

## Copper isotope fractionation during adsorption onto manganese oxides

Y. IJICHI<sup>1\*</sup>, T. OHNO<sup>1</sup>, S. SAKATA<sup>1</sup>

<sup>1</sup>Department of Chemistry, Gakushuin University, Mejiro,  
Tokyo, Japan, 171-8588 (\*yutaidichi@gmail.com)

Ferromanganese oxides are the aggregate which consists iron and manganese oxyhydrites and they scavenge many elements in the ocean. Recently, the variation of isotopic composition of adsorbed elements in natural ferromanganese oxides has been investigated to understand the paleo-ocean redox or elemental circulations in the ocean. To reveal mechanism of copper isotope fractionation between dissolved and adsorbed species, adsorption experiments and X-ray absorption fine structure spectroscopy (XAFS) have been conducted[1-3]. Previous works reported isotopically light value of copper in ferromanganese crusts and nodules, compared to that of modern sea water[4,5]. By contrast, laboratory adsorption experiments reported preferential heavier copper sorption to iron oxyhydroxides[1]. In this study, in order to understand the mechanism of isotope fractionation involving the copper sorption to ferromanganese oxides, we would like to report an experimental observation that associated with adsorption of dissolved copper onto synthesized manganese oxides ( $\delta$ -MnO<sub>2</sub>) and the resulting isotope fractionation.

Adsorption experiments were carried out as a function of pH. At the end of each experiment, copper was isolated from the filtrated samples using anion exchange chromatography. Subsequently, <sup>65</sup>Cu/<sup>63</sup>Cu of each sample was measured by using multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS; Nu Plasma).

The magnitude of observed copper isotope fractionation exhibited no systematic variation with pH, while concentration of dissolved copper in the residual liquid decreased with increasing pH. Lighter copper isotope (<sup>63</sup>Cu) was preferentially adsorbed onto  $\delta$ -MnO<sub>2</sub> ( $\Delta^{65}\text{Cu}_{\text{soln-solid}} = 0.5 \pm 0.3\text{‰}$ ) under our experimental condition (pH = 3~7). Considering natural and experimental data, it is suggested that copper isotopic composition of ferromanganese oxide is mainly affected by adsorption of lighter isotope onto  $\delta$ -MnO<sub>2</sub>.

[1]Balistrieri *et al.* (2008) *Geochim. Cosmochim. AC.* **72** 311-328, [2] Sherman and Peacock (2010) *Geochim. Cosmochim. AC.* **74** 6721-6730, [3]Little *et al.* (2014) *Earth Planet. SC. Lett.* **396** 213-222, [4]Takano *et al.* (2016) *Nature Comms.* **663** , [5] Albarède (2004) *Mineralogy & Geochemistry* **55** 409-427