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Cross-references

Algae (Eukaryotic)
 Bacteria
 Carbon (Organic, Cycling)
 Carbon (Organic, Degradation)
 Cyanobacteria
 Fluorescence In Situ Hybridisation (FISH)
 Metals, Acquisition by Marine Bacteria
 Piezophilic Bacteria
 Protozoa (Heterotroph, Eukaryotic)

BANDED IRON FORMATIONS

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Synonyms

BIFs

Definition

Sedimentary deposits of alternating iron-rich (~20–40% Fe) and iron-poor, siliceous (~40–50% SiO₂) mineral layers that primarily precipitated throughout much of the late Archean (2.7–2.5 Ga) and Paleoproterozoic (2.5–1.8 Ga), but then reemerged in the Neoproterozoic (~0.8 Ga).

BIF characterization, mineralogy, and distribution

BIFs are globally distributed, with some of the larger formations being those of the Hamersley range in Australia and the Transvaal Supergroup in South Africa (Figures 1 and 2). Other major BIFs include Krivoy Rog Supergroup, Ukraine (2.2 Ga); Labrador Trough, Canada; Lake Superior Region, USA; Gunflint and Biwabik, North America

(2.2–2.0 Ga), Carajás Formation (2.6 Ga) and Urucum Region, Brazil (0.8 Ga).

The mineralogy of the least metamorphosed BIFs consists of chert, magnetite, hematite, carbonates (siderite and dolomite–ankerite), greenalite, stilpnomelane, and riebeckite (Klein, 2005): the presence of both ferric and ferrous minerals gives BIF an average oxidation state of Fe^{2.4+} (Klein and Beukes, 1992). It is generally agreed that none of the minerals in BIF are primary, but that instead, the minerals reflect both diagenetic and metamorphic overprinting. For instance, the primary iron minerals were most likely ferric hydroxide (Fe(OH)₃), greenalite ((Fe)₃Si₂O₅(OH)₄), and siderite (FeCO₃) (Klein, 2005).

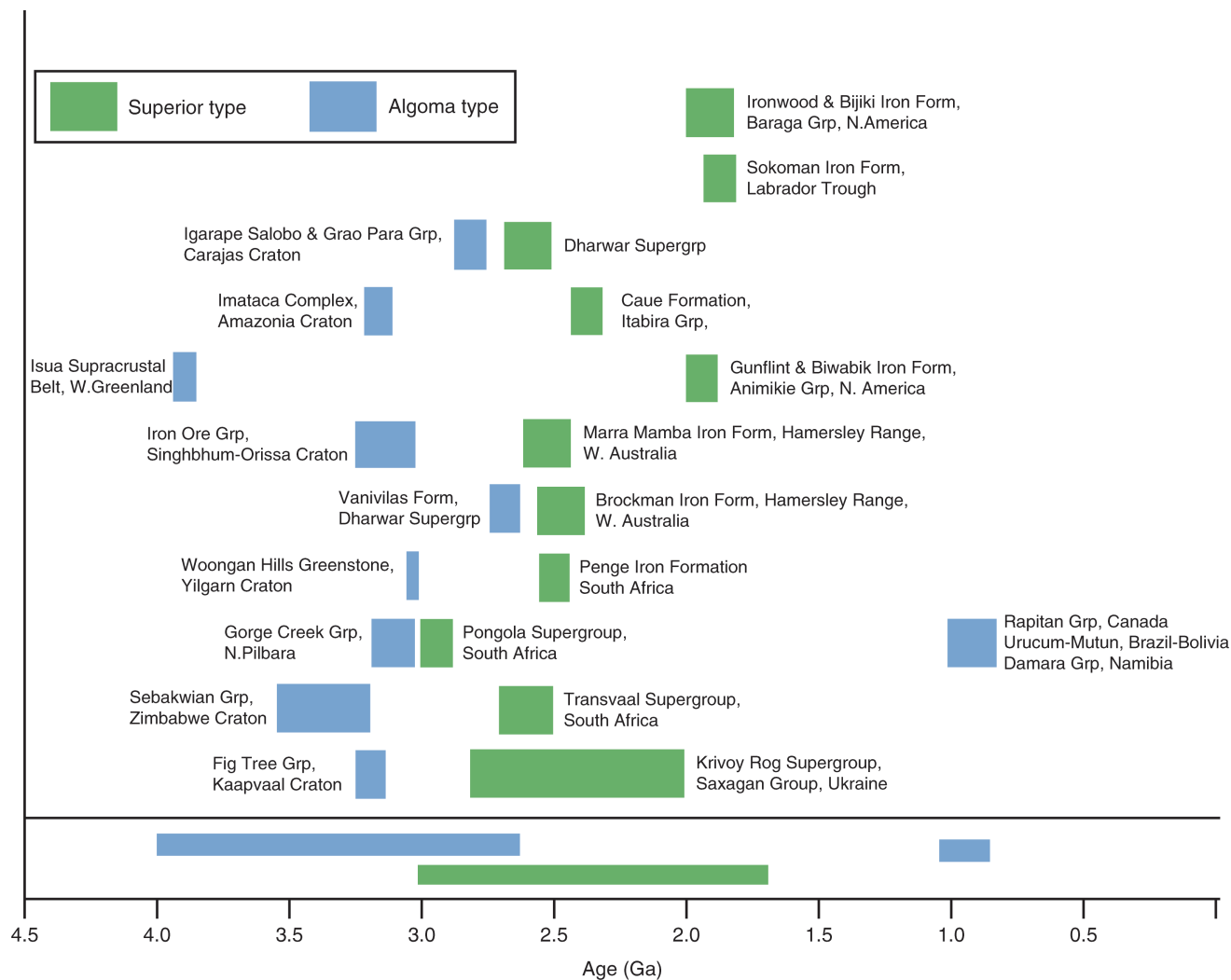
Based on their depositional environment, BIFs have been categorized as Algoma or Superior type. Algoma type BIFs are generally small in lateral extent and display a volcanic association (Gross, 1965, 1980; Huston and Logan, 2004), while Superior type BIFs are found in shelf environments, are vast, and are without a dominant volcanic influence. The “Superior” type BIFs, including those in the Hamersley Group, Western Australia and the Transvaal Supergroup, South Africa, are hundreds of meters thick, over 10⁵ km² in areal extent, and contain >10¹³ t of iron (Trendall, 2002). They are characteristically laminated, with alternating Fe-rich and Si-rich layers (Figures 2 and 3). Banding can 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 Blockely, 1970). Among the latter is the wide variety of varve-like repetitive laminae, known as microbands.

