

Zn stable isotope fractionation during sorption onto todorokite: A molecular perspective from X-ray absorption spectroscopy and density function theory

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Mineral-solution interface reactions control the mobility and fate of trace metals (e.g., Zn) and may drive their associated isotopic fractionation in earth surface environment, but to understand the coupling between interfacial reactions and isotopic behavior requires a molecular-level understanding of these processes. In this study we investigate Zn stable isotope fractionation during sorption to todorokite as a function of reaction time, pH and Zn concentrations. We show that Zn stable isotope fractionation reaches equilibrium at ~12 h reaction time at pH 6. For Zn concentrations of 0.05 and 0.2 mM, Zn isotopic fractionation between sorbed and aqueous Zn ($\delta^{66}\text{Zn}_{\text{sorbed-aqueous}}$) is around $-0.1 \pm 0.04\text{‰}$ at pH 3-5, and $\delta^{66}\text{Zn}_{\text{sorbed-aqueous}}$ gradually increases from $-0.1 \pm 0.04\text{‰}$ to $0.05 \pm 0.05\text{‰}$ at higher pH 6-8. Extended X-ray absorption fine structure (EXAFS) spectroscopy shows that Zn sorbs to the todorokite surface as an outer-sphere octahedral complex with an average Zn-O interatomic distance of 2.06 Å at pH 3. In contrast Zn is predominantly present as a tetrahedral coordinated structure with a shorter average Zn-O interatomic distance of ~2.00-2.05 Å at pH 6 and 8, suggesting the presence of a mixture of octahedral outer-sphere and tetrahedral inner-sphere surface complexes. Density functional theory calculations suggest that outer-sphere surface complexes exist in the center of the structural tunnels of todorokite, yielding a theoretical Zn isotopic fractionation ($\delta^{66}\text{Zn}_{\text{sorbed-aqueous}}$) of -0.2‰ to -0.3‰ , whereas the tetrahedral inner-sphere surface complex results in a large $\delta^{66}\text{Zn}_{\text{sorbed-aqueous}}$ of $+0.5\text{‰}$ to $+0.8\text{‰}$. Combined laboratory experiments and theoretical calculations demonstrate that different magnitudes of Zn isotopic fractionation are controlled by structural differences in the Zn surface complexes formed on todorokite. These results provide important new constraints for understanding Zn isotope signatures in natural Mn-rich sediments and lead to a more complete understanding of Zn isotopes in the ocean.