2B. Banded Iron-Formation: A Continuing Enigma

1.   Introduction

iron formation	a chemical sedimentary rock, typically thin-bedded and/or finely laminated, containing at least 15% iron of sedimentary origin, and commonly but not necessarily containing layers of chert

- American Geological Institute Glossary of Geology

Banded-Iron Formations ('BIFs') are amongst the most controversial of geological deposits. They are characterized by the presence of alternating layers of iron-rich and amorphous silica-rich layers. This dichotomous compositional layering is usually expressed on several scales, from fine sub-millimetre-scale varve-like laminae to metre-scale bands. Even on a microscopic scale, the boundary between the ferruginous and siliceous layers is distinctly abrupt.

This introductory chapter sets out to explore the key aspects of BIFs pertinent to their role in the study of early earth evolution, and outline the major controversies surrounding their interpretation. The focus rests on BIF classification, temporal- and spatial-distribution, constituent behaviour in solution, depositional environment, and origin.

An understanding of the origin of BIFs provides useful insight into conditions existing on, and governing, the early lithosphere, hydrosphere and atmosphere. Iron is used as a metabolic agent by numerous microorganisms. The processes mediated by some of these, including specific species of oxygenic- and anoxygenic-photoautotrophs and chemoferrotrophs, lend credence to the theory of BIF-deposition being, at least in part, a microbially mediated process. Direct evidence for a microbial role in Archaean BIF deposition remains elusive.

All geologists agree that BIFs offer vital insights on the evolution of the early earth. They just can't agree on what those insights are. A brief description, outlining

the general characteristics of BIFs, is instructive. The following discussion draws upon field data from Australia, southern Africa and Greenland.

1.1. Observations of BIFs in Australia, southern Africa and Greenland

1.1.1. Layering and Composition

The quintessential feature of BIFs is the presence of alternating layers of iron-rich and amorphous silica-rich layers. This dichotomous compositional layering is usually expressed on several scales at any given outcrop, from fine sub-millimetre-scale varve-like laminae to metre-scale bands. Haematite and magnetite dominate the iron-rich layers, sometimes accompanied by lesser -oxides and -sulphides of iron and other metals, such as pyrite, chalcopyrite and ilmenite. Varying amounts of carbonate mineral phases, such as calcite and siderite, may or may not be present in both iron-rich and chert-rich layers. Layers of silica may or may not be jaspilitic, frequently patchily. Even on a microscopic scale, the transition between iron- and silica- bands is, as a rule, abrupt.

Compared to other sedimentary and metasedimentary rocks, BIFs appear to be particularly lacking in phosphate-bearing minerals. Organic matter is also scarce.

1.1.2. Vertical and Horizontal Extent

Both the thickness and lateral extent of BIFs vary greatly. Where closely associated with volcanic successions, such as in the Isua Supracrustal Belt in southwest Greenland and in the Kraaipan Greenstone Belt in South Africa's Northern Province, BIF thickness is on the order of tens of metres.

1.2. Mineralogy

BIF has been classified on the basis of mineralogical composition (James, 1954; James, 1966), proposed tectonic setting (Gross, 1965) and depositional environment (Kimberley, 1978; Simonson, 1985). The large variety of available classification schemes undoubtedly reflects our limited understanding of BIF

formation. James' (1954) original facies concept included oxide-, silicate- and carbonate- facies iron formation thought to correspond to different water depths. A fourth so-called sulphide-facies, containing pyrite [FeS_2] and/or pyrrhotite [$Fe_{1-x}S$], was once regarded as syngenetic in origin (Fripp, 1976) but has subsequently been suggested to be epigenetic (Phillips *et al.*, 1984; Groves *et al.*, 1987) - with a replacement rather than primary sedimentary origin for sulphide mineralization.

