

# Mineral ecophysiological data provide growing evidence for microbial activity in banded-iron formations

Yi-Liang Li<sup>1</sup>, Kurt O. Konhauser<sup>2</sup>, David R. Cole<sup>3</sup>, and Tommy J. Phelps<sup>4</sup>

<sup>1</sup>Department of Earth Sciences and School of Biological Sciences, University of Hong Kong, Hong Kong, China

<sup>2</sup>Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta T6G 2E3, Canada

<sup>3</sup>School of Earth Sciences, Ohio State University, Columbus, Ohio 43210, USA

<sup>4</sup>Bioscience Division, Oak Ridge National Laboratory, P.O. Box 2008 MS6036, Oak Ridge, Tennessee 37831, USA

## ABSTRACT

**The phosphorus composition of banded-iron formations (BIFs) has been used as a proxy for Precambrian seawater composition and the paleoredox state of Earth's surface environment. However, it is unclear whether the phosphorus in BIFs originally entered the sediment as a sorbed component of the iron oxyhydroxide particles, or whether it was incorporated into the biomass of marine phytoplankton. We conducted high-resolution mineral analyses and report here the first detection of an Fe(III) acetate salt, as well as nanocrystals of apatite in association with magnetite, in the 2.48 Ga Dales Gorge Member of the Brockman Iron Formation (a BIF), Hamersley, Western Australia. The clusters of apatite are similar in size and morphology to biogenic apatite crystals resulting from biomass decay in Phanerozoic marine sediments, while the formation of an Fe(III) acetate salt and magnetite not only implies the original presence of biomass in the BIF sediments, but also that organic carbon likely served as an electron donor during bacterial Fe(III) reduction. This study is important because it suggests that phytoplankton may have played a key role in the transfer of phosphorus (and other trace elements) from the photic zone to the seafloor.**

## INTRODUCTION

Banded-iron formations (BIFs) are iron-rich (~20–40 wt%) and siliceous (~40–60 wt% SiO<sub>2</sub>) marine sedimentary deposits that precipitated throughout much of the Precambrian. It is generally agreed that the minerals now present in BIFs (chert, hematite, magnetite, carbonates, and ferrous silicates) are not primary, but rather reflect both diagenetic and metamorphic overprinting of some combination of ferric oxyhydroxide, amorphous silica, and ferrous silica and carbonate gels (Klein, 2005). The mechanism by which Fe(II) was initially oxidized to form the ferric iron component in BIFs is still poorly constrained, but almost certainly involved either direct or indirect oxidation via marine bacterial photosynthesis (Cloud, 1965; Konhauser et al., 2002; Kappler et al., 2005). The resulting biomass was then deposited along with the ferric iron-rich sediment to the seafloor, where it served as an electron donor for subsequent metabolic reactions, including Fe(III) reduction (e.g., Johnson et al., 2008) and methanogenesis (Konhauser et al., 2005). Such processes not only account for the extremely low content of organic carbon present in BIFs, but they also explain the presence of some reduced secondary mineral phases in BIFs, such as magnetite and siderite.

Pervasive postdepositional alteration, however, has hindered our understanding of primary microbial productivity of the ocean at the time of BIF deposition and how much biomass settled out with BIF sediments. For example, it has been suggested that during ferric oxyhydroxide deposition from the water column, the highly reactive iron particles could have adsorbed significant quantities of dissolved phosphate from seawater, thereby reducing its concentration to values ~20%–25% of present-day levels (Bjerrum and Canfield, 2002). This reduction in available phosphate would have severely constrained primary phytoplankton productivity during times of BIF sedimentation. In contrast, in Konhauser et al. (2007), it was experimentally demonstrated that dissolved silica, which attained

elevated concentrations in the Archean ocean (Maliva et al., 2005), could compete with phosphate for sorption sites on iron oxyhydroxides such that ferric particle deposition might not be an important pathway for phosphorus uptake. Alternatively, biological uptake of nutrients and their incorporation into microbial biomass might have been the primary mechanism for transferring solutes from the water column to the bottom sediments (Konhauser et al., 2002).

