

# Deposition of banded iron formations by anoxygenic phototrophic Fe(II)-oxidizing bacteria

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## ABSTRACT

**The mechanism of banded iron formation (BIF) deposition is controversial, but classically has been interpreted to reflect ferrous iron [Fe(II)] oxidation by molecular oxygen after cyanobacteria evolved on Earth. Anoxygenic photoautotrophic bacteria can also catalyze Fe(II) oxidation under anoxic conditions. Calculations based on experimentally determined Fe(II) oxidation rates by these organisms under light regimes representative of ocean water at depths of a few hundred meters suggest that, even in the presence of cyanobacteria, anoxygenic phototrophs living beneath a wind-mixed surface layer provide the most likely explanation for BIF deposition in a stratified ancient ocean and the absence of Fe in Precambrian surface waters.**

**Keywords:** banded iron formation, oxidation, anoxygenic photosynthesis, cyanobacteria.

## INTRODUCTION

Banded iron formations (BIFs) are Precambrian sedimentary deposits that generally consist of alternating layers of iron minerals and silica (Beukes and Klein, 1992). How these deposits formed at different periods in Earth history has not been resolved, despite intensive investigation over the last century. Central to this enigma is the controversy over when O<sub>2</sub> evolved on the planet (Buick, 1992; Kasting, 1993; Holland, 1994; Canfield and Teske, 1996), and whether it was present in sufficient concentrations to be responsible for the deposition of the earliest BIFs (ca. 3.8–2.2 Ga).

In the absence of O<sub>2</sub>, only two potential mechanisms for the oxidation of ferrous iron [Fe(II)] to ferric iron [Fe(III)] are known: photochemical oxidation by ultraviolet light (Cairns-Smith, 1978; Francois, 1986) and light-dependent enzymatic Fe(II) oxidation by anoxygenic phototrophic bacteria (Widdel et al., 1993), the most ancient type of photosynthetic organisms (Xiong et al., 2000). Although Fe(II) can be oxidized photochemically in simple aqueous systems (Braterman et al., 1983), such oxidation has not been reported in more complex environments such as seawater. In contrast, both freshwater and marine anoxygenic phototrophs can catalyze the oxidation of Fe(II) (Widdel et al., 1993; Ehrenreich and Widdel, 1994; Straub et al., 1999; Heising et al., 1999; Kappler and Newman, 2004; Croal et al., 2004). Fe(II) serves as the electron donor for these organisms, which convert CO<sub>2</sub> into biomass by using light energy:  $4\text{Fe}^{2+} + \text{CO}_2 + 11\text{H}_2\text{O} + h\nu \rightarrow [\text{CH}_2\text{O}] + 4\text{Fe}(\text{OH})_3 + 8\text{H}^+$ .

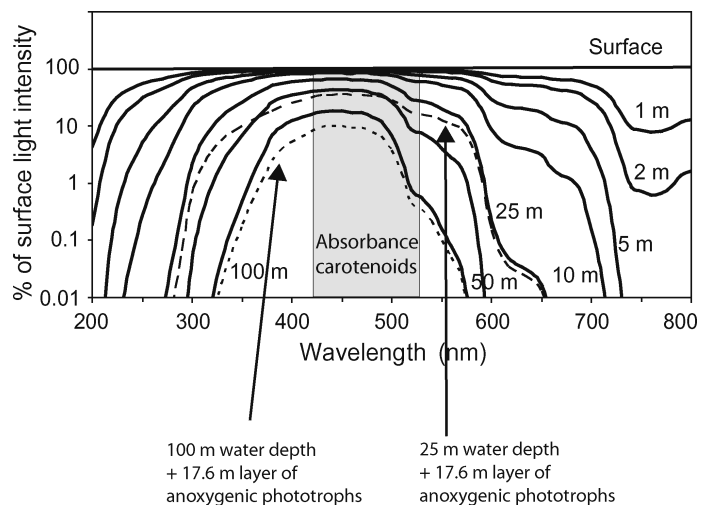
Recently, stratigraphic analyses of a Precambrian Fe deposit (i.e., the Buck Reef Chert, Western Australia) established that a banded iron-rich chert formed offshore, below the base of storm waves at depths of more than 200 m; in addition, a carbon-rich, black and white banded chert unit was inferred to have been deposited in a shallow nearshore environment that was occasionally stirred by storms and large waves

