Geochemical Controls on Microbial Iron(III) Mineral Transformation

Amstätter, Katja[1] Kappler, Andreas[1]
[1]University of Tübingen, Geomicrobiology, Sigwartstr. 10, 72076 Tübingen

Microorganisms change the mineralogy of iron minerals by catalyzing Fe(II) oxidation or Fe(III) reduction. Mineral transformation influences magnetic properties of soils, porosity of aquifers, nutrient availability, and the reactivity of iron minerals in natural environments. In this study we followed the transformation of the poorly crystalline ferric hydroxide 2-line ferrihydrite during growth of the iron-reducing bacterium *Shewanella oneidensis* MR-1 under various geochemical conditions. Data from sequential extractions, μ-X-ray diffraction analysis and Mössbauer spectroscopy show that the identity of the minerals formed and their crystallinity strongly depend on the initial concentration of ferrihydrite, the local ratio of Fe(II) to Fe(III) and the presence of phosphate and natural organic matter (humic substances). Microbial reduction rates and mineral (trans-)formation are strongly influenced by the presence of humic substances. Depending on humic substance concentration, these organic molecules can either sorb to iron minerals and block surface sites for electron transfer or function as dissolved electron mediators between cells and the mineral surface, stimulating the iron mineral reduction. The interaction of adsorbed and dissolved humic substances plays a key role for the competition between inhibiting or accelerating effects. Additionally, in the presence of humic substances we observed the formation of less crystalline iron phases compared to minerals formed in the absence of humic substances. A better understanding of these microbially catalyzed mineral transformations helps to evaluate and predict secondary redox reactions of iron minerals in natural environments.

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