Oxide-rich BIF typically consists of alternating bands of haematite [$Fe^{III}_2O_3$] with or without magnetite [$Fe^{II}Fe^{III}_2O_4$]. Where the iron oxide is dominantly magnetite, siderite [$Fe^{II}CO_3$] and lesser iron silicate are often also present (James, 1966). Silicate-rich BIF is usually dominated by the minerals greenalite, minnesotaite and stilpnomelane. Greenalite [$(Fe^{2+}, Mg)_6 Si_4 O_{10} (OH)_8$] and minnesotaite [$(Fe^{2+}, Mg)_3 Si_4 O_{10} (OH)_2$] are ferrous analogues of antigorite and talc respectively, while stilpnomelane [$K_{0.6} (Mg, Fe^{2+}, Fe^{3+})_6 Si_8 Al(O, OH)_{27}.2\text{-}4H_2O$] is a complex phyllosilicate. The varied primary mineralogy of hydrous iron silicates, carbonates and cherts in silicate-facies BIFs is vulnerable to metamorphic recrystallization at low grades.

Carbonate-rich BIF is usually dominated by the minerals ankerite [$Ca Fe^{2+} (CO_3)_2$] and siderite, both of which display highly variable compositions. The overall mineralogy of carbonate-facies BIFs is relatively simple, with roughly equal proportions of chert and ankerite (and/or siderite) expressed as thinly bedded or laminated alternating layers.

Gross (1965) inferred tectonic settings on the basis of BIF size and lithologic associations. *Algoma*-type iron formations are relatively small, and associated with volcanogenic rocks. Total primary iron content rarely exceeds 10^{10} tons (James and Trendall, 1982). Typical lateral extents are under 10 km, with thicknesses in the range 10-100 m (Goodwin, 1973; Appel, 1980; Condie, 1981). Favoured depositional environments for this type of BIF include island arc/back arc basins (Veizer, 1983) and intracratonic rift zones (Gross, 1983).

Superior-type iron formations are larger, and associated with other sedimentary units. Total primary iron content typically exceeds 10^{13} tons (James and Trendall, 1982). Several BIFs classified as Superior-type have been reported to extend over 10^5 km^2 (Trendall and Blockley, 1970; Beukes, 1973). Deposition is thought to have occurred in relatively shallow marine conditions under transgressing seas (Trendall, 1968; Beukes, 1983; Simonson, 1985; Simonson and Hassler, 1996), perhaps on the continental shelves of passive tectonic margins (Gross, 1965).

2.   BIF Distribution

2.1.   Temporal Distribution

Iron-rich units are not restricted exclusively to the Precambrian geologic record. Younger rocks superficially representing BIFs, commonly termed 'ironstones', are distinctly more Al_2O_3-, P_2O_5- and Fe_2O_3-rich and usually have an oolitic or pisolitic texture (Schopf, 1983) and are conspicuously barren in chert. Unequivocal BIFs appear to be absent from the Phanerozoic record. Table 2 compares characteristics of ironstones and iron formations.

BIFs are found at the very beginning of the rock record, amongst the oldest rocks on Earth. Contrary to earlier belief (Cloud, 1973), there exists a considerable age-spread among Precambrian BIFs. 90% of all iron-formation was deposited between 3.8 Ga and 1.6 Ga, prior to the Paleoproterozoic-Mesoproterozoic boundary (Schopf, 1983; Isley and Abbott, 1999).

Algoma-type tectonic settings are inferred for most older (Early- and Mid-Archaean) BIFs, the vast majority of which are hosted in greenstone-belts. BIFs are generally thicker and of greater lateral extent in the Late Archaean to early Proterozoic basins than in older greenstone belts (Klein and Beukes, 1992), representing a transition to Superior-type BIF deposition. Oxide-facies bands become particularly common during this time, as evidenced by their dominance in some of the largest BIF sites in Western Australia (Groves and Batt, 1984) and Canada (Fyon *et al.*, 1984), both dated at ~ 2.9 – 3.0 Ga. The deposition of the Hamersley Group and Superior region iron-formations marks a prominent volumetric peak in the geological BIF record.

