

Influence of microbial biomass on abiogenic and microbial magnetite formation

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Magnetite (Fe₃O₄) in terrestrial and marine sediments can form through both microbial and abiotic transformations of Fe(III) (oxyhydr)oxides (e.g. ferrihydrite, Fh). However, it is unknown whether biogenic Fe(III) minerals, which contain a significant amount of microbial biomass, can also transform to Fe₃O₄. We have examined whether Fe₃O₄ can be formed via abiotic reduction (aqueous Fe(II)) or biotic reduction (Fe(III)-reducing microorganism *Shewanella oneidensis* MR-1) through transformation of four types of Fh: 1) abiogenic Fh; 2) abiogenic Fh co-precipitated with humic acid (Fh-HA); 3) biogenic Fh produced by the phototrophic Fe(II)-oxidizer *Rhodobacter ferrooxidans* SW2, and 4) biogenic Fh treated with bleach to remove microbial biomass (Fh-bio-NaOCl). We found that the Fe(II)-catalyzed abiotic transformation of abiogenic Fh and Fh-bio-NaOCl led to complete transformation of Fh to magnetite; however, the transformations of Fh-HA and biogenic Fh to magnetite were incomplete. We hypothesize that the microbial biomass in biogenic Fh delayed and/or blocked the reaction between Fh and Fe(II)_{aq}, resulting in a stabilization of Fh. Of the Fh phases that did react with Fe(II)_{aq}, the transformation was faster compared to microbial transformation, implying that the initial Fe(II)_{aq} concentration plays a dominant role in the rate of magnetite formation from Fh. Conversely, all Fh phases were transformed into magnetite to varying degrees during microbial reduction, suggesting that Fh remains bioavailable even when associated with microbial biomass. These results suggest microbial biomass associated with biogenic Fh may influence secondary mineralization pathways, providing insights into biogeochemical cycling of Fe in both modern and ancient environments.