

# Chapter 14

## Role of Microorganisms in Banded Iron Formations

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Banded iron formations (BIF) represent the largest source of iron in the world. They formed throughout the Precambrian, and today are globally distributed on the remnants of the ancient cratons. The first BIF dates back to at least 3.9–3.8 billion years. Little is known about this early period in earth's history, in particular about the presence of molecular oxygen, O<sub>2</sub>, and therefore also about the deposition mechanisms of BIF at that time.

### Composition, Occurance, and Spatial/Temporal Distribution of BIF'S

#### *Mineralogy*

The composition of BIF is dominated by silica (~40–50%) and iron (~20–40%). They are considered to be of sedimentary origin, but always display a diagenetic and metamorphic overprint which sometimes significantly altered the original sediment in terms of its composition and mineralogy. Therefore, the main mineral phases now found in BIF, such as hematite (Fe<sup>III</sup>O<sub>3</sub>), magnetite (Fe<sup>III</sup>Fe<sup>II</sup>O<sub>4</sub>), chert (SiO<sub>2</sub>) and stilpnomelane (K(Fe<sup>II</sup>Mg,Fe<sup>III</sup>)<sub>8</sub>(Si,Al)<sub>12</sub>(O,OH)<sub>27</sub>) are actually of secondary origin. Proposed primary minerals are ferric hydroxide (Fe(OH)<sub>3</sub>), siderite (Fe<sup>II</sup>(CO<sub>3</sub>)) (partially secondary), greenalite ((Fe)<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) and amorphous silica (Klein 2005). The iron in BIF originated as dissolved Fe(II) from submarine hydrothermal vents and was subsequently transformed to dissolved Fe(III) in the upper water column by either

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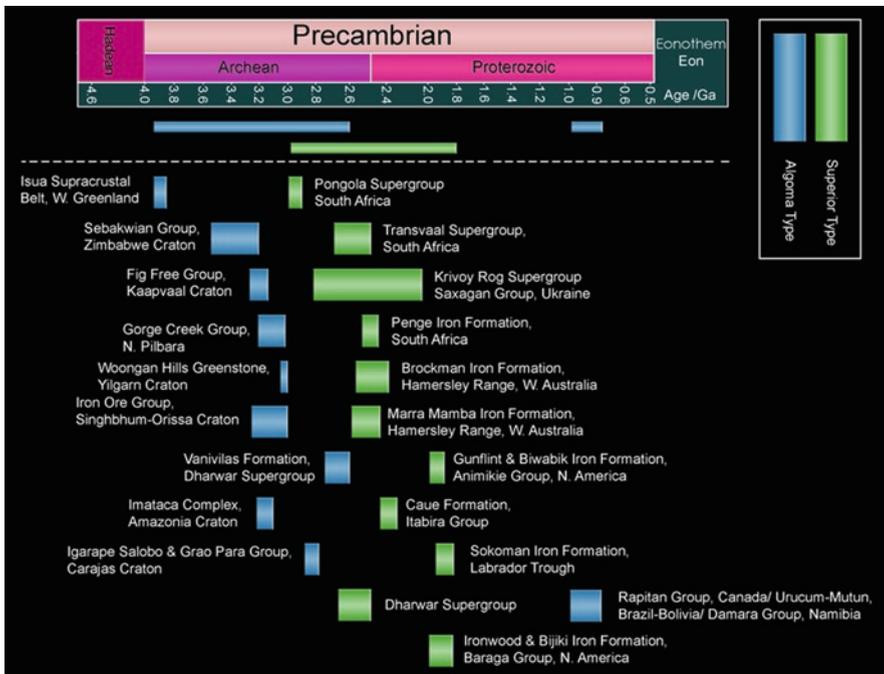
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abiological or biological oxidation. The ferric iron then hydrolyzed rapidly to ferric hydroxide and settled to the sea floor where further transformations ensued.

An early BIF categorization was done by James (1954, 1966) who classified BIF with regards to their mineralogy. Carbonate dominated BIF usually contain alternating chert- and inorganic carbon-rich mineral layers, the latter composed of ankerite ( $\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$ ) and siderite. Those with a high amount of hematite and magnetite are classified as oxide rich BIF, but they may also contain subsidiary amounts of siderite and iron silicates. Silica rich BIF are dominated by chert, a variety of silicate minerals, such as stilpnomelane, minnesotaite ( $\text{Fe}, \text{Mg})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ), greenalite, and carbonates.

