

# Difference in the adsorption behavior of arsenic and antimony on the marine ferromanganese oxides in terms of structural similarity of each ion

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Marine ferromanganese oxides (FMOs) are widely present in various marine environment, which forms nodules and crusts mainly composed of Fe (oxyhydr)oxides and Mn oxides. They are efficient scavengers of trace elements from seawater, so that they are important materials in terms of seafloor metal resources. In addition, the reaction with FMOs colloidal particles in the water column is an important chemical process that dominates the behavior of trace elements in seawater. However, since the chemical factors that govern enrichment mechanisms of trace elements in marine FMOs are diverse, systematical understanding of the enrichment mechanism of each element is not sufficient at present. Therefore, the purpose of this study is to add new findings to the enrichment mechanism of trace elements in marine FMOs. It is suggested that trace element dissolved in seawater as an anion with larger value of the acid dissociation constant ( $pK_a$ ) can be more strongly adsorbed on marine FMOs (Takahashi et al., 2014). However, antimony (Sb) and arsenic (As), although both elements have similar value of  $pK_a$ , are different in the enrichment rate (FMOs/Seawater) about 4 times (Hein et al., 2003). In this study, we focused on the difference in chemical structure between Sb (octahedron) and As (tetrahedron). We investigated the dominant adsorbed structure of Sb and As on Mn oxide and Fe (oxyhydr)oxide at the molecular scale.

Geometry optimization of Sb and As adsorption structures on Fe (oxyhydr)oxide and Mn oxide and the interaction energy in those structures were performed by quantum chemical calculation. In addition, adsorption experiments were conducted by adding Sb and As solutions to synthesized  $\delta$ -MnO<sub>2</sub>, birnessite, and ferrihydrite. Extended x-ray absorption fine structure (EXAFS) spectra of Sb and As in the solid phase of adsorption experiments were obtained to analyze the chemical state at the molecular scale. Furthermore, the enrichment mechanisms of Sb and As in hydrogenetic (HG) and diagenetic (DG) marine FMOs were investigated by comparing EXAFS spectra of Sb and As in natural samples with those in adsorption samples.

EXAFS study suggested that both Sb and As were adsorbed as bidentate-binuclear surface complex to synthesized ferrihydrite and birnessite, while Sb was adsorbed as bidentate-mononuclear surface complex and As was as bidentate-binuclear surface complex to synthesized  $\delta$ -MnO<sub>2</sub>. In natural samples, the distribution to ferrihydrite or goethite was the largest for both Sb and As into HG samples. However, comparing the distribution to Mn oxide in HG samples, it was suggested that Sb was adsorbed on  $\delta$ -MnO<sub>2</sub>, whereas As was adsorbed on birnessite. On the other hand, it was suggested that Sb was largely distributed to birnessite only in DG samples with high Mn/Fe ratio, whereas distribution of As to goethite was large in one DG sample and those to goethite and birnessite were similar in the other DG sample. The main manganese mineral constituting HG sample has low crystallinity and the ratio of edge site/surface site is high. Since Sb was predominantly adsorbed on edge site as bidentate-mononuclear surface complex on  $\delta$ -MnO<sub>2</sub> which has low crystallinity, it was suggested that enrichment mechanism of Sb in HG sample was consistent with the results of enrichment mechanism to  $\delta$ -MnO<sub>2</sub> in laboratory experiments. Considering that the Mn/Fe ratio of DG sample is higher than that of HG sample, it was suggested that the

distribution of Sb to Mn oxide increases as Mn/Fe ratio increases, although As is basically distributed to Fe (oxyhydr)oxide. This difference was considered to be due to the fact that the symmetry and ionic radius of  $\text{Sb}(\text{OH})_6^-$  (octahedron) is similar to those of  $\text{Mn}^{4+}$  in marine FMOs. Therefore, it was considered that the difference in enrichment rate (FMOs/Seawater) between Sb and As is partly due to the difference in adsorption site to Mn oxide.

This study suggested that the trace elements dissolved as anions have different adsorption sites due to the similarity of the chemical structure with the host phase. Therefore, as a new finding of the enrichment mechanism of trace elements into marine FMOs, it was suggested that the enrichment rate (FMOs/seawater) of trace elements with similar structure to the host phase is important.

Keywords: Ferromanganese oxide, Arsenic, Antimony, EXAFS, Enrichment mechanism