

LETTER

Ferrous hydroxy carbonate is a stable transformation product of biogenic magnetite

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ABSTRACT

An ~1:1 mixture of ferrihydrite and nanocrystalline akaganeite (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 PO_4^{3-} 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^{3+} was rapid; with 60% of the total Fe (Fe_{TOT}) reduced in one day. Only an additional 10% of Fe_{TOT} was reduced over the next three years. A fine-grained (~10 nm), cation-excess (CE) magnetite with an $\text{Fe}^{2+}/\text{Fe}_{\text{TOT}}$ 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; $\text{Fe}_2(\text{OH})_2\text{CO}_{3(s)}$], a roasite-type mineral, with time. Ferrous hydroxy carbonate dominated the mineral composition of the three year incubated sample. The $\text{Fe}^{2+}/\text{Fe}_{\text{TOT}}$ 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^{2+} -excess magnetite. The FHC may be an overlooked mineral phase that explains the infrequent occurrence of fine-grained, biogenic magnetite in anoxic sediments.