### Tectonic Setting

BIF have been broadly classified according to tectonic setting, size and lithology as either Algoma or Superior type (Gross 1965). The Superior type (S-type) first appears around 3 billion years ago (Ga) during the Archean and extends to around 1.7 Ga (in the Proterozoic) (Fig. 14.1). Stratigraphically, the S-type BIF occur in almost coeval, large pericratonic basins (Kholodov 2008). They are dominated by



**Fig. 14.1** Temporal distribution of Algoma and Superior Type BIF. The Algoma type occur from 3.9 to 2.6 Ga and then again from 1.0 to 0.85 Ga. While the Superior type commonly occur between 1.7 and 3.0 Ga

hematite, magnetite, siderite, ankerite and greenalite. There is usually no direct association between these BIF and volcanic rocks.

In contrast, Algoma type BIF is often replaced by volcanic rock sequences. Their thickness and lateral expansion is smaller than those of the Superior type BIFs. They usually appear in late Archean, but there are also Algoma type BIF found in late Proterozoic (Fig. 14.1).

### ***Spatial and Temporal Distribution***

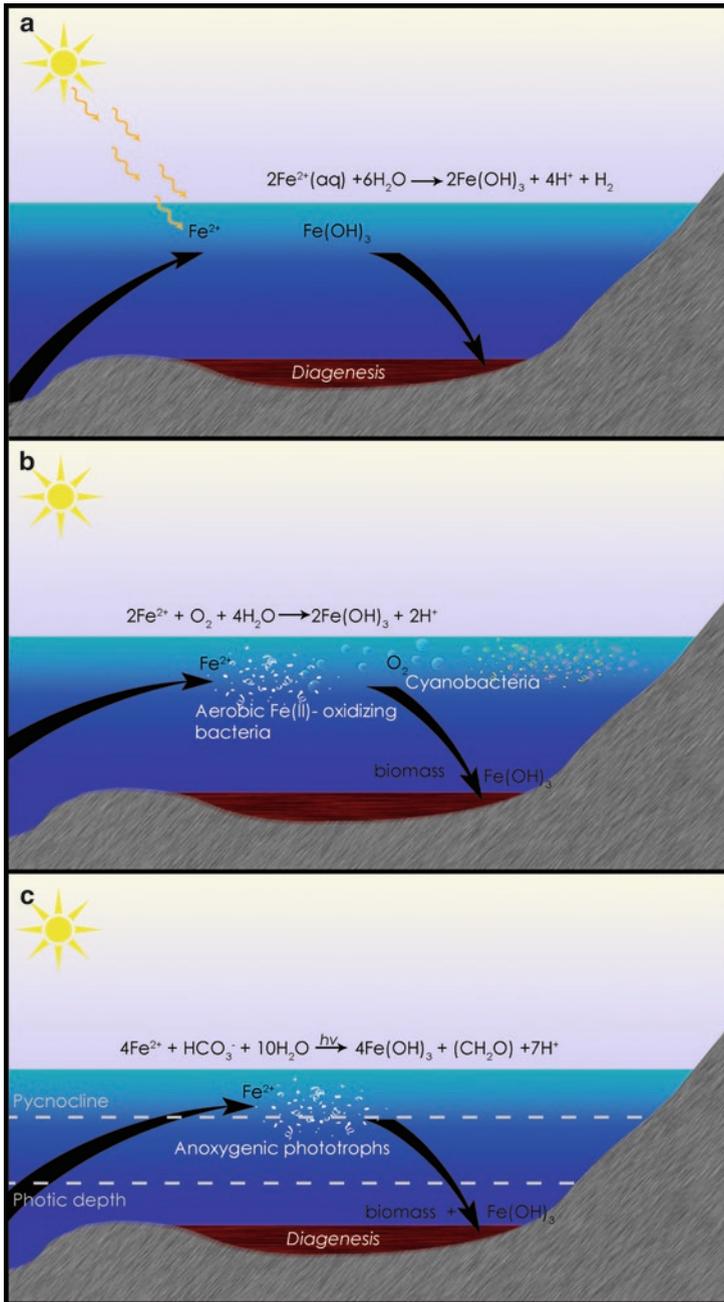
The oldest BIF are those of the Isua Supracrustal Belt in Western Greenland with an approximate age of ~3.8–3.9 Ga (Mojzsis et al. 1996). Further Archean BIF includes the Sebakwian Group in Zimbabwe with an age of ~3.2–3.6 Ga and the late Archean Vanivilas Formation in the Dharwar Supergroup in India with an age of ~2.6–2.8 Ga. The transition zone between the Archean and the Proterozoic is marked by BIF in the Transvaal Supergroup, South Africa, with an age of ~2.7–2.5 Ga and the Brockman Iron Formation at the Hamersley Range in Western Australia with an age of ~2.6–2.4 Ga. The Gunflint & Biwabik Iron Formation in Northern America can be assigned to the Proterozoic BIF with an age of ~2.0–1.9 Ga. BIF then disappear from the rock record until around 750 million years ago with their re-emergence in the Rapitan Group in Canada with an age of ~750 Ma. These latter BIF are associated with Snowball Earth glacial events (Hoffman and Schrag 2000).