2.2. Spatial Distribution

Apart from the aforementioned early-Archaean BIFs at Isua, large mid-Archaean BIFs occur in the Guyana Shield of Venezuela and Guyana, and the Liberian Shield of Sierra Leone, Guinea, Liberia, and Ivory Coast. Algoma-type sequences are common in Archaean greenstone belts around the world, where they are found associated with (ultra)mafic volcanics. Examples include the Vermilion district of northern Minnesota and the Michipicoten district of north-central Ontario. Other BIFs of late-Archaean age are found in the Yilgarn Block of Western Australia and the Zimbabwe Craton.

Superior-type sequences include the Hamersley Group, the Transvaal Supergroup, the Minas Supergroup, and deposits in the Labrador Trough-Animikie Basin including the Sokoman-, Gunflint- and Biwabik- iron-formations. Superior-type BIFs are rare in other sequences. Because these BIFs are usually devoid of readily-dateable volcanogenic rocks, many of them are of ambiguous age. Some workers (e.g., James, 1982; Chemale *et al.*, 1994; Shchipansky and Bogdanova, 1996) have assumed a synchronous age of ~2.45 Ga for several major Superior-type BIFs.

Other noteworthy BIFs, of more ambiguous classification, include those of Russia's Krivoy Rog district and some from Brazil's Minas Gerais.

3. Chemistry and Metamorphism

Major element concentrations in BIFs of various Proterozoic and Archaean ages were studied by Gole and Klein (1981). Iron formation contains on average 30% total iron (FeO + Fe_2O_3). Globally, BIF compositions vary greatly from one to another. However, the bulk-rock major- and trace- element concentrations show remarkable consistency on the unit- and even regional- scale, even for BIFs of different ages and facies (Gole and Klein, 1981). Regional variations do occur in volatile-, S- and Ce-contents (Gnaneshwar and Naqvi, 1994). The regional chemical homogeneity raises the question: how do chemical components in BIFs react to metamorphism? Almost all known BIF exposures are metamorphosed to some degree: was this metamorphism isochemical or did it involve the loss or gain of chemical components? Clearly, an understanding of the behavior of BIFs under changing conditions of pressure and/or temperature is vital to discriminating between primary-/diagenetic- and secondary-minerals and textures. Mineralogical changes incurred during BIF metamorphism lie outside the scope of this paper (see instead Klein, 1983).

3.1. Effects of Metamorphism

Klein (1973) compared the chemistry of late diagenetic to prehnite-pumpellyite facies (low grade) iron-formation samples to those of higher metamorphic grade (up to upper amphibolite facies) from the central and southern parts of the Labrador Trough. It was concluded that the regional metamorphism in the Labrador Trough resulted in loss of volatiles, particularly CO_2 and H_2O. SiO_2 contents also differed significantly between low- and high-grade meta-BIFs, which has been interpreted as reflecting the variable scales of chert- and quartz- banding. Apart from a loss of volatiles, neither the $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ ratio nor major element oxide concentrations appear significantly affected by regional metamorphism.

Kaufman (1996) examined the effects of the intrusion of a ~ 450 ºC diabase sill into the Palaeoproterozoic Kuruman Iron Formation, Transvaal Basin, South Africa. Within 5 m of the intrusive contact, the abundance of iron increases dramatically and

the oxidation state of the sediments fluctuated considerably more than outside the contact aureole. Isotopic and mineralogic systematics within the Kuruman BIF contact aureole resemble those in thermally altered siliceous dolomites and limestones: depletion in carbonate (inorganic) $\delta^{13}C$ and $\delta^{18}O$, and lower total organic carbon (TOC) with enriched $\delta^{13}C_{org}$. Most distinct isotopic and elemental variations occurred within 10 m of the diabase sill, suggesting alteration mainly through volatilization and fluid infiltration.

