

Effect of ionic radii on metal ion species adsorbed in the interlayer of 2:1 phyllosilicate: implications on their migration in environment

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Dissolved concentrations of various trace ions in natural soil/sediment-water systems are regulated by adsorption on phyllosilicates, iron oxides etc., which affects various phenomena observed at earth surfaces. For example, ion-adsorption deposits are the most appropriate deposits for rare earth elements (REEs) industries, since REEs can be readily extracted from the soils by NH_4^+ ion solution. On the other hand, radiocesium is retained at the very surface of soils in Fukushima, which is an important reaction after the nuclear accident in Japan. Thus, the purpose of this study is to reveal the atomic-scale interactions between various metal ions including REE and Cs with clay minerals to understand their macroscopic behaviors in environment.

K-edge EXAFS (extended X-ray absorption fine structure) for various metal ions (K^+ , Rb^+ , Cs^+ , Sr^{2+} , Ba^{2+} , La^{3+} , and Y^{3+}) were performed after their adsorption on vermiculate, montmorillonite, kaolinite, and ferrihydrite to identify their adsorption species. Adsorption experiments were also performed for the adsorbents in three aqueous solutions (0.10 and 1.0 M NaNO_3 , and 1.0 M NH_4Cl), by which adsorption and extraction ratios can be calculated.

Adsorption ratios (NaNO_3 system) to clay minerals increased in the order of K^+ , Rb^+ , Cs^+ < Sr^{2+} , Ba^{2+} < La^{3+} , Y^{3+} due to the larger electrostatic attraction to ions with larger positive charges. EXAFS spectra for the species of Sr^{2+} , La^{3+} , and Y^{3+} adsorbed on vermiculate and montmorillonite are similar to those of hydrated ions, suggesting that they form outer-sphere complex to the mineral surfaces. It was also found that larger ions (Ba^{2+} , K^+ , Rb^+ , and Cs^+) form inner-sphere complex within the interlayer. The extraction ratio by NH_4^+ ion increased in the order of Rb^+ , Cs^+ < Sr^{2+} , Ba^{2+} < La^{3+} , Y^{3+} . Thus, REE ions (La^{3+} and Y^{3+}) are distributed to weathered granite rich in 2:1 phyllosilicates to a large degree, but can be readily leached by NH_4^+ due to the formation of outer-sphere complex, which is known as unique feature of ion-adsorption ore. On the other hand, large ions such as Cs^+ are not readily leached due to the formation of inner-sphere complex, which can explain the strong retention of Cs^+ at the very surface. Thus, this study allows us to understand systematically behaviors of cations in environment.