### **Microbial and Chemical Processes Generating BIF Source Sediment**

The time of BIF deposition spans major evolutionary changes in the Earth's surface composition, from an early anoxic atmosphere dominated by CO<sub>2</sub> and CH<sub>4</sub> to an atmosphere that became partially oxygenated. Therefore, it is likely that BIF formed via different mechanisms throughout the Precambrian. These mechanisms are briefly discussed below.

#### ***Oxidation of Fe(II) by Cyanobacterial O<sub>2</sub>***

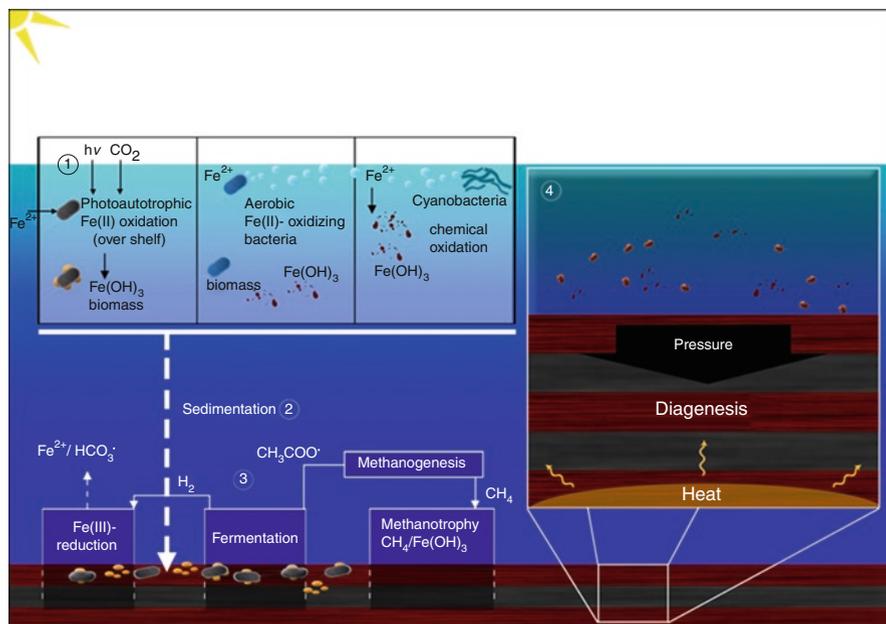
The traditional model of BIF precipitation assumes the oxidation of hydrothermal Fe(II), either via abiotic oxidation by cyanobacterially-produced O<sub>2</sub> (Cloud 1973; Klein and Beukes 1989) and/or biotic oxidation by chemolithotrophic bacteria (aerobic Fe(II)-oxidizers) (Fig. 14.2). Both models suggest the presence of free molecular oxygen in the Precambrian ocean and therefore require the presence of oxygenic photosynthesis at that time of Earth history. This raises the question of when oxygen first appeared and became relevant for Fe(II) oxidation in the ancient



**Fig. 14.2** Summary of Fe(II) oxidation processes potentially involved in BIF deposition. (a) Abiotic photooxidation of hydrothermal Fe(II) by UV light with sedimentation of iron minerals. (b) Chemical oxidation of hydrothermal Fe(II) by cyanobacterial produced  $\text{O}_2$  and Fe(II) oxidation by aerobic Fe(II)-oxidizing bacteria with sedimentation of either iron minerals only (chemical oxidation) or sedimentation of joint biomass and iron minerals (aerobic Fe(II)-oxidizing bacteria). (c) Direct biological oxidation of Fe(II) by anoxygenic phototrophic Fe(II)-oxidizing bacteria with joint sedimentation of biomass and iron minerals

oceans. Previously, microfossils found in the 3.45 billion year old Apex chert of Warrawoona in Australia were suggested as evidence for the existence of cyanobacteria at that time (Schopf 1993), although the biogenicity of those fossils has since been questioned (Brasier et al. 2002). Much younger evidence comes from the 2.7 Ga stromatolitic assemblages of Tumbiana Formation in Western Australia, which suggests that the primary microbial mat community was comprised of cyanobacteria (Buick 1992). Additionally, the analyses of biomarkers, which are organic remains of biological molecules, can be used to identify the former presence of life in rocks. Cyanobacteria display a variety of potential organic biomarker molecules which can serve as a fingerprint. An example are 2 $\alpha$ -methylhopanes, organic molecules that are present in membranes of modern cyanobacteria, which were also extracted from bitumen of the 2.6 Ga Marra Mamba Iron Formation and the 2.5 Gyr Mt. McRae Shale of the Hamersley Group, Western Australia (Brocks et al. 1999; Summons et al. 1999). However, such hopanes have been found in anoxygenic phototrophic Fe(II)-oxidizers as well (Rashby et al. 2007). In addition to hopanes, steranes can be used to track oxygenic photosynthesis. They give direct indication for the existence of oxygen since the biosynthesis of the sterols (precursor to steranes) requires oxygen (Runnegar 1991). These compounds were found in the 2.7 billion-years-old shales of the Jeerinah Formation, Hamersley Group (Brocks et al. 1999, Fig. 14.3).