Without fossil evidence in BIFs, biogenic features associated with the mineralogy might provide indirect evidence for microbial activity during its deposition. For example, the enzymatic reduction of Fe(III) coupled to the oxidation of organic substrates was proposed more than two decades ago to explain the genesis of magnetite in BIFs (e.g., Walker, 1987). Certainly the capacity of extant hyperthermophilic *Bacteria* and *Archaea* (that branch deeply in the universal phylogenetic tree) to reduce Fe(III) (Vargas et al., 1998) and the recent observations of highly negative  $\delta^{56}\text{Fe}$  values in magnetite-rich BIFs with comparable negative fractionations, as observed in experimental culture with dissimilatory Fe(III)-reducing bacteria (DIRB) (Johnson et al., 2008), point toward the antiquity of such an anaerobic respiratory pathway. Moreover, the redox conditions, likely abundance of phytoplankton biomass, and the availability of Fe(III) in ancient ocean sediments were quite suitable for promoting Fe(III)-reducing microbial activity (e.g., Konhauser et al., 2005). Similarly, the presence of apatite and graphite in highly metamorphosed Paleoproterozoic BIFs has recently been interpreted to represent diagenetically altered biomass and, importantly, that diagenetic mineral associations can be preserved through metamorphism up to the amphibolite facies (Papineau et al., 2010).

## METHODS

Magnetite from BIF was extracted and purified by applying a magnet to a ground sample suspended in methanol (for details of the magnetite samples, and pretreatment methods, see the GSA Data Repository<sup>1</sup>). Thermochemical synthesized magnetite was prepared according to methods in Cornell and Schwertmann (1996). Various DIRB were cultured to transform hydrous ferric oxide (ferrihydrite) to magnetite. All *Shewanella* species were incubated at 15–30 °C with ferrihydrite as the electron acceptor and lactate as the electron donor. *Geobacter metallireducens* strain GS-15 was incubated at 30 °C with ferrihydrite as electron acceptor and acetate as electron donor. *Thermoanaerobacter* sp. strains TOR-39, M3, and C1 were incubated at 55 °C with ferrihydrite as the electron acceptor and glucose as the electron donor.

Weighed purified samples were dissolved in 6 M HCl overnight in bottles sealed by butyl rubber stoppers. The solutions were then titrated with 0.3 M K<sub>2</sub>HPO<sub>4</sub> solution to remove iron as white precipitates of Fe(II) and Fe(III) phosphates. The solutions were then filtered by 0.22 μm filter and analyzed for acetate by methods described by Bergmeyer and Möllering (1974) and the protocol provided by R-Biopharm AG

<sup>1</sup>GSA Data Repository item 2011217, details of the magnetite samples shown in Figures 1–3, the pretreatment of samples for enzymatic analysis, Table DR1 (parameters of BIF samples), and Figure DR1–DR3, is available online at [www.geosociety.org/pubs/ft2011.htm](http://www.geosociety.org/pubs/ft2011.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

(www.r-biopharm.com) measuring the absorbance at 340 nm on the spectrophotometer for the formation of NADH (reduced nicotinamide adenine dinucleotide; Bergmeyer and Möllering, 1974).

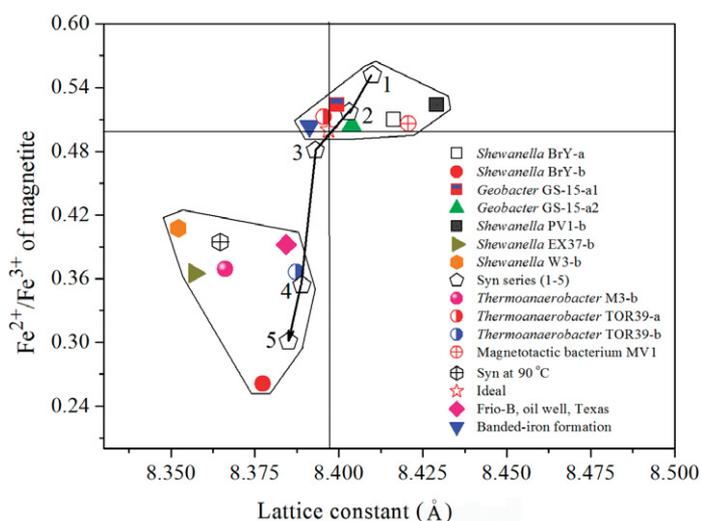
Mössbauer spectroscopy (MS) and X-ray diffraction (XRD) measurements were as described by Li et al. (2009). Infrared spectra were obtained by a Nicolet 5700 Fourier transmission infrared spectroscopy (FTIR) spectrometer equipped with a continuum infrared microscopy. Tecnai G2 20 S-TWIN (STEM) equipped with electron dispersive spectroscopy (EDS) was used to take images and perform selected area electron diffraction (SAED) analysis of fine particles.