(Beukes, 2004; Tice and Lowe, 2004). These observations led to the conclusion that the low abundance of Fe in the shallow-water environment was due to the creation of a CO<sub>2</sub>-rich zone by the activity of microbial mats. According to this argument, downward diffusion of CO<sub>2</sub> would have intercepted Fe(II) upwelling from deep waters, resulting in the precipitation of ferrous carbonates and thus preventing Fe(II) from reaching shallow waters. Here we consider whether a different explanation for the restriction of Fe(II) to deep waters might be possible. Specifically, we test the hypothesis that anoxygenic Fe(II)-oxidizing phototrophs living below a mixed layer inhabited by cyanobacteria could have been responsible for the absence of Fe in shallow waters and for Precambrian BIF deposition in a stratified ancient ocean.

## MATERIALS AND METHODS

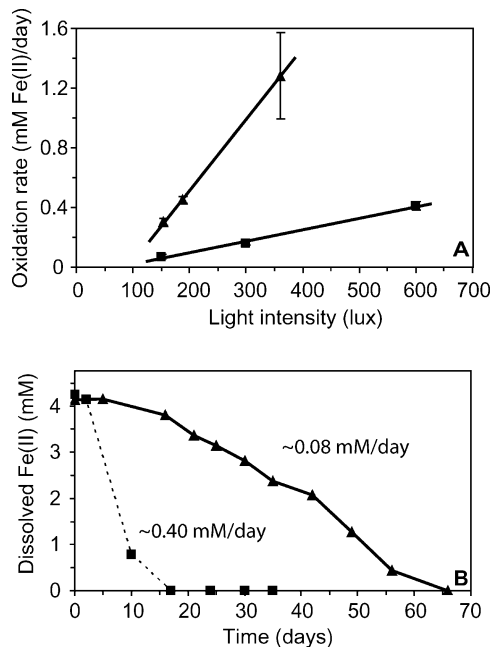
### Source of Organisms, Media, and Growth Conditions

Light is a critical parameter that limits any phototrophic metabolism. Because both light intensity and light quality vary substantially with depth in the water column (Fig. 1), light can be expected to constrain the maximum depth at which anoxygenic phototrophic bacteria can catalyze Fe(II) oxidation. To determine the effect of light intensity on the rate of phototrophic Fe(II) oxidation, we grew two representative



**Figure 1. Wavelength-dependent light intensity at different water depths (indicated by numbers assigned to contour lines). Light intensity is given in percent of surface light intensity, where 100% equals ~30,000 lux (~600  $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$ ), estimated to be 24 h average expected for light intensity on horizontal surface on clear summer day (Thimijan and Heins, 1983). Contour lines were derived using attenuation coefficients given for clear ocean water by Smith and Baker (1981). Dashed lines represent light intensities at 25 and 100 m depth, respectively, including absorption by 25 and 100 m water column and 17.6-m-thick layer of anoxygenic phototrophic Fe(II) oxidizers containing  $10^6$  cells/mL. Shaded area indicates wavelength region where carotenoids absorb light.**

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**Figure 2.** Light dependence of oxidation of dissolved Fe(II) by anoxygenic photoautotrophic bacteria. **A:** Relationship between Fe(II) oxidation rate and light intensity is linear for *Rhodobacter ferrooxidans* strain SW2 (squares) and *Thiodictyon* sp. strain F4 (triangles). Data represent average of three independent experiments with error bars showing standard deviation. **B:** Oxidation of Fe(II) by strain SW2 in presence of full 34W incandescent light bulb spectrum (squares) and in presence of same light bulb in combination with a filter that cuts off wavelengths >650 nm (triangles). In both cases, light intensity was adjusted to 600 lux by positioning culture bottles at appropriate distances from light source. Graphs are representatives of at least two independent experiments.

types of these bacteria at different light intensities (*Rhodobacter ferrooxidans* strain SW2 and *Thiodictyon* sp. strain F4).

