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Enrichment mechanisms of antimony and arsenic in marine ferromanganese oxides: insights from the structural similarity

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The ferromanganese oxides, aggregates of iron (oxyhydr)oxides and manganese oxides, are mainly present in the forms of nodules and crusts in a variety of environments. Marine ferromanganese oxides can be generally classified into hydrogenetic (HG) nodules and crusts on deep sea floor, diagenetic (DG) deposits in sediments, and hydrothermal (HT) deposits close to oceanic ridges, based on the Mn/Fe ratio, growth rate, and constituent Mn minerals. It is generally considered that marine ferromanganese oxides are one of potential mineral deposits as an additional supplement to land-based resources, because they can act as the efficient scavengers for many rare and critical elements like tellurium (Te), cobalt (Co), molybdenum (Mo), and REEs from seawater (e.g., Hein et al., 2013). For example, Te can be extremely enriched in marine ferromanganese oxides with an enrichment factor of ~109 times relative to seawater (Hein et al., 2003; Kashiwabara et al., 2013; Qin et al., 2017). Over the past decades, marine ferromanganese crusts and nodules as potential deep-ocean resources have received increasing attention, however, much lesser knowledge is available concerning the incorporation and enrichment mechanisms for each trace element in marine ferromanganese oxides. However, much lesser knowledge is available concerning the incorporation and enrichment mechanisms for antimony (Sb) and arsenic (As) in marine ferromanganese oxides. The purposes of this work were (i) to reveal the dominant surface complexes for Sb and As adsorbed on Fe and Mn oxides as examples of trace elementd enriched in marine ferromanganese oxides; (ii) to clarify different enrichment mechanisms for Sb and As in marine ferromanganese oxides at the molecular scale; and (iii) to provide new insights into geochemical processes and environment fates of trace elements in marine environment.

In the present study, the dominant adsorbed structure of Sb(V) and As(V) in synthetic ferrihydrite and Mn oxides at the molecular scale were investigated by combination of EXAFS analysis and quantum chemical calculation. Furthermore, the speciation, distribution, and local structure of Sb and As in different types of natural marine ferromanganese oxides were determined by the XAFS spectroscopy. XAFS spectra. XAFS spectra at As K-edge and Sb K-edge were measured at bamlines BL-12C and NW10A, respectively. Micro-XRF-XAFS was measured at BL-4A.

The EXAFS results suggested that Sb(V) was preferentially adsorbed as bidentate-mononuclear complex on δ-MnO_2 due to the symmetry and ionic radius of octahedron $Sb^V(OH)_6^-$ are very similar with Mn4+, but tetrahedral $As^VO_4^{3-}$ was adsorbed as bidentate-binuclear surface complex on δ-MnO_2 (Fig. 1). Both Sb(V) and As(V) were predominantly adsorbed as bidentate-binuclear complex on ferrihydrite and birnessite. In marine ferromanganese oxides, As can be largely distributed to Fe (oxyhydr)oxide, but Sb can be retained by both Fe (oxyhydr)oxide and Mn oxide. The distribution of Sb to Mn oxides could be dependent on the Mn/Fe ratio and constituting mineral in ferromanganese samples, while As is selectively distributed to birnessite in addition to Fe (oxyhydr)oxides in marine ferromanganese oxides. The significant discrepancy of the distribution between Sb and As in ferromanganese oxides can be attributed to their different molecule geometry and preferential surface complexes on Fe and Mn oxides. The findings in this study suggest that the adsorption site is likely to be different for the trace elements dissolved as anions in seawater, and the trace elements with similar structure to the host phases would show higher enrichment factors in marine ferromanganese oxides.

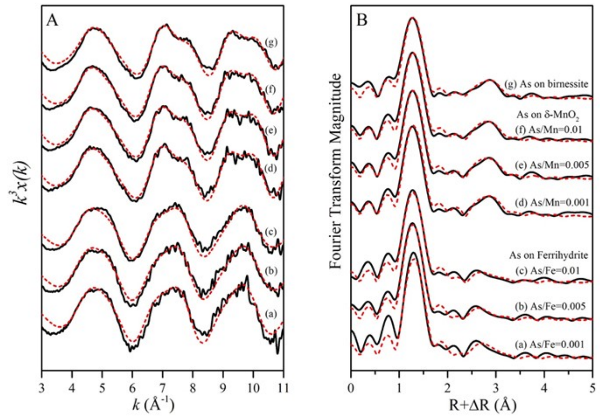

Figure 1. As K-edge EXAFS spectra of adsorbed samples: (A) k^3-weighted x(k) spectra, and (B) their RSFs (phase shift not corrected).

References
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