

# Could bacteria have formed the Precambrian banded iron formations?

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## ABSTRACT

**Banded iron formations (BIFs) are prominent sedimentary deposits of the Precambrian, but despite a century of endeavor, the mechanisms of their deposition are still unresolved. Interactions between microorganisms and dissolved ferrous iron in the ancient oceans offer one plausible means of mineral precipitation, in which bacteria directly generate ferric iron either by chemolithoautotrophic iron oxidation or by photoferrotothropy. On the basis of chemical analyses from BIF units of the 2.5 Ga Hamersley Group, Western Australia, we show here that even during periods of maximum iron precipitation, most, if not all, of the iron in BIFs could be precipitated by iron-oxidizing bacteria in cell densities considerably less than those found in modern Fe-rich aqueous environments. Those ancient microorganisms would also have been easily supported by the concentrations of nutrients (P) and trace metals (V, Mn, Co, Zn, and Mo) found within the same iron-rich bands. These calculations highlight the potential importance of early microbial activity on ancient metal cycling.**

**Keywords:** banded iron formations, Precambrian, sedimentary deposits, photoferrotothropy, chemolithoautotrophic iron oxidation.

## INTRODUCTION

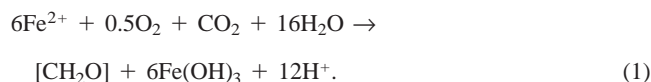
Much of the iron in Precambrian banded iron formations (BIFs) was deposited during the Late Archean to Early Proterozoic (2.7–1.9 Ga). These chemical sedimentary rocks are typically laminated, with alternations of Fe-rich and Si-rich layers. Banding can often be observed on a wide range of scales, from coarse macrobands (meters in thickness) to mesobands (centimeter-thick units) to millimeter and sub-millimeter layers (Trendall and Blockley, 1970). Among the latter are the wide varieties of varve-like repetitive laminae, known as microbands.

Current models on the origin of BIFs suggest that the thick, laterally extensive Proterozoic deposits, such as in the Hamersley Group, Western Australia, formed on partially isolated, submerged platforms on the continental shelves of Archean cratons (Morris and Horwitz, 1983). Pulsed output from distal mid-ocean-ridge settings or hotspots was the major source of iron (e.g., Morris and Horwitz, 1983; Jacobsen and Pimentel-Klose, 1988), possibly supplemented by normal continental drainage (e.g., Canfield, 1998). The hydrothermal waters were brought onto the outer continental shelf by upwelling currents (Klein and Beukes, 1989) or plumes (Isley, 1995), and minerals subsequently precipitated uniformly throughout much of the depositional basin, as made evident by the general pattern of mesoband correlation (Trendall and Blockley, 1970; Ewers and Morris, 1981). The more iron-rich hematite-magnetite me-

sobands formed during major episodes of hydrothermal input that may have lasted a few years to a few decades at most. However, genesis of the silica-rich sequences, including the varves, indicates either periods of relative hydrothermal quiescence (Morris, 1993) or the temporary failure of hydrothermal fluids reaching the BIF depositional basin (i.e., current reorganization).

Most models explaining the primary oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> near the ocean surface have until recently focused on photochemical processes or inorganic reactions using photosynthesis-generated O<sub>2</sub>. Although ultraviolet light clearly contributes to Fe<sup>2+</sup> oxidation in simplified laboratory settings (e.g., Cairns-Smith, 1978; Braterman et al., 1983), it has not been shown to occur in complex, multielement solutions at approximately neutral pH. Dissolved silica, for example, readily reacts with iron to form amorphous iron-silicate gels, thus limiting the effects of photochemical oxidation (Hamade et al., 2000). Such mineralization could have been significant in the early Precambrian when oceans were close to or at saturation with respect to amorphous silica (Siever, 1992); the products of these reactions may now be manifest in the very finely laminated iron-chert beds in BIFs (Morris, 1993). Cloud (1965, 1973) proposed that primitive O<sub>2</sub>-producing photosynthetic bacteria lacked suitably advanced oxygen-mediating enzymes and, consequently, required ferrous iron as an oxygen acceptor. Therefore, these microorganisms would have flourished when Fe<sup>2+</sup> (and nutrients) were made episodically available, allowing for the indirect precipitation of ferric hydroxide. By contrast, the photosynthetic population declined in numbers (yielding a minimal mineralization period) when Fe<sup>2+</sup> availability was limited. Today, plankton growth is still dependent upon iron supply, but as a nutrient (e.g., Hutchins and Bruland, 1998).