BIFs have also been categorized according to their Fe oxide composition, as hematite or magnetite BIFs (Figure 3) (James, 1954). The former refers to BIFs facies consisting principally or entirely of interbedded chert and (primary) hematite, which are in some places oolitic (e.g., the Gunflint range). The latter describes Fe oxide layers of magnetite that may grade imperceptibly into silicate rock in some areas, be mixed with carbonate, or sprinkled with hematite or chert lenses (James, 1954).

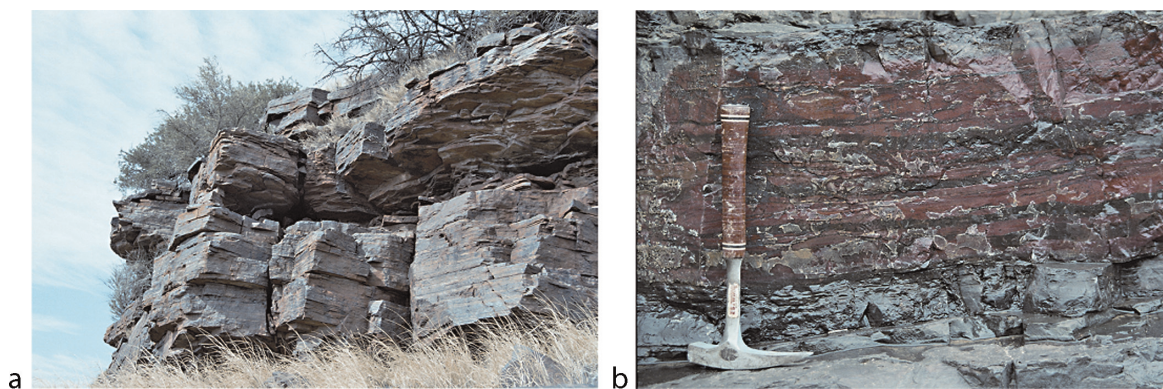
A third categorization of BIF is based on the granular versus nongranular nature of the silica layers. Granules, seen in the 2.0 Gyr Gunflint BIF are approximately 0.5 mm in diameter, irregular, and can be within a chert matrix. They can have a greenalite or magnetite core. These granules, however, do not show the concentric layering seen in hematitic oolites. Non-granular BIFs are typically thin-bedded or laminated and may chiefly be composed of minnesotaite with magnetite and carbonate in some layers (James, 1954).

Banded iron formations and the study of the early Earth

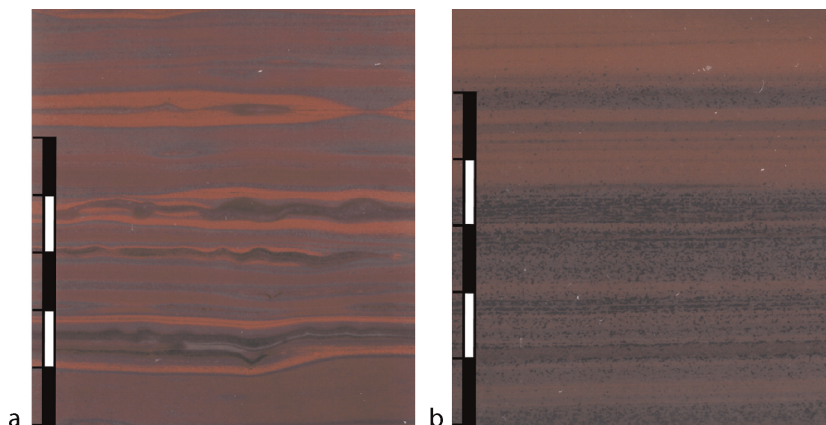
The height of BIF deposition was 2.7–2.4 Ga (Trendall, 2002; Klein, 2005), a timeframe which overlaps with the currently estimated age for the rise of oxygen on the Earth ~2.5 Ga (Anbar et al., 2007). As it is agreed that the



Banded Iron Formations, Figure 1 Appearance of BIFs in geological time and marked as Algoma and Superior types.



Banded Iron Formations, Figure 2 BIF outcrop, Gamohaani Hill, South Africa (a), and White Mfolozi Gorge, Kwazulu Natal, South Africa, Jasper and Magnetite, 3.0 billion-years-old (b). Pictures by Nicole Posth.



Banded Iron Formations, Figure 3 Thin sections of banded iron formation, Mamatwan Manganese Mine, Hotazel, northern Cape Province, South Africa. Samples were taken from a depth of 83.4 m (a) and 87.5 m (b).

source of iron for these deposits was Fe(II), the Fe(III) minerals in BIF indicate that an oxidizing mechanism was present. Once oxygen began its rise due to the advent of cyanobacteria, it is plausible that an oxic mechanism formed BIF, perhaps even in pockets or oxygen oases. In the case of BIF dated prior to 2.7 Ga, however, an anoxic oxidizing mechanism is required to explain the formation of these vast deposits. The latest BIFs (0.8 Ga), which seem to represent a revival later in the geologic record, may be archives of major climate changes related to the Snowball Earth (Kirschvink, 1992; Kopp et al., 2005). Due to the intricacies of the depositional mechanisms, BIFs have been studied for decades regarding their potential as archives of the early Earth environment, but may also prove to be a detailed record of the early Earth biosphere.

BIF deposition

Depositional setting

Early studies of BIF mineral association (James, 1954), as well as comparative BIFs studies (Trendall, 1968; Beukes, 1973; Gole and Klein, 1981; Simonson, 1985; to name a few) postulated that these sedimentary deposits likely formed on the margins of cratons in semi-restricted, marine basins with minimal wave action (for a comprehensive review, Klein, 2005). They also laid a foundation for both theoretical and experimental geochemical modeling based on atmospheric (oxygen and carbon dioxide) and oceanic (iron and silica) concentrations, which are largely linked to mineralogical, petrologic, and isotopic analyses and have been invoked to describe the BIF deposition mechanism (Drever, 1974; Cairns-Smith, 1978; Han, 1978; Braterman et al., 1983; Baur et al., 1985; Francois, 1986; Garrels, 1987; Morris, 1993).