All bacteria strains were cultivated in a freshwater mineral medium with either dissolved Fe(II), hydrogen, or acetate at pH 6.8–6.9 at 24 °C (F4, KoFox) or 16–18 °C (SW2), as described previously (Kappler and Newman, 2004). Cultures were incubated in front of 34W tungsten incandescent light bulbs (Watt-Miser, General Electric, 380 lumens). Experiments with different light intensities were performed by incubating the cultures at different distances to the light bulb. The light intensity was measured with a Traceable dual-range light meter (Control Company, Friendswood, Texas). Wavelength-dependent Fe(II) oxidation rates were determined by incubating the cultures behind a Borofloat light filter (Edmund Optics, Barrington, New Jersey), which cuts off wavelengths >650 nm. Light intensity-dependent Fe(II) oxidation rates were analyzed by linear regression of the oxidation rates observed at different light intensities during exponential growth.

#### Analytical Procedures

To analyze for Fe(II) in cultures of Fe(II)-oxidizing bacteria, 200  $\mu$ L culture suspension was withdrawn with a syringe in an anoxic glove box, filtered with 0.5 mL nylon (0.22  $\mu$ m) filter tubes (Costar, Corning, New York), and analyzed for Fe(II) with the ferrozine assay (Stookey, 1970).

We calculated the light attenuation by a layer of phototrophic

Fe(II)-oxidizing bacteria present in a water column (Fig. 1) as follows. Absorbance spectra of cultures with known cell density were recorded, background absorption by medium components was subtracted, and attenuation coefficients (K) for different wavelengths were calculated using the dependencies (1) of absorbance (A) on light intensity [ $A = \log(I_0/I)$  (I is the light intensity after it passes through the sample;  $I_0$  is the initial light intensity) and (2) of attenuation coefficients on light intensity and thickness of sample (z) [ $K = -(\ln(I/I_0)/z)$ ] for a layer z containing  $10^6$  cells/mL. The attenuation coefficient for the bacterial layer was convoluted with the attenuation coefficients given for pure water (Smith and Baker, 1981) to create the dashed lines in Figure 1.

#### RESULTS AND DISCUSSION

The phototrophic oxidation of dissolved Fe(II) by both the purple sulfur bacterium *Thiodictyon* sp. strain F4 and the purple nonsulfur bacterium *Rhodobacter ferrooxidans* strain SW2 showed a linear dependence on the light intensity, up to 400 and 600 lux, respectively, corresponding to 8 and 12  $\mu$ mol quanta  $m^{-2} s^{-1}$  (Fig. 2A). At higher light intensities the oxidation rates did not increase linearly owing to saturation effects, as has been observed for other anoxygenic photosynthetic bacteria, where saturation at  $\sim 1500$  lux (*Chromatium vinosum*) (van Gemerden, 1980) or 1000 lux (*Rhodospseudomonas palustris*) (Uemura et al., 1961) has been documented.

In addition to light intensity, the metabolic rate of phototrophic organisms is dependent on light quality, owing to the selective absorption of particular wavelengths of light by (bacterio)chlorophyll (Bchl) and carotenoids. For example, Bchl<sub>a</sub>, Bchl<sub>b</sub>, and Bchl<sub>c</sub>, present in purple sulfur, purple nonsulfur, and green sulfur Fe(II)-oxidizing bacteria, have absorption maxima between 800 and 880 nm (Bchl<sub>a</sub>), at 1020 nm (Bchl<sub>b</sub>), and at  $\sim 750$  nm (Bchl<sub>c</sub>). In contrast, the carotenoids of the Fe(II)-oxidizing organisms (SW2: spheroidene, spheroidenone, OH-spheroidene; F4: rhodopinal; KoFox: chlorobactene) maximally absorb at much lower wavelengths (360–517 nm; see Data Repository<sup>1</sup>). Because light of wavelengths lower than 300 and higher than 600 nm will readily be absorbed or scattered by water within the top few meters of the ocean (Fig. 1), this can be expected to limit the rate of Fe(II) oxidation by anoxygenic phototrophs. To determine to what extent phototrophic Fe(II) oxidation could be sustained in deeper water, Fe(II) oxidation rates were measured with strain SW2 using only wavelengths <650 nm (Fig. 2B). The oxidation rate decreased (to 0.08 mM/day) but was still  $\sim 20\%$  of the rate obtained in the presence of the full light spectrum at the same light intensity. This suggests that phototrophic Fe(II) oxidation can be sustained in deeper waters, albeit with decreased efficiency.

