

Connecting Zinc Partitioning and Isotope Fractionation during Fe(II)-Catalyzed Recrystallization of Fe(III) Oxide Minerals

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Fe(III) oxide minerals are abundant in soil, sedimentary, and aquatic systems. The biogeochemical cycling of iron creates conditions where aqueous Fe(II) and solid Fe(III) oxides coexist. These may undergo a series of secondary, abiotic reactions largely driven by electron transfer and atom exchange, which involve coupled oxidative Fe(II) adsorption and reductive dissolution of Fe(III) at spatially separate surface sites. These reactions have been shown to cause the self-recrystallization of stable iron oxide minerals, during which trace metals may be incorporated into the iron oxide structure. Because such incorporation involves a change in bonding environment it may fractionate stable isotopes of trace metals. Such fractionations are potential biogeochemical tracers in modern and ancient systems.

We have investigated factors affecting Zn adsorption onto and incorporation into Fe(III) oxide minerals during Fe(II)-catalyzed recrystallization and identified Zn isotopic fractionations associated with this partitioning. Zn was studied because it is a water contaminant and an essential micronutrient and its content in iron oxides has been used as a proxy for past seawater composition. XAFS spectroscopy was employed to quantify the relative amount of Zn adsorption onto and incorporation into hematite and goethite as a function of pH, Fe(II) concentration, and reaction time. It also provided insight into changes in bonding environment between adsorbed and incorporated forms. Zn isotope fractionations were measured using a MC-ICP-MS and related to Zn speciation determined from XAFS spectroscopy.

XAFS spectroscopy shows that an increase in reaction time (5 to 30 days), pH (7 to 8), and concentration of aqueous Fe(II) were all associated with increased Zn incorporation into the goethite structure, but produced little to no incorporation of Zn into hematite. These factors also enriched goethite in isotopically light Zn, suggesting a connection between fractionation and incorporation; hematite exhibited only a slight enrichment in heavy Zn. These results advance our understanding of trace metal cycling and highlight the importance of Fe redox conditions in fractionating metal isotopes in modern and ancient aquatic systems.