Further evidence for the presence of oxygen comes from the composition of rocks themselves. For instance, the observation of mass-independent fractionation (MIF) of sulfur isotopes in rocks older than 2.4 Ga, but not younger than 2.1 Ga points to changes in the overall sulfur cycle during that time. Specifically, the loss of the MIF signal is directly attributed to the concentration of atmospheric oxygen, and it is widely accepted that the change in sulfur isotopes indicates a shift from anoxic photochemical reactions to an atmosphere with some free oxygen (Farquhar et al. 2000; Mojzsis 2003). Concentrations of more than 10<sup>-5</sup> PAL would have oxidized sulfur to sulfate preventing the preservation of a MIF signal (Pavlov and Kasting 2002) via initiation of bacterial sulfate reduction. Additionally, the presence of oxygen prior to 2.4 Ga would have had an oxidative effect on siderite, detrital uraninite, and pyrite. But since these minerals have been found in rocks such as the siliciclastic sediments of the Pilbara Craton, it has to be assumed that oxygen was not available prior to this point in early earth atmosphere (Rasmussen and Buick 1999). Recent analyses of chromium isotopes in Banded Iron Formations also yield a hint for the rise of atmospheric oxygen around 2.45–2.2 Ga (Frei et al. 2009). Cr is sensitive to the redox state of the environment and therefore provides an excellent oxygen indicator in the rock record. As soon as atmospheric oxygen became available, oxidative weathering set in producing the oxidized and more mobile hexavalent [Cr(VI)], a process that prefers the heavier Cr isotope. The rise in O<sub>2</sub> in the atmosphere can therefore be followed by Cr isotope analysis in sedimentary deposits such as BIF rocks. The mobility of molybdenum (Mo) is also sensitive to the redox status of the environment. In the absence of molecular oxygen, Mo is preserved in crustal sulfide minerals leading to low Mo concentrations in the oceans and in the sediment. A shift in the concentrations of Mo to higher values in the rock record therefore point to an increase of oxygen in the atmosphere leading to an oxidative weathering of the Mo-bearing



**Fig. 14.3** Model summarizing potential biological and chemical processes during BIF deposition. (1) Hydrothermal Fe(II) is oxidized by photoautotrophic anoxygenic Fe(II)-oxidizing bacteria, aerobic Fe(II)-oxidizing bacteria or via chemical oxidation by cyanobacterially-produced  $O_2$ . (2) Biomass and Fe(III) sediment to ocean floor as cell-mineral aggregates. (3) After sedimentation metabolically driven redox processes by fermenters and Fe(III) reducers take place, possibly also involving methanogens and methanotrophs. (4) Pressure and temperature alter the source sediment and cause induced diagenetic/metamorphic overprint

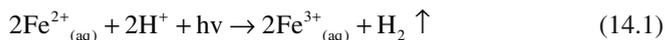
sulfide rocks. Mo analyses in the late Archean Mount McRae Shale in Western Australia carried out by Anbar et al. (2007) point to the presence of small amounts of  $O_2$  in the environment more than 50 million years before the start of the Great Oxidation Event. They assigned the rise of oxygen at around 2.5 Ga  $\pm$  8 Ma.

Collectively, these findings raise the question of how Fe(III) minerals in BIF older than 2.5–2.7 Ga were possible without the presence of oxygen? It is possible that while other processes account for the deposition of major parts of the early BIF, cyanobacteria still could have played a minor role in their formation, but establishing the oxic environment later than their “first” appearance. As mentioned above, biomarkers like steranes, and the fossil record provide evidence for the presence of cyanobacteria around 2.6–2.7 Ga.

### UV-Photooxidation Model

A model which offers a possible explanation for the formation of ferric iron oxides without oxygen involves photooxidation of ferrous iron by UV radiation (Cairns-Smith 1978; Francois 1986). This model is based on the high levels of ultraviolet

radiation on early Earth due to the lack of an ozone layer at that time. Under such conditions, dissolved ferrous iron species, such as  $\text{Fe}^{2+}$  or  $\text{Fe}(\text{OH})^+$ , absorb radiation in the 200–400 nm range, leading to the formation of dissolved ferric iron [reaction 14.1], which in turn, hydrolyzes to form ferric hydroxide at circumneutral pH (Cairns-Smith 1978; Braterman et al. 1983)



However the photochemical oxidation has mainly been observed in simple aqueous systems and the UV light probably was absorbed to a large extent within the ocean surface layer. Also it has been demonstrated that the precipitation of amorphous ferrous silicates and carbonates would have occurred faster than photochemical oxidation (Konhauser et al. 2007). Therefore UV photooxidation can probably be ruled out as primary mechanism to explain the formation of Fe oxide minerals in BIF prior to 2.7–2.5 Ga.