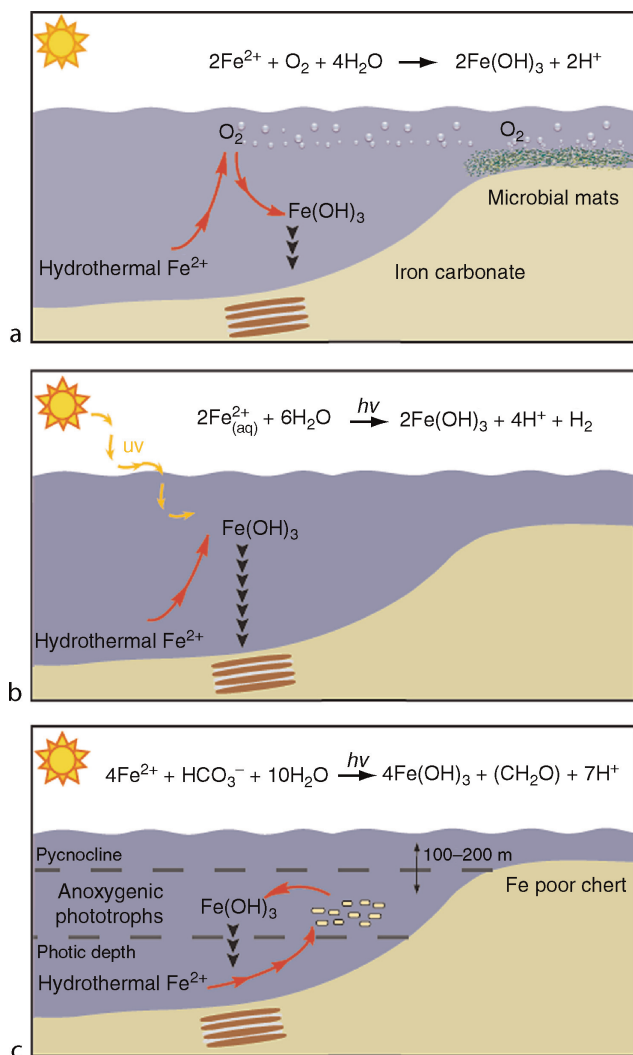
There is ample evidence that the dominant source of Fe (II) into the Archean ocean was hydrothermal (e.g., Jacobsen and Pimentel-Klose, 1988; Bau and Möller,

1993), but it has also recently been suggested that a significant fraction of the Fe in Archean seawater came from the continents (Alexander et al., 2008). The proximity of the Fe(II) source to the site of deposition, however, is still unclear. The estimated Fe(II) concentration for these basins ranges from 0.02 to 0.5 mM (Holland, 1973; Morris, 1993). This Fe(II) may have been delivered from the deep ocean to the outer continental shelf by upwelling currents from a mid-ocean ridge system (e.g., Holland, 1973). Accordingly, BIFs would sediment from below the wave base (free of wave- and storm-induced currents) onto partially submerged platforms of the continental shelves. Alternatively, Fe(II) could have been directly supplied from plumes in a seamount type system (Isley, 1995), which would curtail the difficulties introduced by the high upwelling rates required in the continental shelf model. After deposition, these sediments would undergo diagenesis, with some BIF sediment possibly even being redistributed to deeper waters via turbidity currents (Krapež et al., 2003).

There is significant evidence that Archean oceans also contained elevated concentrations of dissolved silica, possibly even to saturation with respect to amorphous silica (~2.20 mM; Siever, 1992; Maliva et al., 2005). Under such silica-rich conditions, the direct precipitation of amorphous silica could have taken place directly from the water column onto the sea basin floor (Krapež et al., 2003). Moreover, silica could have reacted with dissolved Fe(II) and precipitated as ferrous or ferric-silicates (Konhauser et al., 2007).

Theories of Precambrian BIF deposition

BIF mineralogy dictates that some form of Fe(II) oxidation was necessary for their formation, yet which mechanism(s) dominated is still highly uncertain (Figure 4). While dissolved Fe(II) readily oxidizes in the presence of oxygen at circumneutral pH, to the rise of oxygen on Earth occurred approximately 2.5 Ga (Kopp et al., 2005; Anbar et al., 2007). An alternative, O₂-independent



Banded Iron Formations, Figure 4 Models of banded iron formation deposition: The traditional model of BIF deposition involves the production of oxygen by cyanobacteria, which is released into the water column to chemically react with hydrothermal dissolved Fe(II) (a). The two proposed mechanisms of deposition in an anoxic ocean water column are the abiotic Fe(II) photooxidation by UV light, which has recently been discounted (Konhauser et al., 2007) (b), and direct microbial Fe(II) oxidation via anoxygenic Fe(II)-oxidizing phototrophy (c).

mechanism is therefore necessary to explain the deposition of the earliest BIF.

Both abiotic and biotic mechanisms of BIF deposition have been put forth. The potential role of microorganisms in BIF was first proposed 4 decades ago (Cloud, 1968) and in part addressed the difficulties in explaining these deposits based on geochemical processes alone (Brown et al., 1995). Yet, BIFs contain very little or no organic carbon (0.5% [w/w], Beukes and Klein, 1992) which makes it difficult to constrain the responsible microbial process

simply based on geochemical and petrographic studies. Any fossil information about the presence of life in the Archean has therefore been garnered from contemporaneous formations. For this reason, isotopic, biomarker, and ecophysiological studies with modern analogues have been implemented in order to supplement the geochemical BIF data and test the plausibility of the depositional models and the role of microorganisms.