For the preparation of Fe(III) acetate salt, we dissolved 10 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 150 mL of distilled water. The solution was then titrated with 28%  $\text{NH}_3 \cdot \text{H}_2\text{O}$  until pH 9.0, and showed the formation of dark, grayish-brown precipitate. The precipitate was washed with pure water to remove residual chlorine. The pure ferric hydroxide was dried at 40 °C for 6 h. The dried powder was dispersed in 10 mL acetate and then stirred for up to 16 h. The products were dried in a vacuum oven at 40 °C for 12 h. The product was identified by FTIR.

## RESULTS AND DISCUSSION

The BIF sample for this study comes from the Dales Gorge Member of the Brockman Iron Formation, Western Australia (Pecoits et al., 2009). It has an age of 2.48 Ga (Pickard, 2002) and underwent low-grade metamorphism over a temperature range of 60–160 °C (Gole, 1980; Kaufman et al., 1990). We discovered three new signatures in the BIF that are likely the result of microbial activity: (1) magnetite crystals that are analogous to modern biogenic magnetite in crystallochemistry, (2) (Ca, Sr) apatite nanoparticles that are intergrown with magnetite, and (3) the presence of Fe(III) acetate salt in both BIF and in association with the magnetite formed in cultures with Fe(III)-reducing bacteria.

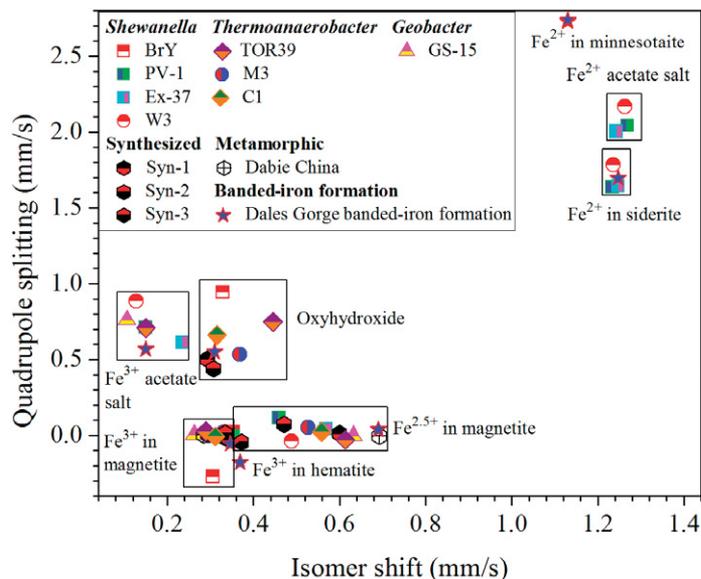
The XRD-based lattice constants and MS-derived  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios are compared in Figure 1 between BIF magnetite and biogenic magnetite crystals collected from various DIRB cultures and those with the other sources. Magnetite crystals of abiotic origin, such as those synthesized (syn) by thermochemical methods previously reported (Zhang et al.,



**Figure 1.** Lattice constant versus  $\text{Fe}^{2+}/\text{Fe}^{3+}$  stoichiometry of magnetite crystallites. Unaltered biogenic magnetite crystallites are labeled by “-a”; biogenic but degenerated (Li et al., 2009) magnetite crystals are labeled by “-b”. Samples 1–5 represent continuous oxidation of synthesized,  $\text{Fe}^{2+}$ -excess magnetite from Zhang et al. (2000). Ideal composition and lattice constant of magnetite is from Zhang and Satpathy (1991). Frio-B magnetite is from petroleum well described by Kharaka et al. (2006). GS-15-a2 and MV1 were from Sparks et al. (1990).

