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Chapter 4. The timescales of mineral redox reactions

by B. Gilbert and G.A. Waychunas

Redox-reactive minerals can serve as electron donors or acceptors for abiotic reactants or microbial metabolic processes, and hence can play important roles in terrestrial and aquatic environments, particularly if their reaction rates are comparable to those of other biogeochemical processes. Under such circumstances, their reactions can control metal and contaminant bioavailability and change the permeability of soils and sediments. While the thermodynamic driving force for a mineral redox reaction is frequently a good predictor of relative rates of reaction, there are many examples in which kinetic factors limit reaction rate. Understanding the thermodynamic and kinetic aspects of mineral reaction rates, and their sensitivity to environmental conditions such as temperature or pH, is important for anticipating the biogeochemical evolution of natural environments subjected to change. Achieving this goal requires knowledge of the reaction pathway, the timescales of intermediate steps, and the lifetimes of metastable reaction states. Mineral redox reactions proceed through a combination of steps that can include electron and proton transfer, the breaking or formation of bonds, and mineral dissolution or phase transformation. The combination of conventional kinetics approaches, newly-developed ultrafast time-resolved methods and molecular simulation can provide elucidation of such complex reaction pathways. This chapter summarizes key concepts in mineral and interfacial redox reactions with illustrations from the rich geochemistry of iron and ironbearing minerals.

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