Oxygenic photosynthesis model

The traditional model of BIF deposition was first postulated by Cloud (1968). Herein, Fe(II) is abiotically oxidized by photosynthetically produced O_2 , allowing for the indirect biogenic precipitation of ferric hydroxide as shown in Equation 1 (Figure 4a). Under an anoxic atmosphere, this O_2 could have been confined to local “oxygen oases” associated with cyanobacterial blooms in coastal settings (Cloud, 1965, 1973). Cloud (1965, 1973) further proposed that such primitive O_2 -producing photosynthetic bacteria, which lacked suitably advanced oxygen-mediating enzymes, required ferrous iron to detoxify oxygen. If so, these microorganisms would have flourished specifically when Fe(II) and nutrients were made episodically available. Once oxygen was present, aerobic Fe(II) oxidizers could also have contributed to biogenic Fe minerals precipitation (Holm, 1989).



The oldest evidence to support the presence of cyanobacteria during the time of BIF deposition came from the 3.45 billion-year-old Apex cherts, Warrawoona, Australia (Schopf, 1993). These findings, however, have since been challenged by Brasier et al. (2002) as being secondary artefacts formed by Fischer–Tropsch type reactions associated with seafloor hydrothermal systems. In fact, Buick (1988) maintained that the chert matrix of the “oldest microfossils” is a secondary hydrothermal deposit of younger age that cross-cuts the primary bedding. The use of kerogen as a marker of past life in these formations has also been challenged by experiments demonstrating the abiotic pathways of kerogen synthesis; simple organic hydrocarbons of abiological origins (e.g., formaldehyde) readily condense onto silica–carbonate inorganic filaments, and subsequently polymerize under gentle heating to yield kerogenous products (García-Ruiz et al., 2003).

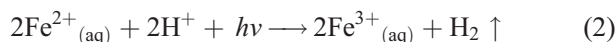
In light of these studies, stronger evidence for the presence of cyanobacteria comes from the stromatolitic assemblages of the 2.7 Gyr Tumbiana Formation, Western Australia. The presence of oxygenic photosynthesis in these formations is based on their likely habitat in sulfate-deficient evaporative lakes (Buick, 1992). This is further supported by the earliest undisputed fossil assemblages of the 2.6 Gyr Campbell Group, South Africa, that include cyanobacterial genera which helped form stromatolitic reefs in shallow subtidal to intertidal settings (Altermann and Schopf, 1995).

Biomarkers, organic compounds derived from more complex precursors which still resemble the original biological molecule after a long burial history, may be used to identify a specific group of organisms in ancient rock. For example, 2 α -methylhopanes are derivatives of prominent lipids in cyanobacteria (methylbacteriohopanepolyols). Abundant amounts were extracted from bitumens of the 2.6 Gyr 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). As these compounds were first solely found in cyanobacteria, their presence was first interpreted as diagnostic of oxygenic photosynthesis, however, they have recently been detected in anoxygenic phototrophs (Rashby et al., 2007), which weakens the use of this biomarker as conclusive proof of oxygenic photosynthesis in ancient rock.

Specific steranes are more indicative of this metabolism. These are 28- to 30-carbon isomers and are unique alteration products of sterols known from extant eukaryotic cell membranes. The only prokaryotes known to synthesize sterols have biosynthetic pathways leading to different structural isomers. Importantly, O₂ is required for the biosynthesis of sterols, hence, their extraction from Archean rock suggests that at least some dissolved oxygen (~0.002 ml O₂ L⁻¹) was present at the time of their production (Runnegar, 1991). To date, there is no experimental evidence to support the alternative theory that steranes may have been produced via an anaerobic pathway utilizing hydrogen peroxide or organic peroxides (Fischer and Pearson, 2007), which make them a specific biomarker of oxygenic photosynthesis. They are found, for example, in the 2.7 billion-years-old shales of the Jeerinah Formation, Hamersley Group (Brocks et al., 1999). Their presence in these shales is particularly intriguing as other redox-sensitive proxies suggest that oxygen arose much later in earth history (Rye and Holland, 1998; Rasmussen and Buick, 1999; Farquhar et al., 2000). Only the presence of localized oxygen oases can explain these conflicting results.

UV photooxidation model

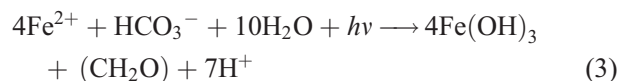
Prior to the rise of atmospheric oxygen and the development of a protective ozone layer, the Earth's surface was also subjected to high levels of ultraviolet radiation. This led to a theory of BIF deposition in which UV radiation drives an abiotic mechanism of Fe²⁺ oxidation and Fe (III) mineral precipitation. Specifically, under conditions of anoxia and high dissolved Fe(II) concentrations, dissolved ferrous iron species, such as Fe²⁺ or Fe(OH)⁺, can absorb radiation in the 200–400 nm range. Dissolved ferric iron is formed (Equation 2), which hydrolyzes to form ferric hydroxide at circumneutral pH (Cairns-Smith, 1978; Braterman et al., 1983) (Figure 4b).



These experiments, however, were recently carried out in complex solution simulating disequilibrium Precambrian ocean water chemistry in which Fe(II)-rich hydrothermal waters react with ambient Si-saturated seawater also containing high HCO₃⁻ concentrations (Konhauser et al., 2007). It was shown that the oxidation effects of either UVA or UVC were negligible in fluids with high dissolved Fe(II), Si, and HCO₃⁻, compared to the precipitation of ferrous-iron-silicates and ferrous carbonate. This suggests that under such conditions Fe²⁺ would have been largely deposited as Fe(II) minerals instead of being oxidized by UV radiation. The fact that Fe (III) minerals are present in BIF therefore suggests that in the absence of O₂ the alternative anoxic depositional mechanism, Fe(II) oxidation by anoxygenic phototrophs, drove Fe oxide deposition.

