Ferrous hydroxy carbonate is a stable transformation product of biogenic magnetite

**LETTER**

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**ABSTRACT**

An ~1:1 mixture of ferrihydrite and nanocrystalline akaganéite (β-FeOOH; 10–15 nm) was incubated with *Shewanella putrefaciens* (strain CN32) under anoxic conditions with lactate as an electron donor and anthraquinone-2,6-disulfonate (AQDS) as an electron shuttle. The incubation was carried out in a 1,4-piperazinediethanesulfonic acid (PIPES)-buffered medium, without PO₄⁻ at circumneutral pH. Iron reduction was measured as a function of time (as determined by 0.5 N HCl extraction), and solids were characterized by X-ray diffraction (XRD), electron microscopy, and Mössbauer spectroscopy. The biogenic reduction of Fe⁺⁺ was rapid; with 60% of the total Fe (FeTOT) reduced in one day. Only an additional 10% of FeTOT was reduced over the next three years. A fine-grained (~10 nm), cation-excess (CE) magnetite with an Fe⁺⁺/FeTOT ratio of 0.5–0.6 was the sole biogenic product after one day of incubation. The CE magnetite was unstable and partially transformed to micrometer-sized ferrous hydroxy carbonate [FHC; Fe₂(OH)₂CO₃(s)], a rosasite-type mineral, with time. Ferrous hydroxy carbonate dominated the mineral composition of the three year incubated sample. The Fe⁺⁺/FeTOT ratio of the residual CE magnetite after three years of incubation was lower than the day 1 sample and was close to that of the stoichiometric magnetite (0.33). To the best of our knowledge, this is the first report of biogenic FHC, and was only reported twice in literature but in a very different context. Ferrous hydroxy carbonate appeared to form by slow reaction of microbially produced carbonate with Fe⁺⁺-excess magnetite. The FHC may be an overlooked mineral phase that explains the infrequent occurrence of fine-grained, biogenic magnetite in anoxic sediments.

**INTRODUCTION**

Dissimilatory Fe⁺⁺-reducing bacteria (DIRB) catalyze the reduction of Fe⁺⁺ to Fe⁺⁺ in soils, sediments, and subsurface materials (Lovley 1993). These organisms utilize Fe⁺⁺ oxides and other Fe⁺⁺-containing minerals as electron acceptors for respiration (Nealson and Little 1997) and transform them to other mineral phases that are reactive with inorganic and organic solutes. Poorly crystalline Fe⁺⁺-oxides, including ferrihydrite and nanooxide (Jambor and Dutrizac 1998) and nanooxide (van der Zee et al. 2003), are the most bioavailable Fe⁺⁺ solid-phase for DIRB. A variety of biomineralization products result from the interaction of DIRB with Fe⁺⁺ oxides, including magnetite, green rust (GR), vivianite, and siderite under specific conditions (Fredrickson et al. 1998). Biogenic Fe⁺⁺ flux rate, the presence of sorbed/coprecipitated ions, medium composition, electron donor and acceptor concentrations, crystallinity and type of Fe⁺⁺-oxide are all important factors influencing the nature of biomineralization products (Zachara et al. 2002; Kukkadapu et al. 2004).

Although magnetite is a commonly observed laboratory transformation product of Fe⁺⁺ oxides by DIRB, there are few reports of biogenic, fine-grained magnetite in soils, sediments, and subsurface materials that have experienced in-situ dissimilatory Fe reduction (Gibbs-Eggar et al. 1999). The reasons for this absence of fine-grained magnetite in natural settings are unknown. Could magnetite be unstable under Fe-reducing conditions due to small size or other properties resulting from biosynthesis? Recently, we noted that the Fe⁺⁺/FeTOT ratio of a fine-grained (10 nm), biogenic magnetite produced by DIRB (Kukkadapu et al. 2004), was in excess (0.5–0.6) of stoichiometric magnetite (0.33; e.g., Greenwood and Gibb 1979) and intracellular magnetite produced by magnetotactic bacteria (Sparks et al. 1990). Biogenic, intracellular magnetites are larger than those produced by DIRB (40–50 nm); they are stoichiometric and single domain in nature, and are more stable as they persist for long periods as microfossils in certain environments (Chang et al. 1987; Vali et al. 1987; Sparks et al. 1990).

Fe⁺⁺-excess magnetites [termed as hyper-, or cation-excess (CE) magnetite], of varying Fe⁺⁺/FeTOT ratio (0.4–0.6) have been reported in the materials/catalysis research areas (e.g., McCammon et al. 1986; Tamaura and Tahata 1990; Tamaura et al. 1994). Cation-excess magnetites are strong reductants and promote the complete reduction of carbon dioxide to carbon (Tamura and Tahata 1990). Allen et al. (2001) recently speculated that CE magnetites are important in nature, playing a significant role in carbon reduction in marine geothermal systems where magnetite formation is rapid.

The high reactivity of CE magnetite for oxidized carbon compounds compared to stoichiometric magnetite and its lack...