### **Direct Biological Oxidation of $\text{Fe}^{2+}$ by Anoxygenic Phototrophic Fe(II)-Oxidizing Bacteria**

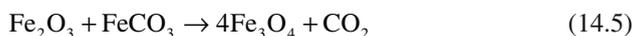
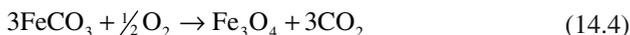
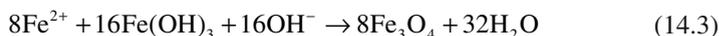
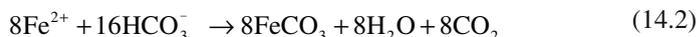
Phototrophic Fe(II)-oxidizing bacteria were discovered about 2 decades ago and might represent an alternative hypothesis to early BIF formation in the absence of  $\text{O}_2$  (Widdel et al. 1993; Heising et al. 1999; Straub et al. 1999; Posth et al. 2010a). These bacteria could have oxidized ferrous iron to ferric iron within the photic zone of the oceans through their photosynthetic process that involves light-energy fuelled  $\text{CO}_2$  fixation coupled to the microbial oxidation of  $\text{Fe}^{2+}$  (Konhauser et al. 2002). The attractiveness of this concept is that it explains BIF deposition in the absence of molecular oxygen using the abundant availability of  $\text{Fe}^{2+}$ , light and  $\text{CO}_2$  at that time. It has even been demonstrated by eco-physiological lab experiments in combination with modeling that these phototrophic bacteria would have been capable of oxidizing enough Fe(II) to explain the large expansion of BIF deposits (Kappler et al. 2005). Growth experiments have even shown that the phototrophs can effectively oxidize Fe(II) up to a few 100 m of water depth (Kappler et al. 2005).

An additional argument in favor of the presence of these organisms in the Archean is the presence of enormous amounts of  $\text{Fe}^{2+}$  that could have served at that time as their electron donors. Interestingly, it has recently been demonstrated that two Fe(II)-rich lakes (Lake Matano in Indonesia and Lake LaCruz in Spain) indeed harbor phototrophic Fe(II)-oxidizing bacteria in the photic zone of the water column (Crowe et al. 2008; Walter et al. 2009). Additionally, phylogenetic analysis of the enzymes involved in the (bacterio-)chlorophyll biosynthesis shows that anoxygenic photosynthetic lineages are more deeply rooted than the oxygenic cyanobacterial lineages (Xiong 2006). However, it has to be noted that to date there is no actual physical or chemical evidence for existence of Fe(II)-oxidizing phototrophs in the Archean (Posth et al. 2010b). A possible approach for such evidence could be finding organic biomarkers that are unique for these bacteria, for example unique pigments

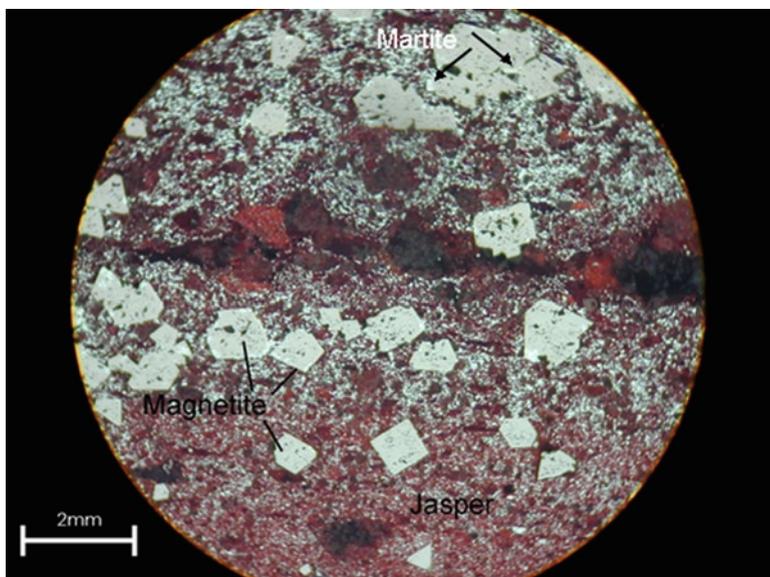
involved in photosynthesis and radical scavenging (radicals forming during Fe-Fenton reactions) – both processes highly relevant in systems where photosynthetic Fe(II)-oxidizers are present.