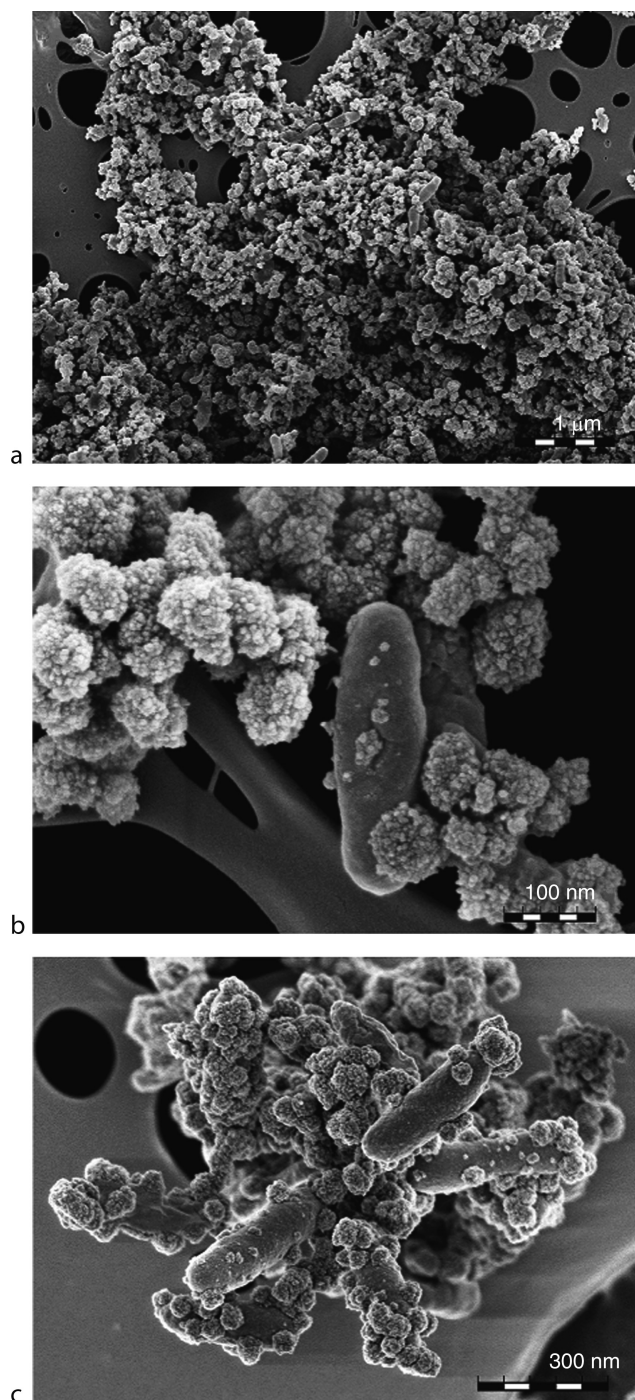
Anoxygenic Fe(II)-oxidizing phototroph model

Anoxygenic photosynthesis was first suggested as a BIF deposition mechanism by Garrels et al. (1973) and Hartman (1984). They proposed that light, not O₂, may have coupled the carbon and iron cycles via photosynthesis that used Fe(II) rather than H₂O as an electron donor and produced Fe(III) rather than O₂ (Figure 2c). It was only 2 decades later that the plausibility of this theory was validated by the discovery of a modern Fe(II)-oxidizing phototroph (Widdel et al., 1993). Seven extant strains of anoxygenic Fe(II)-oxidizing phototrophs are now known to use light energy to catalyze the oxidation of Fe(II) and the corresponding reduction of CO₂, which yields biomass and ferric hydroxide as shown in Equation 3.



In the context of BIFs, anoxygenic Fe(II)-oxidizing photosynthesis (photoferrotrophy) is the only direct biological process that can precipitate Fe(III) minerals in the absence of oxygen.

While no direct evidence exists for the presence of these strains on the Archean Earth, various lines of evidence support the plausibility of anoxygenic phototrophs in BIF deposition. Ecophysiological studies performed with modern anoxygenic Fe(II)-oxidizing phototrophs test the plausibility of this deposition mechanism. It was shown that these strains inhabit a wide range of growth environments; being globally distributed and present in fresh and marine waters (Ehrenreich and Widdel, 1994; Heising et al., 1999; Straub et al., 1999; Croal et al., 2004; Jiao et al., 2005). These organisms do not have a unique form, all being rod-shaped (Figure 5), yet morphological variety is apparent, one example being the presence of vacuoles in one strain, *Thiodictyon* sp. strain F4 (Croal et al., 2004). These strains also utilize a variety of substrates, such as acetate, FeS and H₂, which suggests that they are versatile enough to be an integral group in both



Banded Iron Formations, Figure 5 Anoxic Fe(II)-oxidizing phototrophs "*Rhodospirillum rubrum*" sp. strain SW2 (a, b) and *Chlorobium ferrooxidans* sp. strain KoFox (c) form aggregates with the Fe(III) hydroxides produced by their metabolism. Many cells are not encrusted by, but only associated with, the Fe(III) minerals that may have been the primary minerals in BIFs.

ancient and modern environments. Modeling of the photosynthetic Fe(II) oxidation rates determined in these studies suggest that such microorganisms could have accounted for all of the Fe(III) initially deposited in primary BIF sediment (Kappler et al., 2005). Importantly, while the Fe(II) oxidation rate of these strains is dependent on light intensity, anoxygenic phototrophs can oxidize Fe(II) in light regimes befitting the photic zone of ocean water (of a few hundred meters depth) (Kappler et al., 2005). Also, Fe(II) oxidation is not hindered by high concentrations of dissolved silica (tested at 2 mM Archean ocean concentration) (Siever, 1992; Konhauser et al., 2007).

While modern studies show that cyanobacteria are indeed important in stromatolite building through the trapping and binding of carbonate grains in their filaments and extracellular polymers, several anaerobic pathways, such as sulfate reduction (e.g., Visscher et al., 1998; Paerl et al., 2001), are also integral in carbonate cementation and localized alkalinity generation. Indeed, sequence analysis of small subunit rRNA genes amplified with PCR from genomic DNA showed that anoxygenic phototrophs represent a considerable fraction of biomass in the modern stromatolite communities of Hamelin Pool, Shark Bay, Australia (Papineau et al., 2005). Recently, Bosak et al. (2007) experimentally demonstrated that the anoxygenic phototroph, *Rhodospirillum rubrum*, stimulates the precipitation of calcite in saturated solutions and builds stromatolite-like structures.