4. Component Behaviour in Solution

A key question in the enigma of BIFs concerns the genesis of the characteristic alternating iron-rich and silica-rich bands. Given the deep-marine depositional environment inferred for most BIF deposits, some mechanism is required for transporting iron in its' soluble form and subsequently precipitating it, on a regional scale, out of solution. The chemistry of the Archaean lithospheric, oceanic and atmospheric reservoirs - and the operation of biogeochemical cycles linking these - may well have deviated substantially from conditions observed today. A brief look at the behavior of iron and silica in solution is therefore instructive.

4.1. Iron

Ferrous- and ferric- iron (Fe^{2+} and Fe^{3+}) are the prevailing ionic forms for iron migration. High concentrations of Fe^{3+} are stable only under very acidic conditions (pH = 0-2). An increase in pH causes hydrolysis and precipitation of the insoluble $Fe(OH)_3$ hydroxide. The occurrence of such strong acidic solutions in the ocean at any time during the Precambrian - for example due to weathering of an exotic crust – cannot be accounted for by physiochemical processes, even with an extremely CO_2-rich atmosphere (Belevtsev *et al.*, 1982). Furthermore, ferric iron is also unstable in the presence of many electrolytes, particularly SO_4^{2-}.

Acidic thermal solutions *are* (and presumably also *were*) found in regions of volcanic activity. However, such waters are rich in ferrous rather than ferric iron.

Ferrous iron in solution is highly susceptible to oxidation, mainly due to its reaction with rocks, dilution by meteoric waters and the buffering effect of carbonates and silicates. It seems unlikely, therefore, that at any point in Earth's history iron could be transported in solution in the presence of free oxygen.

The ability of iron to migrate increases tremendously in the absence of free oxygen. Appreciable amounts of iron can be dissolved in slightly acidic to neutral anoxic solutions. Under such conditions, changes in parameters such as pCO_2, pressure ($\equiv$ water depth), pH and Eh (redox potential) determine whether iron is precipitated as a carbonate, oxide, silicate or other salt.

4.2. Silica

In solution, silica exists as the ionic monomer $Si(OH)_4^0$. In contrast to ferruginous species, the solubility of silica is remarkably independent of the acidity, ranging between 80-100 mg/l across a pH range of 2 - 10. In colloidal form, silica becomes far more soluble, particularly at pH < 4 - 5; thermal waters of present-day volcanic regions contain 200 - 300 mg/l dissolved SiO_2, up to 900 mg/l (Zelenov, 1972). Possible 'triggers' leading to silica precipitation include changes in temperature, pH and electrolyte concentrations – particularly Mg^{2+}, Na^+, and to a far lesser extent Fe^{2+} (Belevtsev *et al.*, 1982).

5. Depositional Environment

Holland (1984) interpreted the four different BIF facies (Section 1) as representing different redox conditions existing at different water depths in a stratified ocean. Oxide-facies BIF precipitated under the most oxidizing conditions, while sulphide-facies BIF was precipitated under the most reducing conditions. Silicate- and carbonate- facies were deposited under intermediate redox conditions.

Several workers have noted the lack of iron-rich sedimentary rocks in shallow-water Archaean successions, which instead may contain other orthochemical units such as local bedded barite, sparse carbonate, and evaporites (in the Barberton: Heinrichs

and Reimer, 1977; Lowe and Knauth, 1977; Reimer, 1990; in the Pilbara: Barley, 1979; Groves *et al.*, 1981; Buick and Dunlop, 1990).

On the basis of such observations and other sedimentological constraints derived from intercalated and associated sediments, the majority of models for BIF deposition involved environments ranging from shelf and upper continental slope to the abyssal plain. The greatest depth of deposition thus-far proposed is 900 m in the Barberton (de Ronde *et al.*, 1997). On the basis of P and Fe^{3+} concentrations, Bjerrum and Canfield (2002) have recently proposed a deep ocean setting for both siderite- and Fe-oxide- enriched BIF and associated shales.

