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Time-resolved synchrotron powder X-ray diffraction study of magnetite formation by the Fe(III)-reducing bacterium *Geobacter sulfurreducens*

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Abstract

The Fe(III)-reducing bacterium *Geobacter sulfurreducens* produces nanometer-sized magnetite by transferring electrons from organic matter or hydrogen to ferrihydrite, resulting in the reductive transformation of the ferrihydrite to magnetite, and the generation of ATP for growth. Electron transfer can occur by direct contact between the cell surface and the mineral or via a soluble "electron shuttle," for example a quinone-containing humic species. The minerals produced at different stages of ferrihydrite reduction during two experiments, one with and one without the humic analog anthraquinone-2, 6-disulphonate (AQDS), were measured using high-resolution synchrotron powder X-ray diffraction. Amorphous 2-line ferrihydrite converts to goethite, then to a mixture of goethite and magnetite, and finally to magnetite. Samples with and without AQDS showed the same general mineralogical trends, and the rate of reaction was faster in the presence of AQDS. In addition, two transient minerals structurally similar to goethite and magnetite were observed to form as intermediates between ferrihydrite and goethite and goethite and magnetite, but only in samples produced in the absence of the electron shuttle. These transient minerals were named proto-goethite and proto-magnetite. Proto-goethite has a shorter *c*-axis [4.467(20) Å] than crystalline goethite, a function of size (<2 nm) where quantum properties prevail.

Proto-magnetite is identified by long tetrahedral (2.113 Å) and short octahedral (1.943 Å) Fe-O bonds compared to stoichiometric magnetite, possibly indicative of a coordination crossover caused by charge density [Fe(II)] migration to tetrahedral sites. Fe(II) in solution or sorbed to the mineral surface is considered to be the catalyst causing the mineral transformations. The Fe(II) is thought to form predominantly from the reductive dissolution of 2-line ferrihydrite by *G. sulfurreducens*.

Keywords: Fe(III)-reduction, magnetite, biogenic transformation, ferrihydrite, diffraction, goethite, *Geobacter*