In the water column of modern aqueous environments, such as the Black Sea and stratified lakes, anoxygenic phototrophs are typically found at depths below cyanobacteria because oxygen inhibits anoxygenic phototrophic metabolism (Repeta et al., 1989; Falkowski and Raven, 1997). Note that in these ecosystems cyanobacteria colonize the surface mixed layer down to the depth of a strong pycnocline that prevents (or at least reduces to very low values) the mixing between the surface oxic water and the deeper anoxic water (Özsoy and Ünlüata, 1997). Light is still available below the mixed layer, with an intensity that allows anoxygenic photosynthesis. If organisms like strain SW2 were present in the Precambrian ocean, a similar strong density gradient would have been required to separate the surface mixed layer from the deeper anoxic water in which they were living. We therefore assume that the pycnocline was shallower than the photic depth. Given

<sup>1</sup>GSA Data Repository item 2005170, isolation and identification of pigments, is available online at [www.geosociety.org/pubs/ft2005.htm](http://www.geosociety.org/pubs/ft2005.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

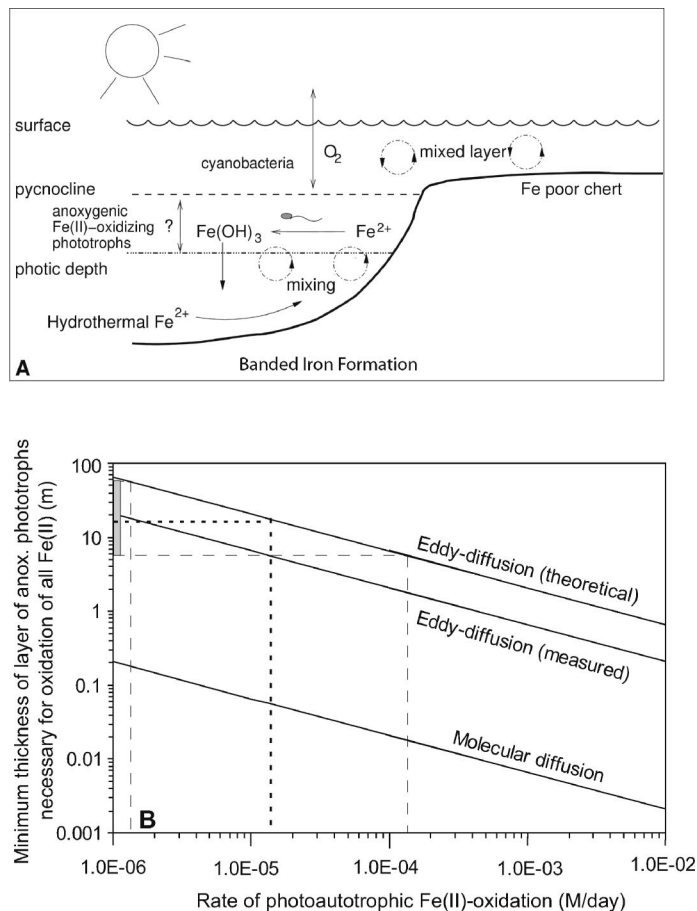
that the source of Fe(II) in the Precambrian ocean is thought to be hydrothermal (Holland, 1973), a relevant question is whether a layer of anoxygenic Fe(II)-oxidizing phototrophs living below a layer of cyanobacteria could have accounted for the complete oxidation of hydrothermal Fe(II) entering the ancient ocean at depth before any Fe(II) potentially could have reached the oxic layers of the water column (Fig. 3A).

