

***In situ* observations of competitive adsorption of monovalent ions at the muscovite (001)-water interface**

S.S. LEE^{1*}, C. PARK^{1,3}, N.C. STURCHIO², K.L. NAGY²
AND P. FENTER¹

¹Chemical Sciences and Engineering, Argonne National Laboratory, Argonne, IL, 60439
(*correspondence: sslee@anl.gov)

²Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, IL 60607

³current address: HP-CAT, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, IL 60439

Robust characterization of ion adsorption and desorption processes is essential for assessing societal risks associated with the bioavailability of nutrients or toxic elements in soils and surface waters. In this study, we monitor the effect of a competing ion (Na^+ or K^+) on the distribution and adsorption thermodynamics of Rb^+ at the muscovite (001)-water interface using *in situ* specular X-ray reflectivity combined with resonant anomalous X-ray reflectivity. Experiments were performed with aqueous solutions containing RbCl and either NaCl or KCl at a fixed ionic strength (3 mM).

These systematic measurements of competitive adsorption reveal insight into the adsorption of Rb^+ and the competing ion. The variation of the average height of Rb^+ with solution composition reveals that the relative proportions of inner-sphere (IS) and outer-sphere (OS) species of adsorbed Rb^+ are not constant. Instead, Rb^+ adsorbs mostly as an IS species in pure RbCl , or when competing with K^+ , but transforms to a distribution with equal proportions of IS and OS when it competes with OS dominant Na^+ . The adsorption thermodynamics results show that the magnitude of the cation adsorption free energy decreases linearly with increasing magnitude of the cation hydration enthalpy. This indicates that cation hydration is an important factor in controlling the adsorption strengths as well as the IS/OS partitioning of these cations. Finally, we estimate the contribution of electrostatic attraction to the monovalent ions' adsorption free energies as IS and OS species. The calculated energy difference between these two species (25-30 kJ/mol) is larger than that estimated (~10 kJ/mol) based on the difference in their adsorption heights (~4 Å) and the dielectric constant (~80) of bulk water. This large discrepancy suggests that a discrete interfacial hydration layer leads to a significant reduction of the interfacial dielectric parameter.

La-Ce and Sm-Nd isotope geochemistry of Early Proterozoic Imweon leucogranite, Korea

SEUNG-GU LEE^{1*}, YOSHIHIRO ASAHARA²,
TSUYOSHI TANAKA², NAM HOON KIM³
AND YONG SUN SONG³

¹Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, Korea (sgl@kigam.re.kr)

²Department of Earth and Environmental Sciences, Nagoya University, Nagoya 464-8601, Japan
(asahara@eps.nagoya-u.ac.jp, tanaka@eps.nagoya-u.ac.jp)

³Department of Environmental Sciences, Pukyong National University, Pusan 608-737, Korea (ysson@pknu.ac.kr)

La-Ce and Sm-Nd isotope systematics in the Precambrian rocks provide a valuable information for the LREE pattern in the source material. The Imweon leucogranite in the northeastern Yeongnam Massif, Korea is strongly peraluminous and S-type granitic gneiss. The leucogranite was generated by partial melting of the metasediments, which consist of quartz+K-feldspar+plagioclase+biotite+muscovite+sillimanite±garnet±tourmaline. Whole-rock Sm-Nd age suggests that the leucogranite should be formed by a magmatic episode at ca. 1.90Ga. One of the main geochemical characteristic of the leucogranite is that some of the granite shows 'tetrad effect' in the chondrite-normalized REE pattern. In this paper, we discuss La-Ce and Sm-Nd isotopic systematics for the Imweon leucogranite with REE tetrad effect to clarify whether the REE tetrad effect of the leucogranite was derived from the differentiation of the source magma or derived from the secondary processes such as metamorphism or hydrothermal alteration.

The present ϵ_{Nd} and ϵ_{Ce} values of the leucogranites with tetrad REE pattern are positive whereas the leucogranites without tetrad REE pattern have the negative ϵ_{Nd} and positive ϵ_{Ce} values. The initial ϵ_{Ce} values of the leucogranite are $-2.5 < \epsilon_{\text{Ce}}(t) < +21.7$ whereas initial $\epsilon_{\text{Nd}}(t)$ values of the leucogranites are similar in the range of $-8.71 < \epsilon_{\text{Nd}}(t) < -4.31$ regardless of the existence of tetrad REE pattern. This suggests that Ce isotopes of the source material should be heterogeneous whereas its Nd isotopes were relatively homogeneous. In addition, such La-Ce and Sm-Nd isotopic data reveal that the leucogranites should be derived from the same source material regardless the existence of the REE tetrad effect.