

# Geochemical study of the microbial and inorganic precipitation of magnetite and siderite at low temperatures

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The origin, mechanism, and fate of fine-grained iron-oxides (magnetite, hematite) and Fe-rich carbonates (siderite, ankerite) in nature are crucial to our understanding of numerous biogeochemical processes and remanent magnetization in the upper crust of the Earth. In recent years, we became increasingly aware of the importance of iron biomineralization in nature, including implications for the atmospheric evolution of the Earth and possible life on Mars. In order to better understand natural processes of iron-oxide and carbonate formation, we have been studying details of the mechanisms and processes of the microbial and inorganic precipitation of magnetite and siderite under well-controlled laboratory conditions (physical chem-

istry, microbiology, mineralogy, and isotopic fractionation). A particular interest in our study is how to distinguish microbial and inorganic origins of fine-grained magnetite and siderite in nature, if possible. This article is a progress report of our activities to date.

## Experimental

Magnetite-rich iron oxides and siderite were precipitated *in vitro* between 45 and 70°C, mediated by thermophilic dissimilatory iron-reducing and fermentative bacteria obtained from deep subsurface environments (Liu *et al.*, 1997; Zhang *et al.*, 1997).

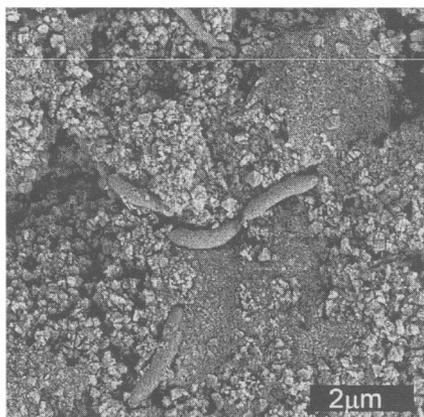


FIG. 1. SEM image of microbially precipitated magnetite-rich iron oxides with rod-shaped bacterial cells at 60°C.

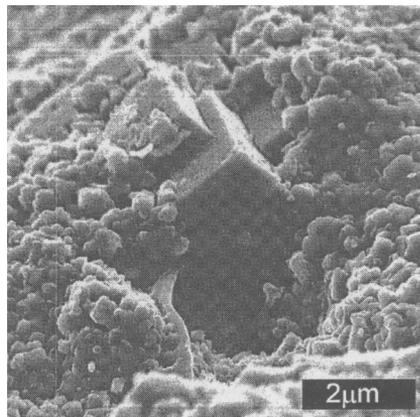


FIG. 2. SEM image of microbially precipitated siderite crystal embedded in fine-grained magnetite-rich iron oxides at 65°C.

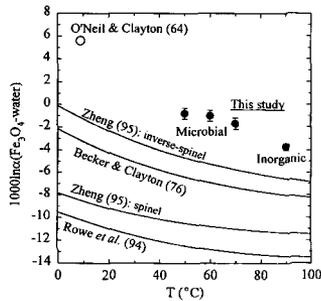


FIG. 3. Oxygen isotope fractionation between magnetite and water at low temperatures.

Two iron-reducing bacteria investigated in this study grow using glucose, acetate, or hydrogen as an electron donor and amorphous Fe(III)-oxyhydroxide as an electron acceptor. Well-crystallized, nm-sized (10–100 nm), magnetite-rich (64–88 wt.%) iron oxides were precipitated extracellularly after a few days of incubation (Fig. 1). A few large crystals of magnetite exhibited a well-developed octahedron. X-ray diffractometry and chemical analyses showed that small, various amounts of maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) were also precipitated. In the presence of  $\text{CO}_2(\text{aq})$ , thermophilic fermentative and iron-reducing bacteria facilitated the precipitation of cubic or rhombohedral siderite (Fig. 2). The Eh, pH, and  $\text{pCO}_2$  values during the incubation were within the stability fields of these minerals.

Magnetite was also precipitated inorganically at 90°C by slowly adding a solution of  $\text{KNO}_3/\text{KOH}$  to a solution of  $\text{FeCl}_2$ . Black, fine-grained (10–100 nm) magnetite was formed instantaneously. The size and shape of the inorganic magnetite were similar to those of the microbial magnetite.

## Results and discussion

Oxygen isotope fractionation during the precipitation of magnetite-rich iron oxides mediated by the two different strains of thermophilic bacteria was reproducible and consistent with each other at 50–70°C. The magnetite is slightly depleted in  $^{18}\text{O}$  compared to the water, and a slight temperature dependence was also observed (Fig. 3). Our experiments of inorganic precipitation of magnetite at 90°C yielded a fractionation factor consistent with those of microbially precipitated magnetite. Our data of microbial and inorganic magnetite-water fractionation are more positive than theoretical or empirical equations in the literature, which grossly disagree with each other (Fig. 3). Results obtained from magnetite ‘teeth’ from the mollusk *Cryptochiton stelleri* (O’Neil and Clayton,

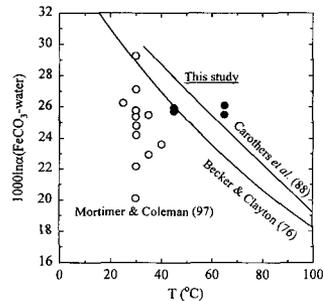


FIG. 4. Oxygen isotope fractionation between siderite and water at low temperatures.

1964) and magnetite formed intracellularly in a magnetotactic bacterium at 27°C (Mandernack *et al.*, 1997) are also consistent with our data. Although it remains unanswered whether the magnetite precipitated biologically and inorganically in this study and from the literature was in isotopic equilibrium with the water, these results strongly suggest that the theoretical/empirical equations of magnetite-water fractionation in the literature are not applicable to low temperature natural environments.

Mortimer and Coleman (1997) reported a wide range of oxygen isotope fractionation during the precipitation of siderite mediated by a mesophilic dissimilatory iron-reducing bacterium (Fig. 4). Their values of siderite-water fractionation were systematically lower than calculated and measured values for inorganic precipitation (Fig. 4). Our preliminary results show that oxygen isotope fractionation during the precipitation of siderite facilitated by a thermophilic fermentative bacterium is reproducible and nearly constant at 45 and 65°C. The observed difference between the two different strains of bacteria could be a biological effect, and is currently under investigation.

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