
Zn Isotope Fractionation during Sorption onto Kaolinite

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Abstract

As bio-essential element, Zinc is necessary for growth and reproduction of living organisms. Toxic levels of Zn are frequently observed in highly polluted sites affected by mining or smelting activities. An accurate understanding of Zn biogeochemical cycle is thus required. Over the last two decades, Zn stable isotope signatures have proved effective in tracking Zn sources. But in ecosystems like soils or rivers, interactions between Zn in solution and in minerals can lead to Zn isotope fractionation that may hamper Zn source identification. Zn isotope measurements can help identify the ways in which Zn interacts between solution and solids. Zn isotope signatures reflect both Zn sources and/or in situ processes. To distinguish between these two factors, isotopic fractionation during Zn complexation by reactive phases has to be addressed. Among the three main groups of reactive phases, metal oxides, organic matter, and phyllosilicates, Zn isotopic fractionation factors during adsorption are only known for the first two. In this study, we quantify zinc isotope fractionation during sorption onto kaolinite, by performing experiments under various pH, ionic strength, and total Zn concentrations. A systematic enrichment in heavy Zn isotopes on the surface of kaolinite was measured, with $\Delta^{66}\text{Zn}_{\text{adsorbed/solution}}$ ranging from 0.11 at low pH and low ionic strength to 0.49 at high pH and high ionic strength. Both the measured Zn concentration and its isotopic ratio are correctly described using a thermodynamic sorption model that considers two binding sites: external basal surfaces and edge sites. Based on this modelling approach, two distinct Zn isotopic fractionation factors were calculated: $\Delta^{66}\text{Zn}_{\text{adsorbed/solution}} = 0.18 \pm 0.06$ for ion exchange onto basal sites, and $\Delta^{66}\text{Zn}_{\text{adsorbed/solution}} = 0.49 \pm 0.06$ for specific complexation onto edge sites. These two distinct factors indicate that Zn isotope fractionation is controlled by the chemical composition of the solution.

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