

## Distinct distribution trends of arsenate and molybdate in marine ferromanganese nodules

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Marine ferromanganese nodules or crusts with the hydrogenetic (HG), diagenetic (DG) and hydrothermal (HT) origins, are important sedimentary substrates for various elements such as lead (Pb), zinc (Zn), cobalt (Co), cerium (Ce), molybdenum (Mo), tungsten (W), arsenic (As), antimony (Sb), tellurium (Te), and etc. However, the distribution behaviors and host phases of tetrahedral arsenate ( $\text{AsO}_4^{3-}$ ) and molybdate ( $\text{MoO}_4^{2-}$ ) oxyanions in the ferromanganese oxides are far from understood. Herein, we combine sequential extraction approach and spectroscopic analyses to explore the mineralogical components of HG ferromanganese nodules collected from the Pacific Ocean and the speciation of arsenate and molybdate therein.

X-ray diffraction (XRD), X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy analyses indicate that the predominant manganese and iron phases were vernadite ( $\delta\text{-MnO}_2$ ) and ferrihydrite, respectively. According to the sequential extraction examination, both As and Mo are associated with the iron (oxyhydr)oxide phases. As K-edge EXAFS analyses indicate the immobilization of arsenate by ferrihydrite via forming inner-sphere complexes in double corner-shared form. This result is consistent with the sequential extraction data. However, Mo  $L_3$ -edge XANES analyses suggest the adsorption of molybdate on vernadite surfaces via the edge-shared complexation, being contrary to the conclusion derived from the sequential extraction results. This inconsistency reveals the unreliability of sequential extraction approach to verify the host phase of trace elements in complicated natural samples due to the potential occurrence of re-adsorption risk.

According to the spectroscopic analyses, chemical binding ( $\Delta G_{\text{chem}}$ ) rather than the previously proposed coulombic interaction ( $\Delta G_{\text{coul}}$ ) is the predominant driving force for the retention of arsenate and molybdate by HG ferromanganese nodules. The disparate distribution trends of arsenate and molybdate are attributed to their different intrinsic properties (e.g., averaged dissociation constants of conjugate acids) and the diverse properties (e.g., surface site density, adsorption equilibrium constant and crystalline structure) of ferrihydrite and vernadite. These research findings will help assess the geochemical behaviors and environmental fate of trace elements in marine environment.

Keywords: Marine ferromanganese nodules, Arsenate, Molybdate, Host phases, Geochemical behaviors