A systematic understanding of adsorption reaction on clay minerals focusing on radium as a key element

Clay minerals, primarily phyllosilicate minerals with layered structures, adsorb numerous cations and are widely distributed on the Earth's surface, thereby influencing the environmental behavior of various elements. For example, radioactive cesium (Cs) released during the Fukushima Daiichi Nuclear Power Plant accident is fixed on the soil surface owing to its strong adsorption onto clay minerals [1,2]. Similarly, rare earth elements (REEs) form ion adsorption-type deposits in weathered granite and adsorb onto clay minerals [3]. However, their mobilities differ significantly: Cs^+ is difficult to extract, while REE^{3+} has a high extraction rate. This difference is attributed to their adsorption structures at the atomic scale. Cs^+ and REE^{3+} are adsorbed onto clay minerals with and without dehydration, forming inner-sphere and outer-sphere complexes, respectively (Fig. 1). Thus, clarifying the factors controlling inner- and outer-sphere complexes is essential for understanding and predicting the environmental behavior of various cations.

To elucidate these factors, we systematically investigated the adsorption structures of various cations, including radium (Ra^{2+}), at the atomic scale using extended X-ray absorption fine structure (EXAFS) [4]. Ra is a decay product of uranium and thorium and can cause environmental pollution in uranium mines. Additionally, ^{226}Ra has recently gained attention as a source for producing actinium (Ac)–225, which is used for α-particle cancer treatment. Therefore, understanding the environmental behavior of Ra is critical in geochemistry. However, Ra lacks stable isotopes, making atomic-scale experiments challenging. To address this, our group developed a novel technique, including a radiation-safe sample holder, enabling the acquisition of Ra-EXAFS data for the first time at SPring-8 **BL22XU** [5]. This method was used to elucidate the adsorption structure of Ra^{2+} on clay minerals. Additionally, EXAFS measurements at SPring-8 **BL01B1** were conducted to examine the adsorption structures of other elements, such as barium (Ba), strontium (Sr), Cs, and rubidium (Rb). For each element, both clay mineral sample with adsorbing ions and hydration solution sample were analyzed.

Figure 2 presents a portion of the EXAFS results. The EXAFS spectrum of a cation adsorbed onto a clay mineral was compared with that of a hydrated cation. When the adsorbed cation forms an outer-sphere complex, its EXAFS spectrum closely resembles that of the hydrated cation, displaying only the first shell corresponding to oxygen atoms in the hydration water molecules. Conversely, if the cation forms an inner-sphere complex, its EXAFS spectrum exhibits a second shell derived from the Si and/or Al atoms in the layered structure of the clay mineral. Accordingly, Fig. 2 reveals that Ra^{2+} adsorbed onto clay minerals formed inner-sphere complexes, while Ba^{2+} and Sr^{2+} primarily formed outer-spheres complexes.

The EXAFS results indicated that Ra^{2+}, Cs^+, and Rb^+ formed inner-sphere complexes, while Ba^{2+} and Sr^{2+} formed outer-sphere complexes. This observation can be attributed to differences in ionic radii, highlighting the significance of size compatibility between the cation and the cavity of the six-membered ring within the layered structure of clay minerals—a phenomenon known as the size-matching effect. In this study, the size-matching effect was determined by the ionic radius and valence of the adsorbed cation, which were evaluated through *ab initio* calculations.

However, the results of systematic EXAFS measurements and *ab initio* calculations revealed that the size-matching effect alone could not fully explain the formation of inner-and outer-sphere complexes.

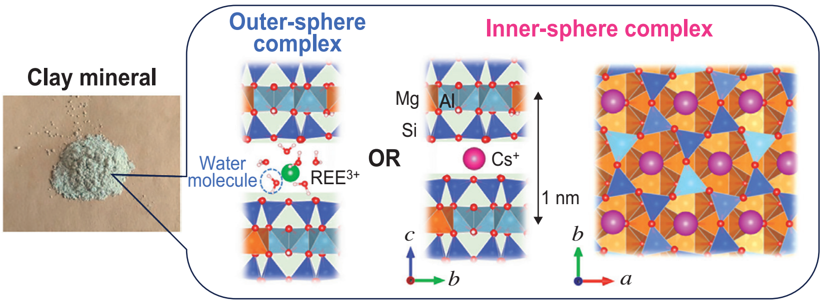

Fig. 1. Adsorption structures on clay minerals at the atomic scale. A cation forming an inner-sphere complex resides within a six-membered ring in the layered structure of the clay mineral.

