Zn isotope fractionation during sorption onto Al oxide: atomic level understanding from EXAFS

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There is increasing interest in using Zn stable isotope signatures to trace pollution in environments, however, interactions between Zn in solution and in minerals in soils and sediments can lead to notable Zn isotope fractionations. Therefore, it is important to understand the mechanisms underlying Zn isotopic fractionation during its sorption onto soil minerals. In this study, we quantified isotopic fractionation of Zn during its sorption onto Al oxide in experiments of various pH and total Zn concentrations. External precision of $^{66/64}$Zn ratio measurement by MC-ICP-MS is better than 0.06‰, and the total procedural blank of Zn was 4-20 ng. We observed a systematic enrichment in heavy Zn isotopes on the surface of Al oxide relative to aqueous solution, with $\Delta^{66/64}Zn_{sorbed\text{-}solution}$ ranging from 0.50 ± 0.16‰ at low pH (e.g., pH 6) and low concentration (e.g., 0.2 mM) to 0.10 ± 0.02‰ at high pH (e.g., pH 7.5) and high concentration (e.g., 0.8 mM). The difference in Zn fractionation behavior is related to the structural difference between sorbed Zn cations. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy analyses reveal that under high pH conditions Zn is octahedrally coordinated by oxygen atoms, whereas at low pH condition Zn is tetrahedrally coordinated by oxygen atoms. EXAFS data suggest formation of Zn-Al layered double hydroxide (LDH) under high pH and high Zn concentration conditions, and the LDH has a Zn-O bond distance of 2.06 Å. In contrast, under low pH or low Zn concentration conditions, results from EXAFS indicate that sorbed Zn atoms occur as inner-sphere surface complexes, with Zn-O interatomic distance of 1.99 Å. Our results suggest that two distinct mechanisms of Zn isotope fractionation take place during sorption of Zn ions, and the chemistry of the solution (pH, concentration) is the main controlling factor, which should be considered in applications of Zn isotopes to track pollution sources.