stoichiometric investigations have revealed that the tendency for ion exchange depends on the atomic weight and electric charge. Ions that are heavier and have larger electric charge adsorb on the clay surfaces more easily than smaller ions with lower charge [1–4]. Moreover, it has been recently suggested that the hydration energy of cation affect the ion exchangeability [5]. However, as clay minerals are nm-scale particles, microscopic phenomena such as the distribution of exchangeable cations on clay surfaces and interfaces and their surface diffusion have not been clarified.

Clay minerals are phyllosilicate crystals with a 2:1 layer. Fig. 1 shows the structure of montmorillonite, a type of smectite clay mineral. The monomolecular layer of the montmorillonite consists of Al-O octahedral sheet in between Si-O tetrahedral sheets. Divalent cations such as Mg^{2+} and Fe^{2+}, when substituted with Al^{3+} in the octahedral layer, produce negative charge on the montmorillonite surface. This negatively charged surface is neutralized by exchangeable cations at the surfaces and interfaces of the silicate sheets. Although the direct observation of

the montmorillonite surface is difficult, the surface of muscovite mica (another 2:1 type phyllosilicate crystal and has a large flat (001) face), has been well observed [6–9]. Through microscopic observation of the muscovite mica surfaces, several new models have been suggested for the distribution of exchangeable cations, which was previously considered to be dominated by the location of divalent cations in the silicate sheets.

Initially, the frayed edge model was suggested, which indicates the exchangeable cations are incorporated into the "frayed edges" of the silicate layers opened by swelling [10]. Recently, experimental evidence of the ion capture at the frayed edges have been provided [11,12]. However, this model is limited to the adsorption of the large cations, such as cesium ions (Cs^+) when the interlayer is closed because the interlayer sites are filled with small cations (e.g., K^+ in muscovite mica). Thus, this model cannot be applied for montmorillonite, whose interlayer easily expands by infiltration of water.

Secondly, it has been reported that the cation distribution depends on the hydration energy through atomic-scale measurement of the muscovite surface by interface dissipation microscopy (IDM) and molecular dynamics (MD) simulation [13]. The hydration energy has been com-

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pared theoretically for the random, row or hexagonal distribution of Rb^+ at the muscovite surface. The calculation of hydration free energy revealed that the hexagonal distribution is more favorable than the other distributions at the muscovite surface. In experiment, the hexagonal and the row pattern of Rb^+ were then observed at the muscovite surface in RbCl solution using IDM. As a result, the authors explained that the surface cations distribute so as to minimize the hydration energy at the muscovite mica surface. This "water-induced correlation model" suggests that the distribution of the cations at the surface is independent of the cation distribution in the silicate sheet.

These investigations have provided several models of cation distribution in muscovite mica. However, the location of the negative charge source is different between clay and mica. In mica, divalent cations, as sources of negative charge, are located in the Si-O tetrahedral layer. However, clay holds the divalent cations in the Al-O octahedral layer. This difference is likely to induce different behavior of the exchangeable cations.

In this study, we aimed to clarify the cation distribution on the montmorillonite surface by visualizing the montmorillonite surface structure at the atomic scale. We observed the 100 nm-scale montmorillonite surface using frequency modulation atomic force microscopy (FM-AFM), which has achieved atomic and molecular scale visualization in a liquid environment.

2. Material and methods

2.1. Sample

Natural montmorillonite (Tsukinuno, Japan) was used in this study. The interlayer of the montmorillonite sample was originally dominated by Na^+ ions. Using chemical component analysis, we confirmed that the other exchangeable cations are rarely present in montmorillonite as described in Section 3.1.

2.2. Solution

We selected Cs^+ as the observable cation because large cations are most suitable for identifying the surface cations on the montmorillonite surface. Therefore, the montmorillonite surfaces were observed in a 500 mM CsCl solution (Wako, 99.0%). The Cs^+ is easily exchanged with surface Na^+ of montmorillonite because of its ion exchange tendency. The exchange of Na^+ and Cs^+ was confirmed by the analysis of the chemical composition of montmorillonite as described in Section 3.1.

