

Dynamic Trace Metal Redistribution by Goethite via Redox and Non-Redox Processes

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Iron (oxyhydr)oxide minerals play important roles in controlling the fate of trace metals in modern and ancient biogeochemical systems. Redox interfaces can promote trace metal entrapment in iron (oxyhydr)oxides, inhibiting micronutrient availability, sequestering contaminants, and producing compositional and isotopic proxies for past conditions. In contrast, iron (oxyhydr)oxides control trace metal fate primarily via adsorption in systems free of active redox processes. Here, we explore two unexpected routes of trace metal redistribution by the iron oxyhydroxide goethite in the absence and presence of redox processes using trace metal isotope exchange methods.

The trace metals nickel, zinc, and cadmium display partially-irreversible binding to goethite after 1 to 4 months of aging. The non-labile fraction of each metal scales with ionic radius, consistent with incorporation into goethite, despite the absence of any catalyst for recrystallization, such as dissolved Fe(II). Surface defects, specifically iron vacancies, may be responsible for this immobilization.

Application of coupled iron and nickel stable isotope tracers shows that nickel incorporation and release during Fe(II)-promoted goethite recrystallization are simultaneous and bidirectional. Surprisingly, 7 to 16% of the goethite-bound nickel exchanges with the dissolved metal pool despite only 3 to 4% of iron atom exchange. Further, these systems display an equilibrium-like control on dissolved nickel concentrations, settling at $\sim 17 \mu\text{M}$ after 30 days regardless of the amount initially present (5 to 40 μM Ni).

These observations demonstrate that there are non-redox mechanisms to drive trace metal entrapment in goethite structures, likely at surface defects. In addition, redox-mediated iron (oxyhydr)oxide recrystallization enables extensive mixing of solid-phase and dissolved metal pools, with net entrapment or release determined by an equilibrium-like relationship. Coupling of these surface- and recrystallization-mediated redistribution pathways for trace metals at redox interfaces may induce dynamic changes in micronutrient and contaminant bioavailability. Further, trace metal concentrations and isotopic compositions recorded by iron (oxyhydr)oxides may reflect irreversibly processes or be rapidly overprinted by later atom and isotope exchange and are thus questionable recorders of initial environmental conditions.