

Novel Zn Stable Isotope Method for Probing Soil Chemical Reaction Kinetics

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Interactions between aqueous Zn and mineral surfaces can lead to notable Zn isotope fractionation, which could be used to track sorption process. In this study, we demonstrate that Zn isotope fractionation ($\Delta^{66}\text{Zn}_{\text{sorbed-aqueous}}$) during Zn sorption onto $\gamma\text{-Al}_2\text{O}_3$ depends on both pH and Zn concentration and ultimately correlates to surface coverage (Γ). At pH values of 6.0–6.5 and/or Zn concentrations of 0.1–0.2 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 values of 7.0–8.0 and Zn concentrations of 0.4–0.8 mM, with a high Γ ranging from 1.5 to 3.2 $\mu\text{mol m}^{-2}$. 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 ($1.5 < \Gamma < 3.2 \mu\text{mol m}^{-2}$). In contrast, at low surface coverage ($\Gamma < 0.8 \mu\text{mol m}^{-2}$), the sorbed Zn occurs as a tetrahedrally coordinated inner-sphere surface complex with an average Zn–O interatomic distance of 1.98 Å. This correlation between isotope fractionation, local bonding structures (i.e., coordination and bond distances), and solution chemistry, allows us to track the Zn sorption kinetics.

We further measured the Zn isotopic fraction as a function of reaction time during its sorption onto $\gamma\text{-Al}_2\text{O}_3$ at pH 7.5, which reveals a change from 0.46 ‰ to 0.05 ‰. This suggests a structural evolution from Zn inner-sphere surface complex to Zn–Al LDH precipitates. In contrast, the Zn isotope signatures remains unchanged (e.g., $\sim 0.47 \text{‰}$) with reaction time at pH 6.0, consistent the surface complexation mechanism. These results demonstrate a great potential of the applications of stable metal isotopes as environmental tracers.