2.3. FM-AFM

We employed FM-AFM to observe the surface of the 100 nm scale particles of montmorillonite with atomic resolution. In the frequency modulation mode of non-contact atomic force microscopy, the interaction force between the tip of the probe and the atoms at the sample surface was detected by the frequency shift (Δf) of the cantilever oscillation. The noise was lowered, and the sensitivity for the detection of the cantilever oscillation in the liquid was improved [14]. With improved sensitivity, imaging of the surface structure with an atomic resolution was achieved [9,15–17]. We used a microscope compatible with SPM-8000FM (Shimadzu, Japan). The probe was an Au-coated silicon cantilever (PPP-NCHAuD, Nanosensors, Switzerland). The eigen frequency of the cantilever was 155 kHz, the quality factor was approximately 8, and the spring constant was approximately 40 N/m in the CsCl solution. The FM-AFM equipment was located in an incubator (CN-40A, Mitsubishi Electric Engineering, Japan) to maintain the temperature at 22 °C.

2.4. Chemical component analysis

The chemical components of montmorillonite before and after the ion exchange were analyzed by energy dispersive X-ray spectrometry
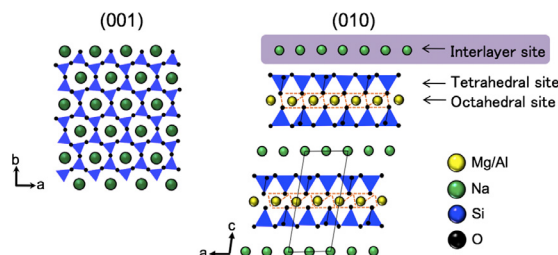

Fig. 1. Crystal structure of montmorillonite. The (001) face is the basal plane of montmorillonite with six-membered rings of silicate tetrahedra. The (010) face shows the 2:1 layered structure of the clay. The green and yellow balls represent the sites of surface/interface and octahedral layer cations, respectively. "(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)".

(EDS; EX-2300, JEOL, Japan) coupled with a field emission-scanning electron microscope (FE-SEM; JSM-6700F, JEOL, Japan) and a field emission transmission electron microscope (FE-TEM; JEM-2100F, JEOL, Japan). The FE-SEM/EDS can analyze all the chemical components of the aggregated montmorillonite blocks. Therefore, it was used to confirm the ratio of Na^+ in naturally occurring montmorillonite. In contrast, the FE-TEM/EDS was applied to analyze the components of a thin montmorillonite particle with a few silicate layers to ensure comparability to the FM-AFM measurement of the montmorillonite surface. The natural montmorillonite block was immersed in purified water for dispersion of montmorillonite by swelling. Next, a drop of the dispersed liquid was loaded and dried on a highly oriented pyrolytic graphite (HOPG) substrate. The remaining dispersed liquid was exchanged with CsCl solution for ion exchange. The montmorillonite particles were then immersed in CsCl solution for 2 h. To avoid precipitation of CsCl salt, the exchanged montmorillonite particles were immersed in ethanol and then loaded on the HOPG substrate for EDS measurement. Note that the montmorillonite particles for FM-AFM observation and those for chemical measurement by EDS were from different blocks, though they were sourced from the same montmorillonite rock.

2.5. FM-AFM observation procedure

First, the dispersed liquid of natural montmorillonite was loaded on the cleaved surface of a muscovite substrate. After the montmorillonite sheets had dried, they were fixed by physisorption of the monomolecular sheets of the montmorillonite on the substrate. Next, a 100 μl droplet of CsCl solution was placed on the dried muscovite substrate along with the montmorillonite sheets. Observation of the montmorillonite surface by FM-AFM was then performed.

3. Results and discussion

3.1. Conformation of Na-Cs exchange by EDS analysis

The averaged chemical formula of the natural montmorillonite block was $Na_{0.80}$, $K_{0.11}(Mg_{1.38}$, $Ca_{0.16}$, $Fe_{0.03}$, $Al_{2.54})Si_{8.08}O_{20}(OH)_4$. This shows that the surfaces and interlayers were dominated by Na^+. The averaged chemical formula of montmorillonite after immersion in CsCl solution was $Cs_{0.42}(Mg_{0.69}$, $Fe_{0.12}$, $Al_{2.93})(Si_{7.93}$, $Al_{0.07})O_{20}(OH)_4$. The chemical formula of cations of tetrahedral and octahedral layers fluctuated before and after immersion in the CsCl solution because different montmorillonite particles were measured in EDS analysis before and after immersion in the CsCl solution, as mentioned in Section 2.4. The EDS analysis showed that exchangeable Na^+ and some other cations at the surfaces and interlayers were completely exchanged with Cs^+ after immersion in CsCl solution. According to the chemical formula of Cs-exchanged montmorillonite, the maximum ratio of Cs^+ at cation sites on the surfaces is about 10%.