

## Stable isotope fractionation of tungsten during adsorption on Fe and Mn (oxyhydr)oxides

Teruhiko Kashiwabara

teruhiko-kashiwa@jamstec.go.jp

In the recent decade, molybdenum (Mo) stable isotope has been one of the most popular proxies for global redox conditions in the ancient ocean. Basis of this utility is the large mass-dependent isotopic fractionation of Mo during adsorption on ferromanganese oxides, which controls isotopic composition of Mo in the modern ocean. Given the chemical similarity between Mo and tungsten (W), potential W isotopic fractionation may offer a new proxy for paleoceanic redox conditions. Here, we experimentally investigated stable isotopic fractionation of W during adsorption on Fe and Mn (oxyhydr)oxides, which are key processes in the global ocean budget of this element.

Our adsorption experiments revealed that W isotopes fractionate substantially on both ferrihydrite and  $\gamma$ -MnO<sub>2</sub>: lighter W isotopes are preferentially adsorbed on the both oxides as a result of equilibrium isotopic exchange between dissolved and adsorbed species. Compared with the case of Mo isotopes, fractionation of W isotopes is (i) of comparable magnitude between ferrihydrite and  $\gamma$ -MnO<sub>2</sub>, and (ii) much smaller than that of Mo on  $\gamma$ -MnO<sub>2</sub>. Our previous XAFS observations and newly-performed DFT calculations indicate that the observed W isotopic fractionations are caused by the symmetry change from *Td* WO<sub>4</sub><sup>2-</sup> to distorted *Oh* monomeric W species via formation of

inner-sphere complexes on both ferrihydrite and  $\beta$ -MnO<sub>2</sub>. Our findings suggest the isotopic composition of W in ancient seawater should have evolved in response to the extent of deposition of both Fe and Mn oxides; this is different from Mo isotopes, in which isotopic fractionation is strongly associated with the occurrence of Mn oxides relative to Fe oxides. Thus, combination of Mo and W isotopes would provide more detailed constraints on global paleoredox conditions in the ancient ocean.