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The Role of Fe(III) Mineralogy on the Morphology of Biogenic Pyrite

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Despite being the most abundant iron sulfide mineral on Earth, the formation of biogenic pyrite (FeS_2) is still not completely understood. In anoxic environments, sulfidation of Fe(III) (oxyhydr)oxides leads to Fe(III) reduction and the formation of iron(II) sulfide minerals. The metastable iron sulfide mineral mackinawite (FeS) is the first product of this reaction. Its transformation to the thermodynamically stable end product pyrite is controlled by the reactivity of the initial Fe(III) mineralogy and solution chemistry[1]. Here we tested ferrihydrite ($Fe(OH)_3$), goethite (α-FeOOH), a mixture of biogenic Fe(III) (oxyhydr)oxides, and magnetite (Fe_3O_4) in the presence of elemental sulfur for biogenic pyrite formation by *Geobacter sulfurreducens*.

The reactivity of Fe(III) minerals and pyritization rates were followed by sequential Fe extraction. We observed that ferrihydrite was the most reactive Fe(III) mineral with respect to Fe(III) reduction rates. However, pyritization kinetics were faster in the goethite experiments. From this we conclude that the reactivity of the initial Fe(III) mineral is not directly related to the pyritization rate. Pyrite formation in the experiments was confirmed by µXRD, ^{57}Fe Mössbauer spectroscopy, and S-XANES (X-ray absorption near edge structure) analyses. SEM (Scanning Electron Microscopy) analyses revealed spherical, euhedral, and framboid-like particles in the setups with the different Fe minerals. Slower pyritization kinetics resulted in spherulitic pyrite formation whereas faster kinetics led to framboid-like morphology. Our current and future work will help us to understand better biogenic pyrite formation and determine the factors influencing pyrite morphology.

1. Zhang, S. Peiffer, S. Liao, X. Yang Z. Ma, X. He, D. Sulfidation of ferric (hydr)oxides and its implication on contaminants transformation: a review. *Sci. Total. Environ.* **816**, 151574 *(2022).*