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 composition 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-MnO2: 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-MnO2, and (ii) much smaller than that of Mo on δ-MnO2. Our previous XAFS observations and newly-performed DFT calculations indicate that the observed W isotopic fractionations are caused by the symmetry change from Td WO42− to distorted Oh monomeric W species via formation of inner-sphere complexes on both ferrihydrite and δ-MnO2. 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.