

Isotope fractionation analysis based on adsorption structure for group 6 elements on Fe/Mn-(oxyhydr)oxides

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Group 6 elements, chromium (Cr), molybdenum (Mo), and tungsten (W), are important trace elements for geochemistry since they are redox sensitive and have several stable isotopes. In particular, Mo has drawn attention in paleoceanography because its geochemical behavior sharply changes depending on the redox conditions (Anbar, 2004). A fractionation for Mo was observed during the adsorption to manganese oxides, i.e. $\delta^{97/95}\text{Mo} = -1.8\%$ (Wasylenk et al., 2011). On the other hand, Cr did not show an isotope fractionation during the adsorption to Fe-(oxyhydr)oxides (Ellis et al., 2002).

Kashiwabara et al. (2011) suggested that the Mo isotope fractionation at water/metal oxides interface is caused by symmetrical change of molybdate from tetrahedral (*Td*) to octahedral (*Oh*) structure during adsorption by XAFS analysis. However, this fact was not confirmed well. In this study, we tried to understand the isotope fractionation of group 6 elements accompanying with adsorption on Fe/Mn-(oxyhydr)oxides by means of density functional theory (DFT) calculations and information of adsorption structure obtained by XAFS.

Adsorption structures of Cr, Mo, and W oxoanions were analyzed by XAFS for ferrihydrite, goethite, hematite, and $\delta\text{-MnO}_2$ (Kashiwabara et al., 2011 and 2013). Isotope fractionations were estimated using the equation based on mass-dependent isotopic differences in vibrational energies (Bigeleisen and Mayer, 1947) with DFT-calculated vibrational frequencies. The several oxoanion structures of hydrated and adsorbed on mineral surface models were examined for DFT calculations.

The results of XAFS analysis suggested that the adsorption structures for chromate and tungstate have *Td* and *Oh* symmetries, respectively, and molybdate has both *Td* and *Oh* symmetrical adsorption structures with various ratios depending on the minerals. From the DFT calculations, the large isotope fractionation was confirmed by the structural change of oxoanions from *Td* to *Oh* symmetry. The evaluated isotope fractionations for each mineral by DFT calculations combined with structural information by XAFS analysis agree with experimental results well. This fact indicates that the isotope fractionations of group 6 elements through the adsorption on minerals are caused by structural change of oxoanions.

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