Other, and perhaps more likely, biological processes can also account for BIF deposition. For example, Holm (1989) speculated that oxidation of Fe<sup>2+</sup> by chemolithoautotrophic species such as *Gallionella ferruginea* in an ocean with limited free photosynthetic oxygen may have been responsible for the precipitation of ferric iron over wide ocean basins:



Today, under microaerobic conditions (e.g., in freshwater with pH = 7, O<sub>2</sub> concentrations = 60 μmol·L<sup>-1</sup>, and Fe<sup>2+</sup> ~200 μmol·L<sup>-1</sup>), iron oxidation by *Gallionella ferruginea* is >60 times faster than the abiotic reactions (Søgaard et al., 2000).

Alternatively, a number of purple and green bacteria couple Fe<sup>2+</sup> oxidation to the reduction of CO<sub>2</sub> during anoxygenic photosynthesis (e.g., Widdel et al., 1993; Ehrenreich and Widdel, 1994; Heising and Schink, 1998; Heising et al., 1999):

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This process has been used to explain iron deposition on early Earth, before free oxygen became widely available as an oxidant (Ehrenreich and Widdel, 1994).

In this study we have developed a biological model for BIF deposition and, for the first time, calculate the number of microbes actually needed to form BIFs. This model takes into account the biomarker (Brocks et al., 1999; Summons et al., 1999) and isotopic evidence (Baur et al., 1985; Kakegawa et al., 1999) from BIF units, such as the 2.5 Ga Hamersley Group, indicating that microbial activity was well advanced and that most microbial taxa were represented in the Precambrian oceans at that time (Awramik, 1992). Similar to today, some of them would have been inextricably linked to iron precipitation (Konhauser, 2000). We consider two bacterial genera that are known to oxidize  $\text{Fe}^{2+}$  as an energy source, namely *Gallionella* sp., a chemolithoautotrophic Proteobacteria, which grows under microaerobic conditions (Hanert, 1992), and *Chromatium* sp., a sulfur oxidizing Proteobacteria, which can also oxidize  $\text{Fe}^{2+}$  during anoxygenic photosynthesis (Ehrenreich and Widdel, 1994).

## METHODS

Intact and convincing microbial fossils have not yet been identified in Fe-rich BIFs. Consequently, any attempt to prove a direct microbial role in iron biomineralization must rely on circumstantial evidence. One such example is using the concentrations of iron, trace metals, and nutrients in BIFs to establish the ecological plausibility of bacteria to oxidize sufficient iron in the water column of the depositional basin. Three ~30-cm-long sections of fresh core were selected from the BIF macrobands of the Dales Gorge Member, Hamersley Group (DDH 44) drilled at Paraburdoo, Western Australia. These cores were chosen to represent a wide range of mesoband types. The samples from BIFs 13 and 15 are dominantly hematite, magnetite, and quartz and have minor carbonates and silicates, whereas those from BIF 16 have a relatively high proportion of carbonates (e.g., ankerite and siderite) and silicates (such as riebeckite and stilpnomelane) as well as hematite, magnetite, and minor quartz. These units were subjected to only low-grade metamorphism with maximum temperatures in the range of 60–160 °C (Kaufman et al., 1990).

The core sections were equally subsampled (20 per BIF macroband) to account for all of the mesobands present. Samples were then powdered, homogenized, and digested by using a standard hydrofluoric-nitric acid digest in Pt-Fe reaction vessels. Aristar, hydrofluoric and redistilled nitric acids were used to minimize contamination. The complete dissolution of the BIF samples was noted in each case. Digest solutions were subsequently analyzed by using a Perkin-Elmer Elan 5000 inductively coupled plasma-mass spectrometer to determine trace metal concentrations. Trace-metal concentrations in reagent blanks were found to be at least three orders of magnitude less than in the samples. Precision (<5%) was determined by replicate analysis, and accuracy (<0.01%) was determined by comparison with the certified standard SDO-1.

## RESULTS AND DISCUSSION

On the basis of available U-Pb dating of zircons in bulk BIF samples from the Hamersley Group, Trendall (2000) reported a depositional rate of 19–225 m/m.y. for the major BIF units. Barley et al. (1997) also measured U-Pb ratios in the Hamersley and concluded that the BIFs may have been deposited at rates as fast as 100–1000 m/m.y. The latter value corresponds to those predicted by Morris (1993), who suggested that during times of maximum iron deposition, ~1 m of iron-dominated mesobands precipitated in 700 yr, from which a realistic maximum annual accumulation rate of 1 mm of hematite equivalent can be adduced. Using these maximum rates (to demonstrate un-

equivocally the feasibility of microbial iron oxidation) and assuming a depositional basin for the Hamersley of  $1 \times 10^{11}$  m<sup>2</sup>, the measured  $\text{Fe}_{\text{total}}$  values of 54.6% (averaged from all Fe-rich BIF mesobands) and the calculated Fe-rich mesoband density of  $4.6 \times 10^6$  g/m<sup>3</sup> lead to a calculated annual precipitation of  $4.53 \times 10^{12}$  mol of Fe (or, normalizing annual Fe precipitation to surface area, 45.3 mol/m<sup>2</sup>) during periods of peak iron deposition.

