

Influence of trace metals on dissolution and Fe(II)_{aq}-promoted recrystallization of iron oxides

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Iron oxides are abundant in soil, sediments, and groundwater aquifers, and they influence the mobility and fate of many geochemically important trace metals through surface sorption and mineral transformation processes. Redox fluctuations can lead to conditions of simultaneous aqueous Fe(II) and solid Fe(III) oxides. Moreover, transition metals such as cobalt (Co), nickel (Ni) and manganese (Mn) frequently co-exist with iron oxides in nature, either in the aqueous phase as dissolved cations, or impurities in the oxide structure.

Effects of trace metals on Fe atom exchange during Fe(II)_{aq}-promoted recrystallization of iron oxides were investigated in this study. In batch reactors, isotopically normal goethite and hematite were exposed to solutions spiked with Fe(II)_{aq} (primarily as ⁵⁷Fe(II)_{aq}) and aqueous Co²⁺, Ni²⁺ or Mn²⁺. Fe(II) sorption and overall aqueous-solid Fe exchange were greatly reduced when aqueous Ni and Co are present. Fe exchange was further suppressed when aqueous Co was pre-sorbed prior to Fe(II)_{aq} addition. Higher concentrations of Co resulted in more diminished Fe atom exchange. Remarkably, the extent of Fe exchange is highly correlated with the extent of Fe sorption for goethite, regardless of the trace metal. These results are consistent with divalent cations passivating Fe atom exchange by occupying Fe sorption sites where Fe exchange could occur.

Experiments were also carried out with trace metal-doped goethite and hematite to understand the effect of solid-phase metal impurities on Fe atom exchange. In contrast to aqueous trace metals, oxides doped with trace metals showed more Fe exchange than pure oxide controls, and the higher metal impurities, the more Fe exchanged over time. The presence of trace metal dopants also improved kinetics of Fe and trace metal release compared to pure oxides within dissolution studies featuring proton-promoted, ligand-promoted, and reductive-ligand-promoted dissolution processes.