## Post-Depositional Processes (Including Microbial Activity) in BIF

The question of what minerals in BIF are of primary or secondary origin has been widely discussed. The formation of quartz from siliceous gelatinous precipitate is mostly accepted at this point, while thermodynamic calculations by Berner (1969) show that hematite can form as a result of the dehydration of either goethite or ferrihydrite under diagenetic conditions. The presence of a number of reduced iron phases in BIF complicates the picture because some are considered to represent primary precipitates that formed within the anoxic water column (e.g., spheroidal siderite), when concentrations of ferrous iron and bicarbonate [reaction 14.2], originating from a combination of hydrothermal sources and microbial respiration of sedimented organic carbon, exceeded siderite supersaturation (Tice and Lowe 2004). Other ferrous iron minerals, including magnetite, rhombic siderite, ferrosilicates (stilpnomelane, chlorite), ankerite, and pyrite, formed during diagenesis and metamorphism (e.g., Ayres 1972; Perry et al. 1973; McConchie 1987). In terms of magnetite, a number of petrographic studies have described the secondary origins of the magnetite, including (1) disseminated grains within but obscuring sedimentary laminae, (2) laminated beds that clearly truncate sedimentary layering, (3) layer-discordant veins, and (4) cleavage fills (Han 1978; McConchie 1987; Morris 1993; Krapež et al. 2003). Much of the magnetite likely formed when Fe<sup>2+</sup>, formed via microbial Fe(III) reduction (see below), reacted with the initial ferric hydroxide precursors [reaction 14.3]. However, the fact that magnetite frequently appears in association with siderite-rich bands also supports the notion that magnetite could have formed via oxidation of siderite (only when O<sub>2</sub> was available) [reaction 14.4] or by reaction with hematite [reaction 14.5] (Figs. 14.4 and 14.5).



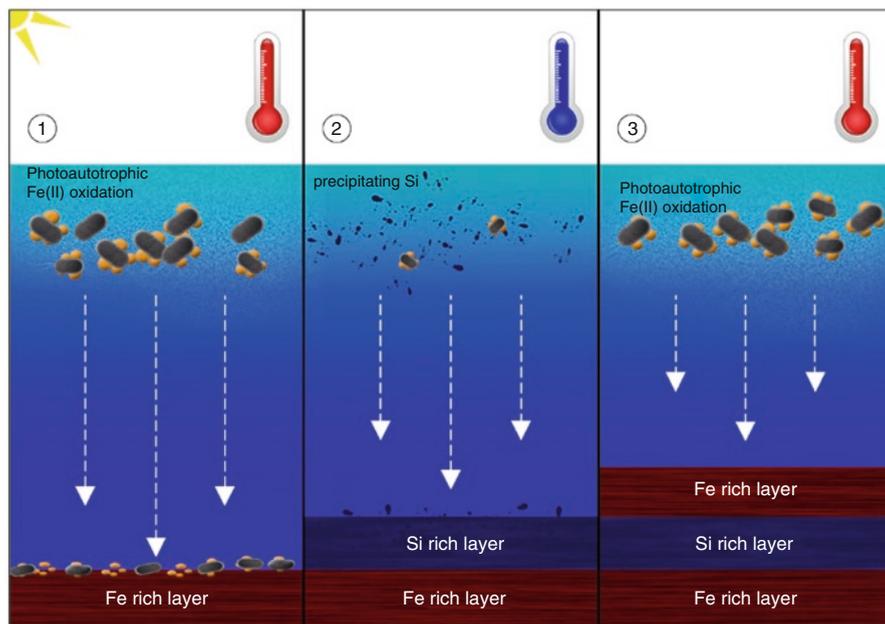
BIF also show an abundance of light carbon isotope signatures within the carbon layers (Garrels et al. 1973; Baur et al. 1985) consistent with the initial presence of microbial biomass during sedimentation. In addition, highly negative  $\delta^{56}\text{Fe}$  values in 2.9 Ga old magnetite (Yamaguchi et al. 2005), with comparable negative



**Fig. 14.4** BIF thin section M1, Mamatwan Manganese Mine, Kuruman, North Cape Province, South Africa. The sample is approximately 2.20–2.22 billion years old. Sample shows white magnetite crystals in a jasperous fine grained matrix. The single magnetite crystals are subhedral to euhedral and their sizes ranges from 1.0 to 0.5 mm. In the *upper part* of the section magnetite forms aggregates with a size of up to 2 mm. Several crystals display narrow bright white rims identified as martite (see arrows). The red color in the jasperous matrix comes from fine grained hematite particles

fractionations as observed in experimental culture with dissimilatory Fe(III)-reducing bacteria (Johnson et al. 2003), point towards the antiquity of such an anaerobic respiratory pathway. Moreover, the recognition that a variety of deeply-branching (and presumed very ancient) hyperthermophilic *Bacteria* and *Archaea* can reduce Fe(III) to Fe(II) (Vargas et al. 1998), strengthens the likelihood that such a metabolism occurred very early on Earth.

