

## Variation of rubidium isotope and its possibility as a tracer of surface environment

Hiroyuki Tsuboi<sup>1</sup>, Rimi Konagaya<sup>1</sup>, \*Yoshio Takahashi<sup>1</sup>

1. Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo

One of important aspects of molecular geochemistry is to develop new isotope tools of various processes by focusing on physico-chemical properties of elements from their atomic scales. There has been no studies so far on the isotope fractionation of rubidium (Rb) caused by Rb behaviour during water-rock interaction, possibly due to general knowledge that the reactivity of  $\text{Rb}^+$ , or alkaline metal ion, is very low. This is not the case, however, if we think about its interaction with phyllosilicates. It has been clarified that cesium (Cs) is adsorbed on 2:1 type phyllosilicates (vermiculite, montmorillonite, and illite) as inner-sphere (IS) complex by analyzing extended X-ray absorption fine structure (EXAFS). It is considered that the specific adsorption structure is caused by the ionic radius of Cs. Therefore, it was predicted that rubidium (Rb) which is close to Cs in terms of ionic radius also forms IS complex on phyllosilicates.

In this study,  $\text{Rb}^+$  was adsorbed on vermiculite, montmorillonite, and illite under various pH and ionic strength conditions, and the adsorption structure was analyzed by EXAFS. For comparison, the same experiment was carried out for the strongly acidic cation-exchange resin (SCR; Dowex 50W X8). After these adsorption experiments, Rb stable isotope ratios ( $^{87}\text{Rb}/^{85}\text{Rb}$ ) in liquid and solid phases were measured with a multi-collector type inductively coupled plasma mass spectrometry (MC-ICP-MS) and the degree of the isotope fractionations were analyzed. The host phase of  $\text{Rb}^+$  in marine sediment in the Pacific Ocean and the standard rock samples (JA-2, JB-1a, JF-1, JG-2, JLK-1, JMS-2, JR-3, JSI-2) were also analyzed with EXAFS and their Rb stable isotope ratios were measured with MC-ICP-MS. In addition, dissolved  $\text{Rb}^+$  and  $\text{Rb}^+$  in suspended particles in river water samples collected in the Tone River were also analyzed with EXAFS and their Rb stable isotope ratios were measured with MC-ICP-MS.

In this study, it was verified experimentally that Rb forms IS complexes in specific phyllosilicates (vermiculite and illite) and Rb stable isotope fractionation occurs during its adsorption ( $\Delta^{87}\text{Rb}_{\text{solid-liquid}} = -0.41 \pm 0.15\%$  and  $-0.29 \pm 0.05\%$  for vermiculite and illite, respectively). The lighter isotope ( $^{85}\text{Rb}$ ) was concentrated in the solid phases in this isotope fractionation. On the other hand,  $\text{Rb}^+$  was mainly adsorbed as outer-sphere complexes in montmorillonite and strongly acidic cation-exchange resin, and the isotope fractionations were too small to be undetected ( $\Delta^{87}\text{Rb} < 0.05\%$ ). The results of adsorption experiments showed that the Rb concentration in seawater (synthetic seawater) is dominated by the partition between seawater and phyllosilicates. EXAFS analysis also revealed that Rb in sedimentary rocks is also dominated by IS complexes with phyllosilicates. In the ocean system, it was revealed that the fractionation ( $\Delta^{87}\text{Rb} = -0.20\%$ ) has occurred between marine sediment and seawater. The lighter isotope was concentrated in the solid phases in these systems. Hence, the Rb isotope fractionation observed in the laboratory experiments was also found in the marine environment.

The mean Rb isotope ratio of seawater-marine sediments is significantly higher than the crustal average, suggesting that the Rb isotope ratio is higher in rivers before its inflow into the ocean. Actually,  $\delta^{87}\text{Rb}$  of the Tone River water was fractionated between dissolved and suspended particle phases and this fractionation was consistent with the fractionation observed in the laboratory experiments for illite and vermiculite. Finally,  $\delta^{87}\text{Rb}$  of seawater and marine sediment can be explained by considering adsorption reaction on phyllosilicates in both rivers and oceans in this study. Based on the results, I proposed that

possible geochemical applications of the  $^{87}\text{Rb}/^{85}\text{Rb}$  isotope ratio are study estimation of the record of sea water fluctuation and the water-rock ratio.

Keywords: Rubidium, Isotope, Weathering