To calculate the thickness of this layer, we set the flux of Fe(II) from the deep ocean ( $J = D \times \partial C/\partial z \cong D \times \Delta C/z$ ) equal to the experimentally determined oxidation rate per cell multiplied by the average planktonic cell density and by the layer thickness ( $z$ ). The value of  $z$  is thus a function of the diffusion coefficient ( $D$ ), the phototrophic oxidation rate (time,  $t$ ) per cell  $\{[1/\rho] [d\text{Fe(II)}/dt]\}$ , the cell density ( $\rho$ ), and the difference ( $\Delta C$ ) between the concentration of Fe(II) in the lowest part of the ocean, i.e., 0.5 mM (Holland, 1973; Morris, 1993), and the zero concentration of Fe(II) assumed in the case of complete oxidation by the bacteria:  $z^2 = (D \times \Delta C)/(d\text{Fe(II)}/dt)$ .

Note that because the cell density is multiplied by the oxidation rate per cell, an explicit term for cell density does not appear in the equation. Figure 3B predicts the thickness of a layer of anoxygenic phototrophs that would be required to completely oxidize Fe(II), assuming a range of values for the photosynthetic Fe(II) oxidation rate per liter of water [ $d\text{Fe(II)}/dt$ , representing the average oxidation rate for the entire layer] to account for different concentrations of bacteria that may have been present, as well as for different oxidation rates per cell associated with different light intensities and different Fe(II) concentrations. The diffusion coefficient has also been varied to account for lack of knowledge of the physical processes responsible for mixing in the deep Precambrian ocean. Using the modern global mean eddy-diffusion rate and an Fe(II) oxidation rate relevant for deeper water [0.014 mM/day: the rate determined at 150 lux ( $3 \mu\text{mol quanta m}^{-2} \text{s}^{-1}$ ), 0.07 mM/day, reduced to 20% to account for the narrow wavelength range in deeper water (Fig. 2B)], a 17.6-m-thick layer would be sufficient to oxidize all of the hydrothermal Fe(II) before it could reach the cyanobacterial-oxic zone. Assuming a higher Fe(II) oxidation rate, a slower Fe(II) diffusion rate or a lower concentration of Fe(II) in the ocean predicts an even thinner layer and vice versa. This is shown for Fe(II) oxidation rates varying one order of magnitude from the experimentally determined oxidation rate (Fig. 3B). A 17.6-m-thick layer of anoxygenic phototrophs as calculated from the experimentally determined Fe(II) oxidation rate (as well as thicknesses of 5.6 and 55.6 m calculated for tenfold lower and higher oxidation rates, respectively) is reasonable given that anoxygenic phototrophs have been reported to extend from depths of ~60 m to ~110 m in the Black Sea (Repeta et al., 1989). This implies that even if cyanobacteria were present in the surface mixed layer, anoxygenic phototrophs could have been responsible for total Fe(II) oxidation.

The amount of Fe(III) minerals that could have been precipitated in an ancient ocean by anoxygenic phototrophs can be estimated using the thickness predicted by this model (17.6 m) and the corresponding Fe(II) oxidation rate [0.014 mM Fe(II)/day]. This is a conservative estimate with regard to light intensity because light-intensity-dependent oxidation rates determined for strain F4 were much higher (~4–7 times) than those obtained for strain SW2 (Fig. 2A). Using an area equivalent to that covered by the Hamersley Basin in Western Australia [ $\sim 10^{11} \text{ m}^2$  (Konhauser et al., 2002)],  $\sim 9.0 \times 10^{12} \text{ mol Fe/yr}$  could have been oxidized and then precipitated by anoxygenic phototrophs. This is the same order of magnitude as the maximum rate necessary to deposit the Hamersley BIF ( $4.5 \times 10^{12} \text{ mol Fe/yr}$ ; Konhauser et al., 2002).

