

DFT 計算を用いた水-金属酸化物表面間におけるモリブデンおよびクロムの同位体分別 Isotope fractionations of molybdenum and chromium at the water/metal oxide interfaces by DFT calculation

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The adsorption reaction to ferromanganese oxides is one of the most important processes that considerably influence the behaviors of trace elements in modern oxalic seawater. In particular, understanding of the adsorption reaction is needed to consider the concentration and isotopic composition of molybdenum (Mo) and chromium (Cr) in seawater, since ferromanganese oxides can be important sink of these oxyanions. For Mo, large isotopic fractionation has been suggested between seawater and ferromanganese oxides where the lighter isotopes of Mo were preferentially adsorbed on ferromanganese oxides ($d^{97/95}\text{Mo} = -2.2 \text{ ‰}$). However, the mechanism of this striking isotopic fractionation of Mo during adsorption to ferromanganese oxides is unclear. Recently, it is reported that this large Mo isotope fractionation is caused by the structural change during adsorption based on the experimental evidences (Kashiwabara et al., 2011). On the other hand, theoretical explanations of this large isotopic fractionation have not been established yet although there are many studies performing quantum chemical calculations. Previous studies using quantum chemical calculations only took into account the dissolved chemical species without considering the interaction with the adsorbent surface. In this study, density functional theory (DFT) calculations are conducted to reveal the large isotopic fractionation of Mo during the adsorption, by which we discussed the relationship between adsorption reaction and isotope fractionation.

DFT calculations were performed with the GAUSSIAN 09 program. Structures (inner- or outer-sphere complex) of molybdate and chromate adsorbed on manganese and iron oxides, which cluster used to consider the interaction with the adsorbent surface directly, were determined through the optimization by DFT calculations with a hybrid functional, B3LYP. After this procedure, molybdate or chromate with clusters of the metal oxide clusters at the surface was taken out from the optimized cluster. For this cluster including molybdate or chromate, vibrational analysis was conducted by single point calculation. Finally, isotope fractionation between hydrated molybdate or chromate and those adsorbed on manganese or iron oxides were calculated from vibrational frequencies.

For molybdate, the largest isotopic fractionation factor ($d^{97/95}\text{Mo} = -1.89 \text{ ‰}$) was obtained when Mo formed inner-sphere complex with octahedral coordination. On the other hand, inner-sphere complex with tetrahedral coordination and outer-sphere complex did not show significant isotopic fractionation. These results support Kashiwabara et al. (2011) which suggested that the isotopic fractionation of Mo during the adsorption on ferromanganese oxide is controlled by the change of symmetry around Mo ion. This study suggested that taking into account of the adsorbent in DFT calculation is needed to estimate the isotope fractionation at the water/solid interface. Similar study on chromate adsorption will be also given in the presentation.

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