

**Molecular geochemistry of interactions of various hard cations and phyllosilicates related to their environmental behaviors and isotope fractionation**

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Interactions of various metal ions with phyllosilicate minerals (clay minerals and micas) affect their geochemical behaviors in various systems in earth and planets. For example, cesium ion forms inner-sphere (IS) complex within the interlayer of 2:1 phyllosilicate minerals, which makes it immobile at soil surface when deposited from the atmosphere [1]. On the other hand, rare earth elements (REEs) form outer-sphere (OS) complexes in the interlayer by adsorbed as hydrated ions [2]. The sharp difference between these hard cations should be explained by any systematic physico-chemical factor. Thus, we have applied EXAFS to various hard cations with various ionic radii including  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Y^{3+}$ ,  $La^{3+}$ , and  $Lu^{3+}$  adsorbed on phyllosilicates [3]. As a result, there is a boundary of the ionic radius around  $Ba^{2+}$ : ions smaller than  $Ba^{2+}$  form OS complexes, while larger IS. The result was confirmed by the interlayer distances of vermiculite adsorbing the cations by XRD. These results suggested that the difference of the interaction with clay minerals among various hard cations can be explained primarily by the ionic radius, implying the importance of the fitness of the siloxane ring size to the ionic radius. The systematic dependence allows us to interpret the difference of environmental behaviors of the hard cations such as (i) higher mobility of  $Sr^{2+}$  ( $< Ba^{2+}$ ) at soil surface [4], which is in contrast to  $Cs^+$  ( $> Ba^{2+}$ ) immobile at soil surface and (ii) readily ion-exchangeable behavior of REE in the ion-adsorption type ore of REE. Moreover, the systematics from the atomic-scale enables us to predict macroscopic environmental behaviors and isotopic fractionation for these cations such as (i) the importance of clay minerals on the migration of  $Ra^{2+}$  ( $> Ba^{2+}$ ) at earth surface [3] and (ii) fractionation of Rb isotope by the formation of IS complex within the interlayer of phyllosilicates [5].

References: [1] Fan et al., *Geochim. Cosmochim. Acta* 135 (2014) 49. [2] Yamaguchi et al., *Geochem. J.* 52 (2018) 415. [3] Yamaguchi et al., to be submitted. [4] Yamaguchi et al., *J. Radioanal. Nucl. Chem.* 317 (2018) 545. [5] Tsuboi et al., to be submitted.