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A XAFS study of isotopic fractionation mechanisms of molybdenum and tungsten at solid/water interface

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Recent development of mass spectrometry has revealed isotopic variations for a number of heavy elements in natural environment. However, a large part of the molecular mechanisms of their isotopic fractionation in natural environment have not been understood, yet. We suggest that X-ray absorption fine structure (XAFS) spectroscopy is a promising approach to understand the *non-traditional* stable isotope systems, especially, at the solid/water interface.

Molybdenum (Mo) shows large mass-dependent isotopic fractionation during adsorption on ferromanganese oxides, which is responsible for isotopic composition of Mo in modern oxic seawater. This fractionation process, although its mechanism is still unclear, is the basis of the utility of Mo isotope system as a paleocean redox proxy. We investigated the structure of Mo species on ferromanganese oxides by XAFS to understand the mechanism of its isotopic fractionation during adsorption on natural ferromanganese oxides.

Ferromanganese oxides are aggregates of amorphous Fe (oxyhydr)oxide (ferrihydrite) and Mn oxide (delta-MnO_2). Our XAFS analyses revealed that (i) Mo forms a T_d outer-sphere complex on ferrihydrite, (ii) distorted O_h inner-sphere complexes on delta-MnO_2, and (iii) delta-MnO_2 is the dominant host phase of Mo in the natural ferromanganese oxides [1]. This structural information provides a molecular explanation for preferential adsorption of lighter Mo isotopes on natural ferromanganese oxides that the structural change from T_d $MoO_4{}^{2-}$ ion, major species in seawater, into distorted O_h species sorbed on delta-MnO_2 phase in natural ferromanganese oxides is the cause of observed isotopic fractionation of Mo, which is supported by quantum mechanical insights [2]. The structure of Mo on a series of other crystalline Fe oxides were also revealed by our studies and showed the excellent correlation with the isotopic fractionation of Mo reported in previous studies: the proportion of *Oh* species in Mo surface species become larger along with the degree of isotopic fractionation [3,4]. These relationships between molecular structure and isotopic fractionation imply that isotopic fractionation as the case of Mo could occur for other elements when the symmetry change occurred between dissolved and adsorbed species. We expect that tungsten (W), which is a congener of Mo, could also show isotopic fractionation during adsorption on ferromanganese oxides because it shows symmetry change between dissolved T_d $WO_4{}^{2-}$ ion in seawater and distorted O_h species on ferromanganese oxides as is the case of Mo [5].

Reference

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