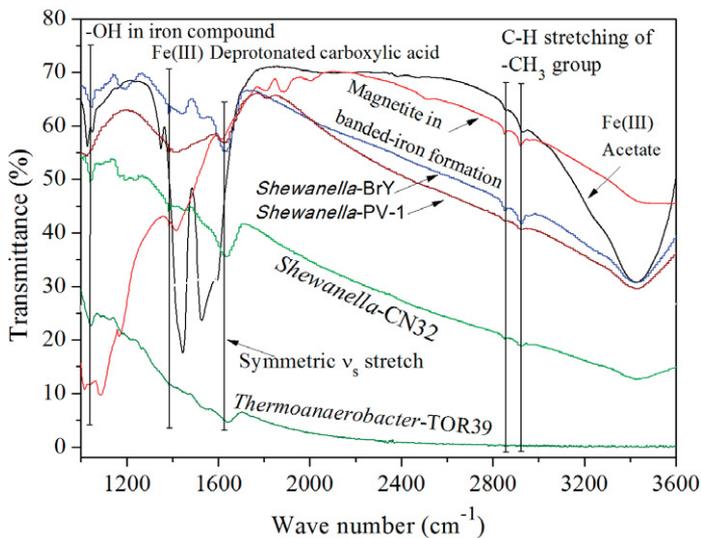
2000) and in this study at 90 °C (syn at 90 °C), and diagenetic magnetite from a petroleum well (63 °C, Frio Formation B sand) (Kharaka et al., 2006), were also measured for their  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and lattice constant values. Lattice constants and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios were recalculated from data reported by Sparks et al. (1990) for magnetite crystallites precipitated by *Geobacter metallireducens* strain GS-15 and magnetotactic bacterium strain MV-1. The theoretical lattice constant of 8.396 Å (Zhang and Satpathy, 1991) and a  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio of 0.5 for perfect stoichiometric magnetite are plotted as a reference in Figure 1. The results shown in Figure 1 suggest that the crystallochemistry of magnetite in BIFs is consistent with a biological origin. Furthermore, the distribution of data in Figure 1 indicates that despite the specific mineralizing mechanisms (Frankel and Bazylinski, 2003) and crystal size, the near-pristine to slightly oxidized biogenic magnetite crystals exhibit  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios and lattice constants closer to, or greater, than perfect stoichiometric magnetite (upper right quadrant). In contrast, magnetite derived from purely thermochemical synthesis (syn at 90 °C) or from natural gneiss rocks such as those in the ultrahigh-pressure metamorphic belts of eastern China, are characterized by lower  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios and lattice constants <8.396 Å (Li et al., 2009).

Fe(III) acetate salt is characterized by its small isomer shifts ( $\delta \approx -0.15$  mm/s) and typical quadrupole splitting of  $\text{Fe}^{3+}$  by MS (Greenwood and Gibb, 1971; Musić et al., 1988; Vértes, 1990) (Fig. 2). In addition, after the BIF magnetite was acid digested and processed by the methods of Bergmeyer and Möllering (1974), the residue showed maximum absorbance at 340 nm when measured by spectrophotometer (analytical protocol by Boehringer Mannheim Co.), indicating the presence of acetate. According to the iron atomic ratios of Fe minerals measured by MS, Fe(III) acetate composes  $\sim 0.5\%$  of Fe atoms in all iron-bearing minerals present in the BIF. It is interesting that Fe(III) acetate salt is a usual component of biogenic magnetite precipitates in various DIRB cultures when amorphous ferric iron and acetate were used as electron acceptor and donor, respectively (Fig. 2). Acetate can also form from bacterial lactate oxidation, as a product of fermentation (e.g., Liu et al., 1997; Li et al., 2009; Perez-Gonzalez et al., 2010), or as a remnant of the incomplete oxidation of acetate by DIRB, such as *Geobacter* (Lovley, 1993). The



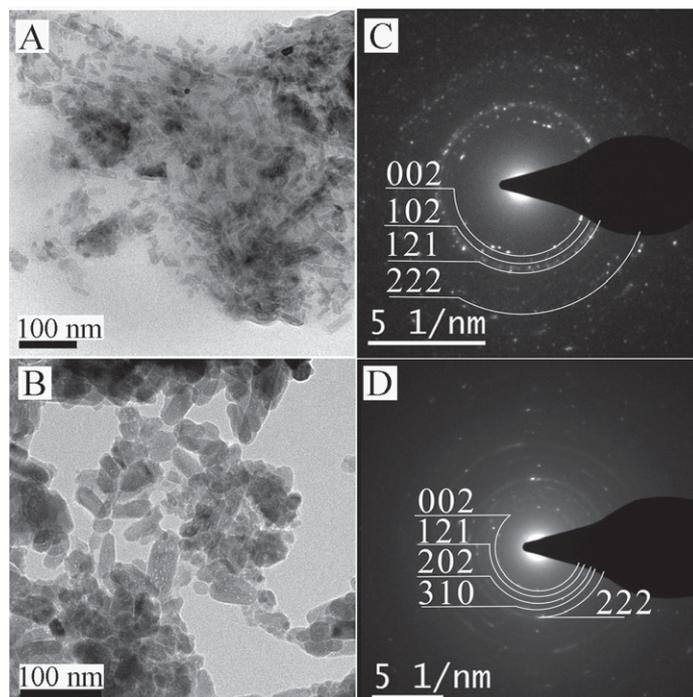
**Figure 2.** Mössbauer isomer shift versus quadrupole splitting indicating existence of Fe(III) salt of acetate in banded-iron formation of Dales Gorge Formation (Hammersley, Western Australia), and Fe(II) and Fe(III) salts of acetate in some cultures of dissimilatory iron-reducing bacteria. Magnetite labeled “Dabie China” is from gneiss of ultrahigh pressure metamorphic belts of eastern China.

