

Impact of Sulfide Supply on Ferric (oxyhydr)oxides Sulfidization and Pyrite Formation

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Sulfidation of ferric (oxyhydr)oxides is a key biogeochemical process in anoxic environments, driving the cycling of Fe and S, and further influencing the mobility of Fe-associated organic compounds and nutrients. The ferric-hydroxide-surface (FHS) pathway also enables fast pyrite formation within a time scale of days or weeks through surface-bound precursors $>\text{Fe}^{\text{II}}\text{S}^{2-}$.^[1] However, in natural environments, ferric (oxyhydr)oxides are often microbially produced and associated with organic matter (OM), while sulfide (S(-II)) fluxes are primarily regulated by sulfate-reducing bacteria rather than single-pulse additions often used in laboratory studies. Here, we compared sulfidization kinetics and pyrite formation rates by reacting abiotic ferrihydrite, goethite and biogenic Fe(III) (oxyhydr)oxides (a mixture of ferrihydrite, goethite, OM, cells, and sorbed phosphate) with aqueous sulfide in an anoxic glove box at pH 6. Sulfide was supplied either as a single 10 mM S(-II) pulse or as multiple 0.5 mM d⁻¹ pulses over 20 days (final Fe(III):S(-II) = 4:1). Changes in Fe and S concentrations and speciation in the aqueous and solid phases were examined through a combination of wet chemistry, Raman micro-spectroscopy, X-ray diffraction (XRD) and Fe X-ray absorption spectroscopy (EXAFS). Our results show that ferrihydrite transformed primarily into lepidocrocite, goethite, and pyrite under single-pulsed sulfide addition, whereas goethite and pyrite dominated under multiple-pulsed conditions. Pyrite formed in both ferrihydrite and goethite treatments under two S(-II) supply modes. Rietveld fitting of XRD patterns and Fe K-edge EXAFS spectra revealed that continuous multiple-sulfide supply mode delayed pyrite formation. However, no pyrite was detected in experiments with biogenic Fe(III) (oxyhydr)oxides, where sulfide was instead converted to zero-valent sulfur. Additionally, phosphate from cultivation medium was scavenged as vivianite. This suggests that the presence of OM and/or phosphate in the biogenic Fe(III) mineral inhibited pyrite formation perhaps by blocking reactive surface sites. These findings highlight the importance of surface-associated components (e.g., OM and phosphate) and sulfide supply rates in controlling pyritization, with implications for Fe and S cycling in reduced environments. [1] M. Wan et al., 2017, *Geochim. Cosmochim. Acta*, 217, 334-348.