

# Selective isotope fractionation of rubidium during adsorption on phyllosilicate minerals as a tracer of water-rock interaction

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It has been clarified that cesium (Cs) ion is adsorbed on 2:1 type phyllosilicates (vermiculite, montmorillonite, and illite) as inner-sphere (IS) complexes by extended X-ray absorption fine structure (EXAFS). It is considered that the IS complexation caused by the large ionic radius of Cs<sup>+</sup> leads to isotopic fractionation, but is not observable due to the absence of multiple isotopes for Cs. Thus, we studied rubidium (Rb) isotope, since Rb with ionic radius close to Cs also forms IS complexes on phyllosilicates.

In this study, Rb<sup>+</sup> was adsorbed on vermiculite, montmorillonite, illite, ferromanganese oxides, and strongly acidic cation-exchange resin (Dowex 50W X8) under various pH and ionic strength conditions, and the adsorption structure was analyzed by EXAFS. After these adsorption experiments, Rb stable isotope ratios (<sup>87</sup>Rb/<sup>85</sup>Rb) in aqueous and solid phases were measured with MC-ICP-MS to analyze the degree of the isotope fractionation. The chemical state and stable isotopes of Rb in the natural sediment samples and seawater in the Pacific were also analyzed with XAFS (EXAFS and XANES) and MC-ICP-MS, respectively.

It was verified experimentally that Rb<sup>+</sup> forms IS complexes in specific phyllosilicates (vermiculite and illite), for which Rb stable isotope fractionation occurs during the adsorption ( $\delta^{87}\text{Rb}_{\text{solid-liquid}} = -0.41 \pm 0.15\text{‰}$  and  $-0.29 \pm 0.05\text{‰}$  for vermiculite and illite, respectively). On the other hand, Rb<sup>+</sup> mainly adsorbed as outer-sphere complexes on montmorillonite, ferromanganese oxides, and strongly acidic cation-exchange resin did not show large isotope fractionation ( $\delta^{87}\text{Rb} < 0.05\text{‰}$ ). The results of the adsorption experiments suggested that the Rb concentration in seawater is dominated by the partition between seawater and phyllosilicates, which that in ferromanganese oxides reflect that of seawater. EXAFS analysis revealed that Rb in natural sediments is also dominated by IS complexes with phyllosilicates. In the natural system, it was revealed that the fractionation ( $\delta^{87}\text{Rb} = -0.17 \pm 0.07\text{‰}$ ) is found between sediment and seawater in the ocean. Based on these results, we propose here geochemical application of the <sup>87</sup>Rb/<sup>85</sup>Rb isotope ratio to estimate past seawater fluctuation and the water-rock ratio in the system.