

An Inverse Correlation Between Zn Stable Isotope Fractionation and Zn-O Bond Distances Revealed from Synchrotron-based X-ray Absorption Spectroscopy

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Sorption of Zn onto mineral surfaces can lead to notable Zn isotope fractionation, however, the fractionation mechanism remains poorly understood at the molecular scale. In this study, we demonstrate that Zn isotope fractionation ($\Delta^{66}\text{Zn}_{\text{sorbed-aqueous}}$) during Zn sorption onto Al oxide depends on the surface coverage (Γ) and eventually on its bonding structure. At low pH (6.0–6.5) and/or low concentrations (< 0.4 mM), where $\Gamma < 0.8 \mu\text{mol m}^{-2}$, $\Delta^{66}\text{Zn}_{\text{sorbed-aqueous}}$ is $0.47 \pm 0.03\text{‰}$, whereas $\Delta^{66}\text{Zn}_{\text{sorbed-aqueous}}$ decreases to $0.02 \pm 0.07 \text{‰}$ at pH 7.0–8.0 and large Zn concentrations (≥ 0.4 mM), with a high $\Gamma > 1.5 \mu\text{mol m}^{-2}$. Using extended X-ray absorption fine structure (EXAFS) spectroscopy, we elucidated that a Zn–Al layered double hydroxide (LDH) with a Zn–O bond length of 2.06 Å forms at high surface coverage. In contrast, at low surface coverage, the sorbed Zn occurs as a tetrahedrally coordinated inner-sphere surface complex with an average Zn–O interatomic distance of 1.98 Å, suggesting that shorter Zn–O bond distance correlated to the large isotope fractionation.

We further experimentally determined the Zn isotopic fraction during its sorption onto manganese oxides (todorokite and birnessite) and the corresponding Zn–O distances. After summarizing these data with previous studies on other mineral surfaces (e.g., quartz, goethite, ferrihydrite), we reveal that Zn stable isotope fractionation decrease from 0.92 ‰ to -0.46 ‰ when Zn–O distance increases from 1.92 Å to 2.12 Å. This inverse correlation between isotopic fractionation, local bonding structures and solution chemistry would shed light on a fundamental understanding of metal stable isotope geochemistry.