While 2 α -methylhopanes were first considered diagnostic of oxygenic photosynthesis, they may have a structural function and are not related to cell metabolism. Indeed, several facultative and obligate anaerobes possess the genes for hopanoid biosynthesis, and *Geobacter sulfurreducens* produces a wide variety of complex hopanoids structurally related to 2 α -methylhopane under strictly anoxic conditions in pure culture (Härtner et al., 2005; Fischer and Pearson, 2007). Moreover, it was recently demonstrated that an anoxygenic Fe(II)-oxidizing phototroph, *Rhodospirillum rubrum*, generates substantial quantities of 2-methylhopanoids in the absence of oxygen (Rashby et al., 2007), which renders their presence in ancient rocks alone as an unsatisfactory marker for a specific metabolism.

Pigment biomarkers may offer further evidence of a microbial role in BIF. Okenane, the fossil hydrocarbon biomarker of the carotenoid pigment precursor, okenone, was recently found in the 1.64 billion-year-old Barney Creek Formation in northern Australia, a marine, sub-wavebase base succession. This pigment is exclusively found in purple sulfur bacteria and in recent sediments under euxinic conditions (Brocks, 2005).

Isotopic evidence and the BIF depositional mechanism

The Fe isotope composition of iron minerals in BIFs is markedly different from the homogenous values seen in

igneous rocks and many modern marine sediments ($\delta^{56}\text{Fe}$ $0.00 \pm 0.05\%$). Specifically, the hematite, magnetite, Fe-carbonate, and pyrite Fe isotope compositions reflect the various processes contributing to BIF formation; equilibrium fractionation of minerals, a variation in the fluid isotope composition from which the minerals precipitated, as well as microbial processes (Johnson et al., 2003; Johnson and Beard, 2005).

In an effort to elucidate the role of microorganisms in the formation of BIF, the Fe isotope fractionation carried out by Fe metabolizing microorganisms was analyzed in controlled laboratory studies of both pure and enrichment cultures. These show that ferric hydroxides are enriched in the heavy isotope relative to Fe(II) for anoxygenic Fe(II)-oxidizing phototrophy ($1.5 \pm 0.2\%$) (Croal et al., 2004), microbially catalyzed aerobic Fe(II) oxidation at low pH (Balci et al., 2006), aerobic chemical oxidation (Bullen et al., 2001), and UV Fe(II) oxidation (Straton et al., 2006), suggesting that all major processes produce similar Fe isotope fractionations.

The isotopic fractionations reported from laboratory experiments correlate well in part with the values recovered from Archean to early Proterozoic banded rocks of the Transvaal Supergroup, South Africa. $^{56}\text{Fe}/^{54}\text{Fe}$ values in hematite are as high as $+0.75$ to $+1.0\%$ (Johnson et al., 2003) when compared to the Fe from hydrothermal vents ($\pm 0\%$). As UV photooxidation was recently ruled out as a significant BIF deposition mechanism (Konhauser et al., 2007), these positive to near-zero $\delta^{56}\text{Fe}$ values are even consistent with (although not proof of) phototrophic Fe(II) oxidation in the early Archean oceans. However, the similarity in values from anoxygenic phototrophs with those of Fe(III) oxides formed by chemical oxidation and microbially catalyzed aerobic Fe(II) oxidation make it difficult to distinguish the key biotic and abiotic processes (Bullen et al., 2001; Balci et al., 2006). Iron isotope fractionation during oxidation itself is obviously independent of the oxidation mechanism (chemical or biological) because of the very rapid isotopic exchange between aqueous Fe^{2+} and Fe^{3+} , allowing isotopic equilibrium to be attained between reduced and oxidized aqueous species. Moreover, in these ancient formations interpretation of the isotopic signature is complicated by the complexity of the depositional environments, the diagenetic processes which have altered the Fe mineralogy, including the infiltration of external fluids during diagenesis and/or low temperature metamorphism which may have erased the primary isotope record (Hoefs, 1997; Johnson et al., 2003). Indeed, the large variation of $\delta^{56}\text{Fe}$ (-2.5 to 1.0% relative to the bulk Earth) in late Archean and early Paleoproterozoic BIFs from the Transvaal Supergroup, South Africa incorporates the entire range of values measured on the Earth.

The carbon isotopic record of BIFs is constrained by the low occurrence of organic carbon (0.5% [w/w], Beukes and Klein, 1992) in these structures. Carbon isotope signatures observed in contemporaneous formations may offer information about organisms which were present at the

time of deposition, but whose record was erased, for example, by postdeposition diagenetic processes. In such ancient formations, negative carbon isotope signatures are often interpreted as an indicator of life. Organisms transform inorganic carbon (e.g., CO_2 or HCO_3^-) via autotrophic pathways into organic carbon, preferentially incorporating the lighter isotope, ^{12}C , into the organic phase and producing residual CO_2 enriched in the heavier isotope, ^{13}C . Cyanobacteria, for example, display a $\delta^{13}\text{C}$ range of -4 to -35% (Schidlowski, 2000). For example, early photosynthesis has been linked to mat-forming communities in microfossiliferous units within Archean formations from Western Australia and South Africa (e.g., Altermann and Kazmierczak, 2003; Tice and Lowe, 2004) by carbon isotopic values ranging from -20% to -35% , as well as the $-31.0\% \pm 4.7$ values from organic carbon in early Proterozoic cherts (Strauss et al., 1992).

Key to this approach is the consideration of overlapping degrees of fractionation produced by various carbon fixation pathways (reductive acetyl-CoA, reductive citric acid, Calvin cycle, and hydroxypropionate). This makes it impossible to determine whether these putative biological residues were remnants of chemolithoautotrophs, evidence for early photosynthesis, or abiological C-isotopic fractionations, such as those associated with Fischer-Tropsch type processes ($\Delta^{13}\text{C}$ between -50% and -100%).

