

# Investigation of factors controlling adsorption structures of cations on clay minerals based on EXAFS and *ab initio* calculation

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Clay minerals are important adsorbents for the environmental behavior of various cations at the Earth's surface. The details of the adsorption reactions strongly depend on the species of cations. For example, radioactive cesium (Cs) emitted from nuclear power plant accidents was strongly adsorbed on clay minerals, causing the fixation of Cs within 5 cm at the soil surface [1]. On the other hand, rare earth elements (REE) in ion-adsorption type deposits are adsorbed on clay minerals, which leads to high extraction rates of REE by the ion-exchange reaction [2, 3]. The difference in affinity is caused by adsorption structures at the atomic level: inner-sphere and outer-sphere complex. Cs<sup>+</sup> is adsorbed on clay minerals without hydrated water molecules, forming an inner-sphere complex. REE<sup>3+</sup> is adsorbed with hydrated water molecules, forming an outer-sphere complex. These correspondences imply that the formations of inner-sphere and outer-sphere complexes are the origins of the strong and weak adsorption by clay minerals, respectively.

This study systematically compared various cations, including radium (Ra<sup>2+</sup>), to investigate the factors controlling the adsorption structures. Extended X-ray absorption fine structure (EXAFS) is a powerful tool to clarify the adsorption structure. However, Ra EXAFS measurement had not been conducted because Ra has no stable isotopes. Thus, this study established a method to obtain Ra EXAFS spectra in a safe manner [4]. Furthermore, the stabilities of clay minerals were evaluated by *ab initio* numerical simulations. The EXAFS results showed that some cations, including Ra<sup>2+</sup>, form inner-sphere complexes. The *ab initio* calculations suggested that the clay mineral adsorbing larger cations is more stable, meaning the importance of structural matching between the adsorbed cation and cavities at tetrahedral layers in the clay minerals. These results suggest that the formation of the inner-/outer-sphere complexes is controlled by structural matching in addition to hydration energy. These systematic understandings help us predict and understand various cations' environmental behaviors.

References: [1] K. Tanaka *et al.*, *Geochem. J.* **46**, 73 (2012). [2] A. Yamaguchi *et al.*, *Geochem. J.* **52**, 415 (2018). [3] A.M. Borst *et al.*, *Nat. Commun.* **11**, 4386 (2020). [4] A. Yamaguchi *et al.*, *iScience* **25**, 104763 (2022).