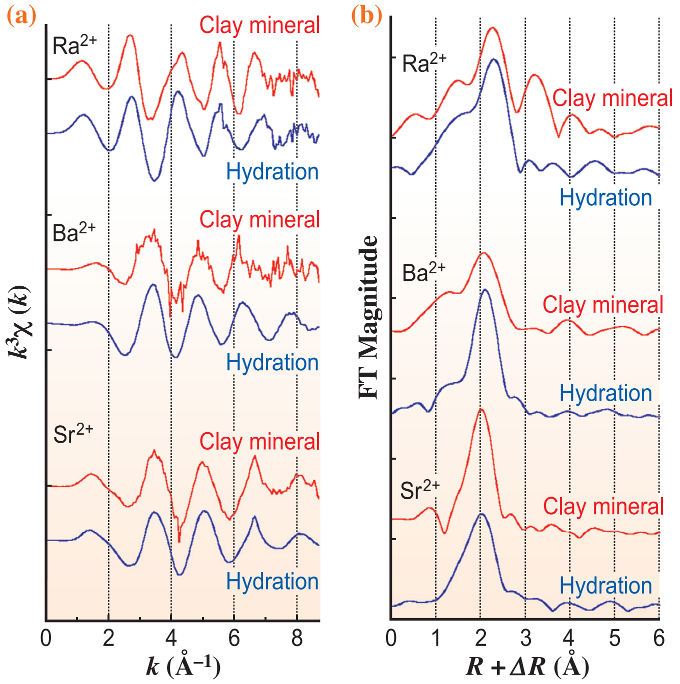

Fig. 2. EXAFS spectra of Ra, Ba, and Sr (**a**) in k-space and (**b**) in R-space. The intensities of Sr-EXAFS are plotted after division by 3.

These findings suggest that the hydration energy of the adsorbed cation also plays a crucial role, as the formation of inner-sphere complexes requires a dehydration reaction when hydrated cations in solution are adsorbed onto clay minerals. The hydration energy can be evaluated using hydration enthalpy. Consequently, this study concluded that the combined influence of the ionic radius and hydration enthalpy of cation governs the formation of inner- and outer-sphere complexes (Fig. 3).

This systematic understanding of adsorption reaction on clay minerals provides valuable insights for predicting the environmental behavior of various elements. To validate this framework, soil samples collected from the Ningyo-toge uranium mine were analyzed to investigate the mobility of several elements, including Ra. Chemical analyses, such as quantification of chemical composition and sequential extraction, indicated that Ra^{2+} is adsorbed onto clay minerals and immobilized within a weathered granite layer. These findings are consistent with the EXAFS results and the systematic model presented in Fig. 3. This study confirms that this approach effectively explains and predicts the environmental behaviors of various cations.

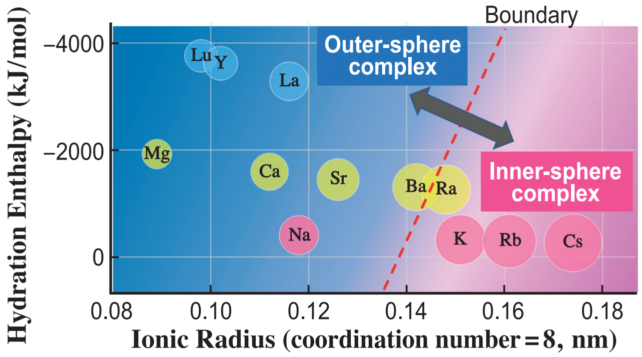

Fig. 3. Factors controlling the formation of outer- and inner-sphere complexes.

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