Dependence of ion exchange on the hydration structure of montmorillonite surfaces probed by atomic-scale observation of solid-liquid interface

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Cations of clay mineral are exchangeable depending on the atomic weight and electric density. Because of this ion exchange property, the clays are expected to capture the radionuclide which is diffused in the soil. Recently, the effect of water molecules on the ion exchange tendency has been suggested (S. Charles et al., 2006). In order to clarify the behavior of the water molecules at the clay-solution interface, we conducted the atomic-scale observation of the hydration structure in the vicinity of the montmorillonite surfaces in several ionic solutions.The frequency modulation atomic force microscopy (FM-AFM) which was modified based on the commercial AFM (SPM-9600, Shimadzu Corp., Japan) was employed for the atomic scale observation of interfacial structure (T. Fukuma et al., 2005). This FM-AFM technique has achieved the visualization of the 2D or 3D density map of the water molecules in the vicinity of crystal surfaces (K. Kimura et al., 2010; T. Fukuma et al., 2010). We observed the natural montmorillonite surfaces by FM-AFM in the 0.1 M KCl, CsCl, $CaCl_2$ solutions, respectively. The 100 nm plate-like particles of the montmorillonite were fixed on the mica substrate surfaces, then the (001) face and the interface were observed (Fig.1).The upper images in Fig.1 show the topography of the montmorillonite surfaces. The protrusions (brighter areas) indicate the cation sites of the montmroillonite surfaces which were located in the center of the six-membered rings of silicate tetrahedra. The interface of the montmorillonite and the solutions were observed along the dashed line in the upper images (bottom images in Fig.1). The bottom images showed the three brighter layers presented by arrows. These brighter areas indicate the distribution of the hydrated water molecules.Our results revealed that the hydration structure in the vicinity of the montmorillonite surfaces is uniform regardless of the cations in the solutions. It is suggested that the water molecules around the surface would not affect the ion exchange at the clay surfaces.

Keywords: clay mineral, ion exchange, hydration, frequency modulation AFM (FM-AFM)