

Zn isotope fractionation sorption during sorption and its implication in understanding for Zn cycling in the Earth surface

WENXIAN GOU

Chengdu University of Technology

Zinc (Zn) is an essential micronutrient involved in various biological processes, but it becomes toxic at elevated concentrations. Its mobility and bioavailability on Earth's surface are largely controlled by sorption at solid-water interfaces. Zn isotopes readily fractionate during sorption, offering a promising tool for tracing Zn cycling. However, the mechanisms driving Zn isotope fractionation during sorption remain poorly understood, limiting its broader applications.

To address this gap, we conducted controlled Zn sorption experiments on aluminum (oxyhydr)oxides—representative of natural Al hydroxides and Al-rich clays. Using experimental probes, modeling, and advanced X-ray absorption fine structure (XAFS) spectroscopy, we quantified Zn isotope fractionation and elucidated the coordination chemistry of sorbed Zn. Our kinetic experiments revealed that Zn isotope fractionation is primarily controlled by equilibrium processes, with transient kinetic effects occurring only in the early stages of sorption. At equilibrium, Zn isotope fractionation is dictated by Zn's coordination chemistry, particularly the Zn–O bond length, which exhibits a linear relationship with isotope fractionation. Furthermore, distinct sorption mechanisms have different Zn–O bond length and accordingly characteristic isotope fractionation signatures: inner-sphere complexation induces a 0.47‰ fractionation, whereas precipitation as Zn–Al layered double hydroxide (LDH) results in negligible fractionation (~0‰). These findings highlight the potential of Zn isotope fractionation as a tracer for distinguishing sorption mechanisms.

Using Zn isotope fractionation as a tracer, we gained deeper insights into the kinetic formation of Zn–Al LDH and the role of silicates in its precipitation. Moreover, discrepancies between experimental and natural Zn isotope fractionation suggest that Zn transport in the environment is influenced by additional processes beyond sorption, such as mineral lattice incorporation. These findings underscore the need for further investigation into the broader controls on Zn isotope behavior in natural systems.