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

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In the recent decade, molybdenum (Mo) stable isotope has been one of the most popular proxies for paleoceanic redox conditions. Basis of this utility is the large mass-dependent isotopic fractionation of Mo during adsorption on ferromanganese oxides, which controls isotopic compostion of Mo in the modern ocean[1]. 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[2].

Our adsorption experiments revealed that W isotopes fractionate substantially on both ferrihydrite and δ-MnO_2: 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 δ-MnO_2, and (ii) much smaller than that of Mo on δ-MnO_2. 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_4^{2-} to distorted *Oh* monomeric W species via formation of inner-sphere complexes on both ferrihydrite and δ-MnO_2. 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 [3]. Thus, combination of Mo and W isotopes would provide new insights into paleoceanic redox conditions.

[1] Barling et al. (2001) *Earth Planet. Sci. Lett.* **193**, 447-457. [2] Kashiwabara et al. (2013) *Geochim. Cosmochim. Acta* **106**, 364-378. [3] Kashiwabara et al. (2017) *Geochim. Cosmochim. Acta* **204**, 52-67.