

## Isotope fractionation of Mo-like elements during adsorption to ferromanganese oxides

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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 molybdenum (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. The coordination number relates to its ionic radius. Thus, the elements which have similar ionic radius to Mo are expected to show the similar phenomena to Mo, i.e. the large isotope fractionation. Germanium (Ge) and Vanadium (V) can be candidate of such elements because they have similar ionic radius to Mo (Ge(IV):  $r = 0.53 \text{ \AA}$ , V(V):  $r = 0.54 \text{ \AA}$ , and Mo(VI):  $r = 0.59 \text{ \AA}$  for 6-fold coordination). In this study, we examine the adsorption structure of Ge and V on Fe-/Mn-(oxyhydr)oxides by XAFS spectroscopy. Furthermore, the isotope fractionation during adsorption on the minerals is estimated by quantum chemical calculations.

XAFS analysis indicated that the adsorbed species of Ge on Fe- and Mn-(oxyhydr)oxides have Td geometry. On the other hand, the adsorbed structure of V on ferrihydrite is Td whereas that on  $\delta\text{-MnO}_2$  is distorted Oh. This trend of V in adsorbed species is similar to that of Mo. The geometries of hydrated species of Ge and V are Td. Thus, it is expected that a large V isotope fractionation occur during adsorption on Mn oxide, but a small fractionation in the case of Ge. In fact, a large isotope fractionation for V and a small isotope fractionation for Ge were estimated by quantum chemical calculations. This finding indicates that the requirement to show a Mo like large isotope fractionation during adsorption is not only an appropriate ionic radius. Recently, we found that two elemental properties of Mo(VI), namely  $d^0$  electronic configuration and appropriate ionic radius, lead to the large isotope fractionation. In fact, V(V) possesses  $d^0$  electronic configuration, but Ge(IV) does not. Tungsten (W)(VI) also satisfies the two properties and shows a large isotope fractionation during adsorption on Fe-/Mn-(oxyhydr)oxides. Thus, the elements which have the two elemental properties (Mo-like elements) can exhibit a Mo like large isotope fractionation during ferromanganese oxides.

Keywords: molybdenum, ferromanganese oxide, isotope fractionation, quantum chemical calculation, vanadium, germanium