Theories of iron and silica mineral layering

One of the characteristic features of BIF are the alternating Fe-rich (hematite, magnetite, and siderite) and the silicate/carbonate (chert, jasper, dolomite, and ankerite) layers that form bands varying in thickness from the microscale (μm in thickness) to meter-thick units (Trendall, 1968; Klein and Beukes, 1992; Klein, 2005). Some deposits, such as in the Dales Gorge Member, Hamersley Group, Western Australia, show laterally contiguous layers up to a 100 km in distance. This suggests that some unifying trigger of iron and silicate mineral precipitation exists over large areas with some regularity, most likely one which largely subdues the precipitation of one mineral while stimulating that of the other. Furthermore, given the range of band thickness from the micro- to macro-scale, as well as the complex mineralogy, it is most likely that layering in BIF is determined by a multilayered mechanism; one producing primary layering and a second mechanism acting post deposition via diagenesis.

Following this observation, many models attribute the primary genesis of micro and mesobands to seasonal stratification, or to yearly or decadal climatic cycles. Episodic hydrothermal pulsation and upwelling of Fe(II)-rich waters into depositional basins already saturated with dissolved silica have been invoked to explain these bands; silicification is driven by seasonal evaporation of basin waters (Holland, 1973; Garrels, 1987; Jacobsen and Pimentel-Klose, 1988; Siever, 1992). This mechanism, however, does not explain the laterally contiguous fine-scale banding, nor does it resolve why the iron and silica

do not co-precipitate but rather form distinct mesobands (Trendall, 1968; Garrels, 1987; Morris, 1993). Furthermore, in light of increasing evidence for an active microbial component in the Fe cycle (Johnson et al., 2003), the potential importance of microorganisms in BIF deposition models has been suggested. Indeed, a mechanism of alternating Fe and silicate mineral layer deposition with a microbial driver triggered by temperature has been recently presented (Posth et al., 2008).

Diagenesis in BIFs: oxidation and the reduction of Fe(III) minerals

The average oxidation state of $\text{Fe}^{2.4+}$ can be described by the simultaneous deposition of Fe(II) and Fe(III). Yet, this mixed oxidation state can also be explained by partial biotic or abiotic diagenetic re-reduction of precipitated Fe(III) to Fe(II). Experimental studies testing such diagenetic mineral transformations in the presence and in the absence of biomass have not yet been reported. Nonetheless, the presence of magnetite as (1) disseminated grains within but obscuring sedimentary laminae, (2) laminated beds that clearly truncate sedimentary layering, (3) layer-discordant veins, and (4) cleavage fills, suggests such a secondary origin (Ewers and Morris, 1981; Krapež et al., 2003).

The diagenetic or microbial modification of Fe(III) after sedimentation to produce siderite (FeCO_3) and magnetite (Fe_3O_4) requires a reductant. Even if a surface water oxic zone was generated by cyanobacterial activity (Summons et al., 1999), deep waters remained anoxic (e.g., Canfield, 1998). The dominant anaerobic respiratory processes would have oxidized fermentation products in the bottom waters and/or shallow sediments (Rothman et al., 2003). The scarcity of O_2 limited both nitrate and sulfate. This is supported by both negligible sulfur isotopic fractionations between late Archean and early Paleoproterozoic sulfide and sulfate minerals (Strauss, 2003), as well as the absence of pyrite in BIF, except in association with interlayered shaley units (Ewers and Morris, 1981). The significance of manganese pathways is also refuted by the low relative concentrations of Mn(II) released in hydrothermal effluent, as well as the lack of phototrophic or nitrate-independent Mn(II) oxidizing bacteria in modern environments. In contrast, abundant ferric hydroxide deposited as BIF may point to the importance of a microbial process which coupled the oxidation of organic carbon, dead planktonic bacteria, to the reduction of ferric iron producing such reduced iron mineral phases.

Evidence of BIF diagenesis via ancient microbial Fe(III) reduction comes from Fe isotopic ratios in Fe-bearing minerals from Archean sedimentary rocks that closely mimic those observed during modern dissimilatory Fe(III) reduction. For instance, analyses of carbon- and magnetite-rich rocks, from the 2.9 Gyr Rietkuil Formation, Witwatersrand Supergroup, South Africa, revealed $\delta^{56}\text{Fe}$ values as low as -2.3‰ (Yamaguchi et al., 2005). These negative fractionations are very similar to what might be expected from multiple stages of Fe(III)

reduction (Johnson et al., 2004), where each single-step bacterial Fe(III) reduction leads to isotopically light ($\delta^{56}\text{Fe} < 1.2\text{‰}$) aqueous Fe(II) relative to the initial ferric hydroxide substrate (Icopini et al., 2004). The importance of Fe(III) reduction as a means to explain the iron fractionations has, however, been challenged by Rouxel et al. (2005). They suggested that highly variable, but negative values in pyrite from black shales (0.5‰ to -3.5‰) between 2.8 and 2.3 Ga more likely reflect the initial deposition of Fe oxides (e.g., BIFs) which preferentially removed isotopically heavy ^{56}Fe , driving the ocean waters to the negative $\delta^{56}\text{Fe}$ values recorded in pyrite. This interpretation is consistent with the notion that partial biological and abiological processes oxidized the dissolved Fe(II) brought into the shallow waters, but is problematic in light of recent studies showing significant isotopic variations for minerals within close proximity and thus, time of deposition (Johnson et al., 2008). This variation is perhaps most easily explained if the Fe isotopes reflect diagenetic pathways and not the bulk seawater (Johnson et al., 2008).

BIF diagenesis and the Archean marine Fe cycle

BIFs have recently been studied to develop a model of the Archean marine Fe cycle. In doing so, Konhauser et al. (2005) made two assumptions. First, they assumed that the bulk of the Fe(II) component in Fe-rich BIF-type macrobands formed diagenetically through biological Fe(III) reduction, i.e., the magnetite is not primary. Based on a predicted rate of Fe(III) deposition annually (1 mm year^{-1}), they then quantified the electrons that were needed to generate the amount of magnetite as reported in BIF (one third of Fe minerals; Morris, 1993). Second, they quantified the amount of photosynthetic Fe(II)-oxidizer biomass that may have been generated in the photic zone of the water column (based on Kappler et al., 2005), in order to estimate the amount of Fe recycled prior to burial. The results demonstrated that under ideal growth conditions, as much as 70% of the biologically formed Fe(III) could have been recycled back into the water column via fermentation and organic carbon oxidation coupled to microbial Fe(III) reduction. It was also suggested that some of the biomass may have been ultimately consumed via methanogenesis, i.e., coupling the oxidation of acetate or H_2 to methane formation. The hypothesis is to some extent corroborated with the analyses of kerogens (extracted from rocks 2.8 and 2.6 Gyr) with highly negative $\delta^{13}\text{C}$ signatures (between -40‰ and -60‰) that possibly formed as the result of methanogenic ^{12}C -rich gas production, the incorporation of the methane into the biomass of methanotrophic bacteria and inevitably the preservation of ^{12}C -enriched organic matter (Hayes, 1983).

