

# Molecular geochemistry of rubidium: a possibility of $^{87}\text{Rb}/^{85}\text{Rb}$ ratio as a signature of sedimentary environment and seawater amount

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## Introduction

There are some examples that the chemical species control element concentrations and isotopic fractionation, and in this research, it is a goal to investigate such elements and to scrutinize whether they can be a new geochemical tool. Firstly, it was aimed to clarify whether concentrations and isotope ratios of rubidium (Rb) vary by the formation of inner-sphere complexes in phyllosilicates similarly to the case of cesium (Cs). If they are confirmed, there is a possibility that we can reveal how the depths and distances from land of various sediments and sedimentary rocks relatively changed. The information can give new insights into elucidation of sedimentary environment. Furthermore, considering the global mass balance of Rb, the distribution ratio between the ocean and the sediments may reflect the Rb isotope ratio in the sediments and may be an index reflecting the amount of water in the seawater. So far, the possibility of fluctuations of Rb isotope ratio and the geochemistry using the ratio are not developed at all. This research may be the pioneer of new isotope geochemistry.

## Methods

As the samples in the laboratory system, an aqueous solution of  $\text{Rb}^+$  was added into suspended solution of vermiculite at various pH and ionic strength to obtain adsorption envelope for the system. As for the seafloor sediment samples, the Sea of Japan sediment samples (GH 87-2 series) were received from the National Institute of Advanced Industrial Science and Technology (AIST). For the purpose of obtaining molecular-scale information on Rb adsorbed on clay mineral and Rb species of the Sea of Japan sediment samples, measurement and analysis of Extended X-ray adsorption fine structure (EXAFS) were carried out. For the measurement samples, hydrated Rb in water, Rb adsorbed on vermiculite, and the sediment samples from the Sea of Japan were prepared. In addition to the information obtained with EXAFS, the species of Rb in adsorbed on vermiculite was estimated by adsorption experiments. In order to obtain information on a capacity of adsorption site of Rb on vermiculite, adsorption experiments were conducted by changing initial concentrations of  $\text{Rb}^+$  and solid adsorbent, respectively. The relationship between liquid phase concentration at equilibrium and adsorption amount was investigated. For the samples to be measured for isotope ratio, a part of the samples prepared by experiments on adsorption isotherm was used. For each sample, liquid and solid isotope ratios were measured. Isotope data were reported as  $\delta^{87}\text{Rb}$  relative to  $\text{RbNO}_3$  (Wako, Japan).

## Results & Discussion

The independence of pH and the ionic strength suggests that Rb forms inner-sphere complex with vermiculite surface with lesser contribution of electrostatic term in the adsorption reaction. EXAFS spectra also suggested that Rb forms inner-sphere complexes on vermiculite. Variation of Rb isotope ratio at

various fractions of adsorbed Rb in the system [%], which shows the systematic increase of the  $\delta^{87}\text{Rb}$  as the increase in the adsorbed fraction. The isotope fractionation can be well explained by Rayleigh fractionation model with  $\Delta_{\text{solid-liquid}}^{87}\text{Rb} = -0.41 \pm 0.15\text{‰}$ , which suggests that the adsorption reaction is more or less irreversible, and that the kinetic isotopic effect may be occurring in this reaction. These results supported the conclusion of preferential retention of lighter isotope on the solid phase. It was revealed that this isotope fractionation can be an indicator of the distance from the land and the water depth of marine sediment and can show variation of the seawater quantity. Based on these molecular-level structural information and isotopic results, it is concluded that the Rb isotope ratio is useful as a new tool for geochemistry.

Keywords: Isotope, Adsorption, Rubidium, Clay mineral