Total cell production from such iron oxidation can be determined from documented growth rates for both *Gallionella* and *Chromatium*. On the basis of experiments mimicking iron-containing groundwater seeps, in which an inoculum of microbial mat cells was dispersed into bacterial aggregates in a fluid up-flow reactor, Emerson and Revsbech (1994b) reported that under microaerobic conditions ( $\text{O}_2 < 40$  μmol/L), iron concentrations between 80 and 100 μmol/L, and pH = 7, *Gallionella* populations ( $10^9$  cells/cm<sup>3</sup> of original mat) oxidize to 1200 nmol of  $\text{Fe}^{2+}$  per hour. This result leads to an annual  $\text{Fe}^{2+}$  oxidation rate of  $1.1 \times 10^{-11}$  mol/cell. If we use these rates and assume continuous growth during sustained hydrothermal activity at times of Fe-rich mesoband deposition, then  $4.3 \times 10^{23}$  cells would have been needed to precipitate all of the  $\text{Fe}^{3+}$  in BIFs annually (an order of magnitude fewer cells would have been required to precipitate the iron at slower sedimentation rates, e.g., 100 m/m.y., or to precipitate the smaller amounts of iron in the varved mesobands). In actuality the number of iron-oxidizing bacteria growing in the water column may have been two to three times higher than those required to precipitate BIFs because iron recycling would have taken place during sedimentation. Unfortunately, recycling processes in BIF depositional basins are poorly defined. Despite these uncertainties, our calculations show that if chemolithoautotrophic  $\text{Fe}^{2+}$  oxidation occurred over a 100-m-deep active zone, then a minimum cell density of  $4.3 \times 10^4$  cells/cm<sup>3</sup> was required throughout the basin. This density would more likely vary with depth such that denser *Gallionella* populations would have been present slightly above the chemocline, where microaerobic conditions exist, and there would be fewer cells near the ocean surface.

Ehrenreich and Widdel (1994) showed that in a solution containing the iron-oxidizing phototroph *Chromatium*, the oxidation of  $9.5 \times 10^{-3}$  mol  $\text{Fe}^{2+}$  per liter of solution yielded  $2.4 \times 10^{-3}$  mol of dry cell biomass (as  $\text{CH}_2\text{O}$ ) over a 15 d experiment. On the basis of an average *Chromatium* cell volume of 2.65 μm<sup>3</sup> and a proportionate mass to *Gallionella* (where each cell has a volume of ~1 μm<sup>3</sup>, a wet mass of  $1 \times 10^{-12}$  g, and contains  $1.3 \times 10^{-14}$  mol of C; Hallbeck and Pedersen, 1991), over the course of a year, Ehrenreich and Widdel's (1994) experimental result translates into an average annual oxidation rate of  $8.0 \times 10^{-12}$  mol of  $\text{Fe}^{2+}$  per cell. This value leads to a maximum of  $5.7 \times 10^{23}$  cells (or  $5.7 \times 10^4$  cells/cm<sup>3</sup> over a 100-m-thick photic zone for *Chromatium*) required to precipitate an annual BIF layer. Their actual distribution in the water column would depend on the balance between the depth of the chemocline and light availability, with cells growing preferentially beneath the chemocline (Pfennig, 1978).

The *Gallionella* and *Chromatium* cell densities are much less than the modern populations of mixed bacteria and other plankton assemblages growing in the photic zone of marine coastal waters ( $10^6$  cells/cm<sup>3</sup>; Azam et al., 1983), the open ocean ( $10^5$ – $10^6$  cells/cm<sup>3</sup>; Campbell et al., 1997), and the total bacteria found distributed throughout the water column of the euxinic Mariager Fjord in Denmark ( $10^6$  cells/cm<sup>3</sup>; Ramsing et al., 1996). Furthermore, where  $\text{Fe}^{2+}$  is abundant, i.e., in iron-containing groundwater seeps, *Gallionella* densities have been reported to reach  $10^9$  cells/cm<sup>3</sup> of mat (Emerson and Revsbech, 1994a), while in anoxic lake water *Chromatium* species can compose >98% of the total microbial population and reach densities > $10^6$  cells/cm<sup>3</sup> (Camacho et al., 2000).

