

## Mechanism of large isotope fractionation of molybdenum (VI) between seawater and ferromanganese oxides

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Various trace elements are contained in ferromanganese crusts and nodules. The distribution of molybdenum (Mo) between seawater and marine ferromanganese oxides is one of the most important processes that influence the concentration of Mo in seawater. In this process, a large mass-dependent isotope fractionation between seawater and ferromanganese oxides was observed, where lighter isotopes of Mo were preferentially incorporated into ferromanganese oxides. The large isotopic fractionation of Mo is most likely caused by geometrical change from tetrahedral (Td) to distorted octahedral (Oh) during adsorption on manganese oxides based on X-ray absorption fine structure (XAFS) spectroscopy. However, the mechanism to form distorted Oh adsorption structure still does not understand.

In this study, we used adsorbed species models of Mo on manganese oxide which relate to a proposed adsorption mechanism and investigated its structural parameters and isotope fractionations by density functional theory (DFT) calculations. Results indicated that the modeled adsorbed species could reasonably explain both highly distorted geometries observed by XAFS spectra and the large isotope fractionation. In consideration of highly distorted adsorbed species with DFT calculation results, we concluded that two elemental properties of Mo(VI), namely  $d^0$ -electronic configuration and appropriate ionic radius, lead to the large isotope fractionation. The former governs the geometrical characteristics of both Td and distorted Oh geometry, whereas the latter restricts its coordination environment.

The specific interaction of molybdate to manganese oxide can explain various natural phenomena: (i) manganese oxide is the host phase of molybdate in marine ferromanganese oxides, though most of negatively-charged ions are preferentially adsorbed on Fe (oxyhydr)oxides, (ii) the large isotope fractionation of molybdenum during its adsorption on natural ferromanganese oxides by the formation of distorted adsorbed species on manganese oxide.

Keywords: molybdenum, ferromanganese oxide, isotope fractionation