Assuming that sedimentation of biomass and Fe(III) took place during anoxygenic phototrophic or aerobic Fe(II) oxidation in the Archean, it could be argued that the electrons present in the biomass associated with the sedimented Fe(III) minerals could theoretically re-reduce all Fe(III) leaving no remains for a later formation of hematite (Konhauser et al. 2005). However, since the Fe(III) oxide hematite and also the mixed Fe(II)-Fe(III) oxide magnetite are major constituents of many BIF it can be assumed that only minor amount of organic carbon were initially deposited with the Fe(III)-rich sediment. Alternatively, the biomass and electrons could have been removed from the sediment by Fe(III)-independent redox processes, e.g. by fermentation or methanogenesis. Calculations by Konhauser et al. (2005) showed that only about 3% of the biomass reached final burial. Indeed, Konhauser et al. (2005) further suggested that some of the initially produced biomass was transformed by hydrolysis and fermentation leading to a possible



**Fig. 14.5** Possible deposition of alternating iron and silicate mineral layers triggered by temperature fluctuations in the ocean water: (1) and (3) Moderate/higher temperatures yield relatively high photoautotrophic bacteria oxidation rates and thus iron(III) mineral formation. Therefore, biomass and Fe(III) settle together to the seafloor. (2) With decreasing temperatures photoautotrophic oxidation rates slow down and at the same time lower temperatures initiate abiotic Si precipitation from Si oversaturated ocean water. Si minerals then settle to the seafloor

removal of electrons in form of reduced compounds (e.g.  $H_2$ ) away from the sediment that otherwise would have been available to reduce Fe(III). Furthermore, some of the  $H_2$  or organic compounds could have been used by methanogens. The highly negative  $\delta^{13}C$  values of around  $-40\text{‰}$  to  $-60\text{‰}$  in 2.8–2.6 Ga old kerogens point to intensive methane formation at that time (Hayes 1983).

### Limitation of Microbial Processes in BIF's by Nutrients and Trace Metals

Phosphate is essential to life due to its important role in many biomolecules such as DNA, RNA and ATP, as well as a constituent in cellular membranes. It was suggested that the strong affinity of phosphate to Fe(III) hydroxides could have depleted the Archean ocean of phosphate leading to a “phosphate crisis”, i.e. constraining microbial activity due to limiting bioavailable concentrations of phosphate in the water column (Bjerrum and Canfield 2002). However, since Archean oceans had high concentrations of dissolved and amorphous silica, the silica would have competed with phosphate for sorption sites at the ferric hydroxide particle

surface lowering sorption of phosphate compared to silica-free systems. Additionally, the co-precipitation of iron and silica changes the particle's point of zero charge (PZNC) also lowering phosphate binding and phosphate removal from the ocean water (Konhauser et al. 2007). Overall, it was therefore suggested that phosphate in the Archean was probably not limiting.

Besides nutrients such as phosphate, trace metals are important for microorganisms due to their role as metal-cofactors. Although the microorganisms usually need only small quantities, trace metals such as nickel, copper, and cobalt can represent a limiting factor for microbial growth. A possible approach to constrain the plausibility of a certain bacterial activity at the time of BIF formation is therefore to estimate concentrations of trace metals required by a certain physiological group of microbes in the Archean ocean from the abundance of these trace metals in BIF. However, to use this approach to constrain certain microbial processes, several questions have to be addressed.

1. Is the trace metal distribution in BIF representative of the composition of the Archean ocean or has there been major remobilization due to diagenesis and/or metamorphism?
2. Do certain trace metals show different sorption behavior to abiogenic versus biogenic Fe(III) minerals and is there a difference in co-precipitation during abiotic versus biotic Fe(II) oxidation?
3. Is there an influence by silica on the sorption and co-precipitation behavior of trace metals?

Recently, analysis of Ni concentrations in BIF, in combination with quantification of Ni sorption behavior to Fe(III) (hydr)oxides (similar to the ones assumed to be the primary minerals of BIF), suggested a decrease in the amount of bioavailable Ni around 2.7 Ga ago probably due to a cooling of the mantle. As a consequence, microbial methane production could have slowed since Ni is essential for these microbes ((Jaun and Thauer 2007), potentially initiating the so-called Great Oxidation Event around 2.4 Ga (Konhauser et al. 2009). Another potentially interesting trace metal is cobalt, which has been identified as being involved in Fe(II) oxidation in phototrophic Fe(II)-oxidizing bacteria and thus possibly limited photoferrotrophic activity in the Archean (Jiao et al. 2005). However, sorption behaviour of Co to abiogenic and biogenic Fe(III) (hydr)oxides has not been correlated with BIF Co concentrations thus far.