A caveat to consider is whether light attenuation by cells in the water column positioned above the Fe(II) oxidizing phototrophs would



**Figure 3. A:** Simple box model of ancient stratified ocean with cyanobacteria colonizing surface mixed layer, above layer of anoxygenic photoautotrophic Fe(II)-oxidizing bacteria, with a hydrothermal source of Fe(II) underneath. Concentration of dissolved Fe(II) is assumed to be ~0.5 mM (Holland, 1973; Morris, 1993). Question mark and double arrow point to thickness of layer (calculated in B) of anoxygenic phototrophs supported by Fe(II) input. **B:** Calculation of thickness of layer of Fe(II)-oxidizing anoxygenic photoautotrophs supported by Fe(II) flux from deep ocean. Shown is dependence of this thickness on Fe(II) oxidation rate for different diffusion coefficients ( $D$ ): (1) molecular diffusion of dissolved Fe(II) ( $D = 1 \times 10^{-5} \text{ cm}^2/\text{s}$ ; Sobolev and Roden, 2001); (2) eddy diffusion measured for open oceans ( $D = 0.1 \text{ cm}^2/\text{s}$ ; Ledwell et al., 1993); and (3) theoretically predicted eddy diffusion coefficient for modern ocean ( $D = 1 \text{ cm}^2/\text{s}$ ; Wunsch and Ferrari, 2004). Dotted lines indicate predicted thickness for this layer (17.6 m), assuming Fe(II) oxidation rate at low wavelength conditions as determined experimentally ( $1.4 \times 10^{-5} \text{ M/day}$ ). Dashed lines and gray bar indicate thicknesses for this layer (5.6 and 55.6 m) if oxidation rates were one order of magnitude lower or higher.

appreciably affect the rate of Fe(II) oxidation that we have assumed. Accordingly, we determined the spectral absorption cross section of phototrophic Fe(II) oxidizers (i.e., the cell-number normalized absorption spectra), and calculated how much a 17.6-m-thick layer of anoxygenic phototrophs would reduce the light intensity. Our calculations suggest that this effect would be minimal and would still allow enough light to be present for efficient Fe(II) oxidation, even at the base of this layer (Fig. 1). Similarly, the light intensity attenuation coefficients of phytoplankton and of natural waters containing cyanobacterial chlorophylls (Kirk, 1994) suggest that Fe(II) oxidation rates would be negligibly affected by an overlying layer of cyanobacteria (not shown in Fig. 1). Because our calculations are based on conservative assumptions, even considering limiting factors such as temperature, nutrients,

lower concentrations of Fe(II), and light attenuation by cells and/or (in)organic particles, it appears that anoxygenic phototrophic bacteria alone could have precipitated enough Fe(III) to account for the immense amounts of Fe minerals present in BIFs. Given that the cells closely associate with the Fe(III) precipitates (Kappler and Newman, 2004), it seems likely that deposition of these cell-mineral aggregates would have fostered diagenetic re-reduction of Fe(III) coupled to the mineralization of cell material. As hypothesized by Walker, such processes not only could explain the low content of organic carbon in most BIFs, but also the presence of magnetite and siderite (Walker, 1984).

In conclusion, our experimental and theoretical results suggest that, in a stratified Precambrian ocean, a layer of anoxygenic phototrophic bacteria living beneath the wind-mixed surface layer was the most likely catalyst for BIF deposition, even in the presence of cyanobacteria, and could explain the absence of Fe that has been inferred for shallow-water environments (Tice and Lowe, 2004), as well as account for the deposition of BIFs on the continental shelf. Even in the event of pycnocline deepening due to strong winds or intense surface cooling, upwelling of Fe(II) into the surface layer would have been limited by the metabolism of the anoxygenic phototrophs, serving effectively as a buffer to separate the deep iron reservoir from O<sub>2</sub> at the surface. If Fe(II) was consumed prior to reacting with cyanobacterial oxygen, the dominant sink for oxygen on the early Earth becomes even more enigmatic.

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