If bacteria were involved in the precipitation of iron in BIFs, we need to assess whether there were sufficient trace metals (i.e., V, Mn,

TABLE 1. TRACE METAL REQUIREMENTS OF MICROBIAL IRON OXIDIZERS

	P	V	Mn	Co	Cu	Zn	Mo
<b>Fe-rich mesoband composition</b>							
Average concentration (mg/kg)	713.1 (4.2)	37.60 (0.05)	1118 (1)	3.10 (0.02)	14.4 (1.2)	36.6 (1.8)	0.91 (0.07)
Amount in annual BIF layer (mg)	$3.3 \times 10^{14}$	$1.7 \times 10^{13}$	$5.2 \times 10^{14}$	$1.5 \times 10^{12}$	$6.7 \times 10^{12}$	$1.7 \times 10^{13}$	$4.2 \times 10^{11}$
<b><i>Gallionella</i></b>							
Cell wet mass (g)	$1.0 \times 10^{-12}$	$1.0 \times 10^{-12}$	$1.0 \times 10^{-12}$	$1.0 \times 10^{-12}$	$1.0 \times 10^{-12}$	$1.0 \times 10^{-12}$	$1.0 \times 10^{-12}$
Single-cell requirement ( $\mu\text{g/g}$ )*	9000.00	0.20	9.00	0.15	12.60	45.00	0.45
Single-cell concentration (mg)	$9.0 \times 10^{-12}$	$2.0 \times 10^{-16}$	$9.0 \times 10^{-15}$	$1.5 \times 10^{-16}$	$1.3 \times 10^{-14}$	$4.5 \times 10^{-14}$	$4.5 \times 10^{-16}$
Number of cells needed to form BIF	$4.3 \times 10^{23}$	$4.3 \times 10^{23}$	$4.3 \times 10^{23}$	$4.3 \times 10^{23}$	$4.3 \times 10^{23}$	$4.3 \times 10^{23}$	$4.3 \times 10^{23}$
Annual biomass requirement (mg)	$3.9 \times 10^{12}$	$8.6 \times 10^7$	$3.9 \times 10^9$	$6.5 \times 10^7$	$5.6 \times 10^9$	$1.9 \times 10^{10}$	$1.9 \times 10^8$
Number of supportable populations	85	200 000	133 000	23 000	1200	890	2200
<b><i>Chromatium</i></b>							
Cell wet mass (g)	$2.7 \times 10^{-12}$	$2.7 \times 10^{-12}$	$2.7 \times 10^{-12}$	$2.7 \times 10^{-12}$	$2.7 \times 10^{-12}$	$2.7 \times 10^{-12}$	$2.7 \times 10^{-12}$
Single-cell concentration (mg)	$2.4 \times 10^{-11}$	$5.4 \times 10^{-16}$	$2.4 \times 10^{-14}$	$4.1 \times 10^{-16}$	$3.4 \times 10^{-14}$	$1.2 \times 10^{-13}$	$1.2 \times 10^{-15}$
Number of cells needed to form BIF	$5.7 \times 10^{23}$	$5.7 \times 10^{23}$	$5.7 \times 10^{23}$	$5.7 \times 10^{23}$	$5.7 \times 10^{23}$	$5.7 \times 10^{23}$	$5.7 \times 10^{23}$
Annual biomass requirement (mg)	$1.4 \times 10^{13}$	$3.1 \times 10^8$	$1.4 \times 10^{10}$	$2.3 \times 10^8$	$1.9 \times 10^{10}$	$6.8 \times 10^{10}$	$6.8 \times 10^8$
Number of supportable populations	25	55 000	37 000	6500	350	250	620

Note: Values in parentheses represent one standard deviation. Single-cell requirements modified from dry weight values in Bowen (1979). BIF is banded iron formation. \*Single-cell requirements for *Chromatium* are considered identical to those of *Gallionella*.