formation of Fe(III) acetate in both the BIF sample and DIRB cultures implies that the biochemical reactions that took place in Precambrian sediments were similar in many respects to DIRB cultures in terms of bioavailability of Fe(III) and sources of carbon for Fe(III) respiration. The presence of acetate in BIFs and various biogenic magnetite assemblages was further confirmed by FTIR (Fig. 3). A comparison of FTIR spectra between synthesized Fe(III) acetate, biogenic mineral assemblages, and BIF samples (Fig. 3) indicates the existence of a C-H stretching mode characteristic of  $-\text{CH}_3$  groups, as well as symmetric  $\nu_s$  stretching and Fe(III) deprotonated carboxylic acid in both BIFs and biogenic magnetite precipitates (Fu and Quan, 2006).



**Figure 3. Fourier transmission infrared spectroscopic spectra indicating vibrations from acetic function groups and their interaction with iron in banded-iron formation sample and magnetite crystals from various dissimilatory iron-reducing bacterial cultures.**

Although the existence of apatite (Gole, 1980; Ewers and Morris, 1981) and the presence of phosphorus (Lepp and Goldich, 1964) in some BIFs have previously been reported, its mineralogical characterization and its role as a macronutrient in Archean–Paleoproterozoic Precambrian oceans have never been adequately addressed. In contrast, phosphatization is a common mineralization mechanism for the biogenic phosphorus observed to be widely present during and after the Neoproterozoic (e.g., Westall, 1999; Xiao and Schiffbauer, 2008). Aggregates of apatite intergrown with magnetite are evident in the Dales Gorge BIF (Figs. 4A and 4B). The crystal size is  $60 \pm 40$  nm in the long axis and  $26 \pm 5$  nm in the short axis. SAED analyses (Figs. 4C and 4D) yield (hkl) of (200), (201), (120), (121), (310), and (320), matching the powder diffraction file of (Ca, Sr) apatite (PDF 82–1429). Sr in the structure of apatite is corroborated by EDS analysis. The source of the Ca may have been cellular polyphosphate (Brown and Kornberg, 2004) because Ca content in magnetite and surrounding material is much lower than the apatite aggregates; the presence of Sr may also have been sourced from biomass because of its strong partitioning into apatite during organic respiration (Holmden et al., 1996; Rakovan and Hughes, 2000; Verberckmoes et al., 2004). EDS analyses further indicated the presence of carbon, which may be from structural  $-\text{CO}_3$  or coexisting calcium carbonate. The size and morphology of apatite crystallites are similar to heterotrophic bacterial-precipitated apatite (Kajander and Çiftçioglu, 1998; Sánchez-Navas and Martín-Algarra, 2001; Nemliher, 2005), while the fact that apatite occurs as an intergrowth in magnetite implies a genetic link between iron oxide formation and the processing of biomass.



**Figure 4. Transmission electron microscopic characterization of (Ca, Sr) apatite from banded-iron formation of Dales Gorge Member (Hamersley, Western Australia). A and B are morphologies of apatite aggregates. The (hkl) indexes of selected area electron diffraction patterns of crystal aggregates in C and D indicate that crystals are (Ca, Sr) apatite.**

The detection of both apatite and Fe(III) acetate, coexisting with magnetite exhibiting crystallochemical characteristics consistent with a biogenic origin, comprise three key lines of evidence that BIFs were, in part, biological products. In terms of the source for phosphorus in BIFs, our data further suggest that it was derived from the mineralization of cellular phosphate during metabolism (Brandes et al., 2007), rather than the absorption of phosphorus to ferric oxyhydroxides particles during the oxidation of Fe(II) (Bjerrum and Canfield, 2002), because hematite in the BIF of this study is highly pure without any phosphorus detectable by either EDS or high-resolution STEM.

The implications of this study are significant in that they show Precambrian phytoplankton as key intermediates in the transfer of nutrients from the marine photic zone to the seafloor. In this regard, future efforts in using BIFs as proxies for ancient seawater chemistry should consider the absorption and metabolic capacity of biomass in addition to the surface reactivity of ferric oxyhydroxides particles.

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