## **Mechanisms of Altering Iron and Silica Mineral Layering – A Potential Role of Microorganisms?**

BIF show a characteristic layering of Fe-rich and silica/carbonate-rich bands. The thickness of the layers varies between micro-scale to meter-thick units (Trendall 1968; Beukes and Klein 1992; Klein 2005) and some BIF show a wide lateral continuity of up to hundreds of kilometers. This raises the question of whether the

alternating banding has a unifying trigger (Posth et al. 2008), and whether the precipitation of either iron or silica somehow influences the formation of the other. It has been suggested that the layering is due to seasonal stratification or yearly climate cycles (Morris 1993), in which periodic upwelling or hydrothermal pulsation of Fe(II)-rich waters was punctuated by seasonal evaporation of silica (Holland 1973; Garrels 1987; Jacobsen and Pimental-Klose 1988; Siever 1992).

However, these models have been questioned since they do not explain the lateral banding of both Fe(III) and silica minerals. Additionally, they do not explain why iron and silica do not co-precipitate to a large extent (Trendall 1968; Garrels 1987; Morris 1993). Accordingly, a new model has been suggested that links temperature-induced bacterial Fe(II)-oxidation to abiotic silicification as a way of explaining the banding (Posth et al. 2008). The activity of phototrophic Fe(II)-oxidizing bacteria (Fe(II) oxidation rates) shows a strong temperature dependency (Hegler et al. 2008; Posth et al. 2008). When the bacteria were incubated under changing temperature conditions and in the presence of silica, at water temperatures of 25–30°C, the Fe(II) oxidation rate and the ferric hydroxide precipitation was high. Below and above these temperatures, Fe(II) oxidation and the precipitation of the biogenic iron(III) minerals decreased. At lower temperatures when Fe(III) mineral precipitation decreased, however, the precipitation of amorphous silica was triggered. As temperatures increased to 25–30°C, Fe(III) minerals were again precipitated by the Fe(II)-oxidizing phototrophs, effectively allowing the alternating layering of silica and Fe minerals. Interestingly, the rate of Fe(II) oxidation was not affected by the silica and Fe(III) precipitation seems to be decoupled from silica precipitation. This is probably due to the change in Fe(III) mineral surface charge from positive to negative due to the sorption of cell organic matter preventing silica sorption (Posth et al. 2008). This decoupling suggests that a separate deposition of Fe-rich and silica-rich layers in BIF could have been triggered by one unifying parameter, temperature.

These findings raise the question of whether ocean temperature cycles in the Archean existed and were strong enough to trigger the banding. Estimates of water temperature in the Archean are poorly constrained, and range from 10°C to 85°C (Knauth and Lowe 2003; Knauth 2005; Robert and Chaussidon 2006; Kasting et al. 2006; Jaffrés et al. 2007; Shields and Kasting 2007). An additional difficulty in constraining these past temperature is the high potential for diagenetic overprinting, which might distort the data. Based on the most recent interpretations, the general climate in the Archean was around 10–33°C (Kasting et al. 2006) and consequently, mesophilic Fe(II)-oxidizing phototrophs, as used in the experiments by Posth et al. (2008), would prosper in such an environment.

Nevertheless, two independent lines of evidence suggest that such temperature fluctuations took place in the ancient ocean. First, modern ocean temperature cycles depend on incoming currents and seasonal variations and show temperature changes as needed for the effects observed by Posth et al. (2008). Second, a tilt in Earth's axis (obliquity) could have caused seasonal temperature changes (Laskar and Robutel 1993).

## Conclusions

Banded iron formations not only serve as possible archives for the Precambrian atmosphere and hydrosphere but they shed insights into the biotic processes occurring at that time. It is generally believed that the large amounts of oxidized Fe present in the BIFs were formed by oxidation of hydrothermal Fe(II). The oxidation of the Fe(II) after 2.7–2.5 Ga ago could be due to cyanobacterial O<sub>2</sub>, however, the formation of BIF older than 2.7–2.5 Ga requires an anoxic mechanism for Fe(II) oxidation. Currently, anoxygenic photosynthetic bacteria provide the most plausible explanation of Fe(III) mineral deposition in the anoxic Archean. The role of microorganisms in BIF deposition also goes beyond providing the O<sub>2</sub> for Fe(II) oxidation or direct Fe(II) oxidation. Biomass and ferric hydroxides deposited at the sea floor provide the necessary substrates for Fe(III)-reducing bacteria, fermenters and methanogens. These microorganisms probably reworked the sediments to a significant extent before ultimate lithification.

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