Co, Cu, Zn, and Mo) and nutrients (i.e., P) available in the depositional basin water column to support their growth. The total amounts of each element can be determined from their average concentrations in the Fe-rich mesobands multiplied by the volume of material presumed to have been deposited each year. For example, the average concentration of V in an Fe-rich mesoband is 37.6 mg/kg, yielding a maximum annual deposition of  $1.7 \times 10^{13}$  mg (Table 1). Bacteria require  $\sim 0.2$   $\mu\text{g/g}$  (i.e., wet cell mass) of V, which on the basis of a wet *Gallionella* cell mass, amounts to  $2.0 \times 10^{-16}$  mg of V in each cell. If we use the total cell counts required to form the  $\text{Fe}^{3+}$  in BIFs, e.g.,  $4.3 \times 10^{23}$  cells, the overall biomass requirement of V would have been  $8.6 \times 10^7$  mg. The amount of V preserved in the equivalent BIF is  $\sim 2 \times 10^5$  times this value. Similar calculations show that during periods of maximum deposition, the Fe-rich mesobands have excess P (85 $\times$ ), Mn (133,000 $\times$ ), Co (23,000 $\times$ ), Cu (1200 $\times$ ), Zn (890 $\times$ ), and Mo (2200 $\times$ ) relative to the microbial nutritional needs. Comparable trace metal excesses are calculated for *Chromatium* (Table 1).

The excesses are necessary for three reasons. First, in addition to supporting the active community in the water column, an unknown proportion of metals and nutrients would also be immobilized in dead biomass. Of those metals and nutrients, some would become buried and incorporated into the sediment, while the remainder would be recycled back into the water column (Van Cappellen and Gaillard, 1996). Second, at any given time in the Precambrian oceans other types of bacteria (and maybe eukaryotes) would have required nutritional support. The actual population structure in the ancient oceans is unknown, but assuming that the overall density was similar to modern, chemically stratified marine waters ( $\sim 10^6$  cells/cm<sup>3</sup>; Ramsing et al., 1996), it appears that sufficient nutrients (e.g., phosphorous) were available to support the calculated *Gallionella* and/or *Chromatium* populations. Third, the actual availability of trace metals in the water column would have been diminished by the scavenging properties of the Fe-rich particles as they settled down to the sediment. The extent of adsorption would subsequently be controlled by factors such as salinity, fluid composition, and pH, the latter relating to surface-charge characteristics such as the point of zero charge (PZC). Silica-containing ferric hydroxides have PZCs of 5.3–7.5 (Schwertmann and Fechter, 1982), signifying that at the estimated pH range for the Late Archean–Paleoproterozoic oceans, i.e., 6.5–7.4 (Grotzinger and Kasting, 1993), mineral surfaces were likely less sorptive than under present-day conditions. This circumstance implies that during the primary deposition of the ferruginous sediment in the Hamersley basin, the solid-phase partitioning of trace metals may have been largely limited to those incorporated into microbial biomass. The exception was phosphate (Berner, 1973), which

would have been scavenged by the iron oxides and made potentially unavailable to microbial biomass.

As the Fe-rich particles and planktonic biomass settled out of the water column, each new layer would isolate the biomass and sediment of earlier layers from the overlying seawater, and trace-metal mobility in an iron-oxide-rich sediment would have been limited (McConchie, 1987). What is most important from our perspective, the concentration of trace metals in the ferruginous sediment provides an indication of their availability to ancient  $\text{Fe}^{2+}$ -oxidizing microbial populations growing in the overlying water column. With time, buried microorganisms would have been degraded in situ and their constituent metals released to the sediment pore waters by a combination of diagenetic processes such as fermentation and iron reduction (Walker, 1984; Baur et al., 1985; Nealson and Myers, 1990) and metamorphic mineralization (Perry et al., 1973). Concomitantly, dissolution-precipitation or crystallization of biogenic ferric hydroxides, along with segregation of silica, would have led to a secondary stage of metal immobilization (Holm, 1987). The secondary minerals formed would have included (1) magnetite or iron carbonates when organic mineralization was coupled with  $\text{Fe}^{3+}$  reduction in the sediments, (2) hematite, when organic material was completely depleted, or (3) clays, when coprecipitated silica, entrained by the iron-rich particles during their deposition, reacted with other cationic species in high-pH pore waters (Morris, 1993). The various respiratory processes may reconcile the apparent paradox of having nutrient upwelling-induced planktonic blooms in the surface waters, yet no cellular remains generally associated with the iron oxides in BIF mesobands today.

## CONCLUSIONS

This work is the first to show quantitatively that direct microbial  $\text{Fe}^{2+}$  oxidation had the potential to generate the bulk, if not all, of the ferric iron in BIFs. This work, however, does not even consider the passive roles that other bacteria may have played, such as biologically induced biomineralization, whereby bacterial surfaces would have simply served as nucleation sites for iron mineralization (Konhauser and Ferris, 1996; Warren and Ferris, 1998; Konhauser, 1998). Clearly, microorganisms had the means to be important agents in iron deposition, and their effect must now be considered as a demonstrable mechanism for BIF development in the Precambrian.

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