Summary

Banded iron formations (BIFs) have been studied for decades in regard to their importance as an economically

viable source of iron ore, but their significance also extends to their potential as archives of the early Earth environment.

In spite of this effort, the mechanism of their deposition and in particular whether microorganisms drove the precipitation of BIF minerals, is still uncertain. Increasing evidence of a predominantly anoxic Earth until ~2.5–2.4 Ga forces the investigation of O₂-independent mechanisms for BIF deposition. For this reason, recent studies have explored the long-standing proposition that Archean BIFs may have been formed, and diagenetically modified, by anaerobic microbial metabolisms.

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Cross-references

Algae (Eukaryotic)
 Biological Control on Diagenesis: Influence of Bacteria and Relevance to Ocean Acidification
 Biomarkers (Molecular Fossils)
 Biosignatures in Rocks
 Critical Intervals in Earth History
 Cyanobacteria
 Fe(II)-Oxidizing Prokaryotes
 Fe(III)-Reducing Prokaryotes
 Gallionella
 Geobacter
 Hydrothermal Environments, Marine
 Isotope Fractionation (Metal)
 Isotopes and Geobiology

Microbialites, Stromatolites, and Thrombolites
 Nanocrystals, Microbially Induced
 Ores, Microbial Precipitation and Oxidation
 Photosynthesis
 Salinity History of the Earth's Ocean
 Sediment Diagenesis – Biologically Controlled
 Snowball Earth
 Stromatolites

BASALT (GLASS, ENDOLITHS)

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Synonyms

Endolithic microorganisms in basaltic glass; Microbial life in glassy basalt

Definition

Basalt endoliths. Microorganisms that colonize and live inside fractures, vesicles, and other cavities in basaltic rocks.

Basalt. The most common volcanic rock formed by eruptions of magma of basaltic composition.

Seafloor basalt. Basalt that is exposed at the seafloor, most commonly in or close to the ocean spreading ridge axes where the crust is young, or at intraplate seamounts.

Subseafloor basalt. Basalt that has been buried by younger lava flows and/or deep-sea sediments, as the crust aged and moved away from the spreading ridges.

Basaltic glass and endolithic microorganisms

Introduction

Basalt is continuously formed during volcanic eruptions along the global mid-ocean ridge system, and constitutes the upper 0.5–1 km thick layer of the ocean crust which covers more than 50% of the Earth's surface. When the basaltic magma is extruded into the cold seawater, the 1–2 cm thick outermost surface layer is cooled so rapidly that its chemical species do not have enough time to be arranged into minerals, but freeze to an amorphous glass rind. These glassy margins become heavily fractured due to cooling-related contraction, and the fracture networks provide an immense surface area for rock-water interactions and colonization by microorganisms. As the basaltic glass dissolves and alters more quickly than the minerals (pyroxene, plagioclase) in the crystalline interior of the lava, the glassy proportion plays an important role in the alteration of the ocean crust and the chemical exchange with the ocean water. The alteration is not only controlled by physiochemical factors but also by microbial processes, implied by the presence of endolithic microorganisms (see *Endoliths*) within the glassy margins. The microbial

activity may, on the other hand, be controlled by the geological environment, which includes a variety of complex fluid temperature and chemistry conditions ranging from seafloor weathering to various hydrothermal systems.

Basaltic glass alteration

Low-temperature alteration of basaltic glass results in the formation of concentrically zoned rims of a yellow-brown, hydrous residual alteration product, frequently called palagonite, along the outer surfaces, and internal vesicles and fractures of the glassy margins of lava flows. The altered glass is amorphous (gel-palagonite) to poorly crystalline with clayish character (fibro-palagonite) (e.g., Stroncik and Schmincke, 2001), and is usually highly enriched in oxidized Fe and Ti, and depleted in Si and alkaline and alkaline earth elements compared to the fresh, parental glass. The term palagonite was used for the first time by von Waltershausen in 1845 for the brown groundmass of a tuff from Palagonia, Sicily, and was then thought to be a new mineral phase. Although palagonite was later shown to be a heterogeneous material, the term has commonly been used in the literature. However, several authors now recommend referring to this material as altered glass. During the last 2 decades, various field and laboratory studies have shown that the alteration rate and the chemical and crystalline characteristics of the altered glass strongly depend on the physiochemical and hydrological conditions (e.g., Crovisier et al., 2003). The understanding of how the endolithic microorganisms in the glassy margins of basaltic lava flows influence and interact with the alteration process is, however, still poor.

Evidence of microbial life in glassy basalt

The first in situ observations of endolithic microorganisms in basaltic glass was reported from a scanning electron microscopy (SEM) study of recent (<1 million years old (Ma)) volcanic glass deposits from Iceland (Thorseth et al., 1992). Microbial biofilms together with irregular alteration fronts at the fresh-altered glass boundary lead to the suggestion that the degradation of the volcanic glass could be biocatalyzed by the development of more aggressive microenvironments in the near vicinity of the microbial cells. This was subsequently supported by experimental alteration studies, where development of corrosion marks in the glass surface only was observed in combination with biofilm formation and not in sterile controls (Thorseth et al., 1995a; Staudigel et al., 1995, 1998). Similar alteration textures resembling microbial cell morphologies observed in glassy margins of 6 Ma ocean basalt, sampled 432 m below the seafloor at the Costa Rica Rift during the Ocean Drilling Program (ODP) Leg 148, were then stained using DNA-specific dyes to confirm the presence of DNA within these structures (Thorseth et al., 1995b; Giovannoni et al., 1996; Furnes et al., 1996). Further fluorescence in situ

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