Isotopic Fractionation of Cu and Zn During Sorption by Fe and Mn (hydr)oxides: first-principles theory

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In aquatic environments, the aqueous concentrations of Cu and Zn are strongly controlled by sorption onto iron (hydr)oxides such as goethite (α-FeOOH) and manganese oxides such as birnessite (δ-MnO$_2$). It is hypothesised that sorption of Cu and Zn on these phases should be associated with a significant isotopic fractionation and that this may, for example, explain the difference in isotopic composition of dissolved Cu and Zn in seawater relative to ferromanganese crusts. However, experimental investigations of isotopic fractionation are inconsistent; it appears that the laboratory experiments are achieving chemical equilibrium but not isotopic equilibrium. To resolve this problem, we need an ab initio (quantum mechanical) prediction of the vibrational modes and, hence, reduced isotopic partition functions for Cu and Zn surface complexes on Fe-Mn (hydr)oxides. EXAFS studies show that sorption of Cu and Zn on FeOOH and MnO$_2$ occurs via inner-sphere surface complexation. On goethite, Cu and Zn are sorbed to form bidentate double corner-sharing and edge-sharing complexes with surface oxygens and a coordination number of 5. On birnessite, both Cu and Zn sorb via tridentate complexes over the vacancy sites with a coordination number of 3 to 4. In the work reported here, I calculate the equilibrium isotopic fractionation of surface-complexed Cu and Zn from the relevant vibrational modes of finite clusters (e.g., Cu(H$_2$O)$_3$(OH)$_2$Fe$_2$(OH)$_2$(H$_2$O)$_6$$^{+4}$) used to approximate the surface complexes. Calculations were done using density functional theory with both traditional gradient-corrected exchange-correlation (PBE) and hybrid (B3LYP) functionals. Relative to the Zn(H$_2$O)$_6$$^{+2}$ or Cu(H$_2$O)$_5$$^{+2}$ aquo complexes in the aqueous phase, goethite will preferentially sorb the heavy isotopes of Zn and Cu, but the fractionation ($^{66\text{-}64}\Delta_{Zn}$ or $^{65\text{-}63}\Delta_{Cu}$) is only 0.3 ‰. In contrast, sorption to birnessite will favor the heavy isotope with a fractionation of 1.0 ‰ for Zn. We anticipate a similar value for Cu (work in progress). The strong fractionation associated with sorption to birnessite is mostly driven by the decrease in coordination number. It should be noted that, in natural systems, complexation by organic ligands can shift the fractionation to favor the heavy isotope in the dissolved phase. Laboratory experiments, even when aged for several months, appear to be out of isotopic equilibrium.