The ages of BIFs and volcanic super-plume events are often statistically indistinguishable (Isley and Abbott, 1999). The petrology of these diverse volcanics ranges from ultramafic through felsic, while chemical affinities to ocean island basalts (OIBs), enriched mid-ocean ridge basalts (MORBs) and normal MORBs (NMORBs) have been reported (Hoffman, 1988). It has been argued that increased hydrothermal activity resulting from these enormous volcanic events promoted BIF deposition (Barley *et al.,* 1997). Units from the Barberton contain massive sulphides and collapsed chimney deposits, indicating proximal high-temperature hydrothermal activity.

The greenstone belt sedimentary successions commonly hosting Algoma-type iron-formations resemble the facies distributed around modern ocean spreading centers and island arcs. Favoured depositional environments for this type of BIF include island arc/back arc basins (Veizer, 1983) and intracratonic rift zones (Gross, 1983).

Mature shelf assemblages, including well-developed carbonate platforms, are found in intimate association with Superior-type iron formations. Thus, BIF deposition occurred in relatively shallow marine conditions under transgressing seas (Trendall, 1968; Beukes, 1983; Simonson, 1985; Simonson and Hassler, 1996), on the continental shelves of passive tectonic margins (Gross, 1965). Limited clastic input suggests that these platform environments were isolated. Schopf (1983) interpreted the coeval development of large continents, continental glaciation and Superior-type BIFs as

representing the transition from local Algoma-type deposition to deposition on extensive oxygenated continental shelves.

To summarize, the majority of Algoma-type BIFs were deposited as parts of volcanosedimentary successions in greenstone belts. For Superior-type BIFs, a depositional environment consisting of a partly isolated, submerged platform on the continental shelf of an Archaean craton is currently in favour with most workers (Konhauser *et al*., 2002).

6.   Origin

Despite almost a century of geological studies into the origin of BIFs, a depositional mechanism that adequately explains both their geology (Section 1) and extent (both in space and time - Section 2) remains unclear. The sources of BIF iron and silica, and possible mechanisms of iron precipitation (and, by extension, the phenomenon of alternating iron/silica banding) are discussed next.

6.1.   Sources of Iron and Silica

As with other aspects of BIFs, the source(s) of iron have been disputed. Both continental (e.g., Alibert and McCulloch, 1993) and hydrothermal (e.g., Holland, 1973; Simonson, 1985; Dymek and Klein, 1988) settings have been put forward as likely Fe-sources. On the basis of depleted rare earth element (REE) patterns and Nd isotopic signatures, it is now widely accepted that mid-ocean-ridge or hotspot tectonic settings act as a distal hydrothermal source of iron (e.g., Holland, 1973; Morris and Horwitz, 1983; Jacobsen and Pimental-Klose, 1988). This iron output is pulsed, and possibly supplemented by normal continental drainage (e.g., Canfield, 1998). Upwelling currents (Klein and Beukes, 1989) or thermal plumes (Isley, 1995) deliver hydrothermal waters onto the outer continental shelf.

The absence of silica-secreting organisms in Precambrian oceans likely gave rise to conditions at or near the silica saturation point (Siever, 1992). Silica

precipitation can then be achieved through evaporative supersaturation (Garrels, 1987) or coprecipitation with solid-phase iron minerals (Ewers, 1983).

Uniform, regional-scale precipitation of minerals within the depositional basin gave rise to the extensive horizontally continuous mesobands (Trendall and Blockley, 1970; Ewers and Morris, 1981). Until recently, the genesis of the siliceous sequences was attributed either to temporary failure of hydrothermal fluids reaching the depositional site due to changes in ocean circulation (termed 'current reorganization' by Konhauser *et al.*, 2002) or to periods of relative hydrothermal quiescence (Morris, 1993).

In the above scenario, the magnitude and periodicity of hydrothermal activity and influx thus control the relative thicknesses of the iron and chert layers (Morris, 1993). Ge/Si ratios in BIFs suggest that iron and silica fluxes were decoupled, with the latter being predominantly derived from the weathering of continental landmass rather than of hydrothermal origin (Hamade *et al.*, 2003). In such a scenario, alternating chert- and iron- rich layers would reflect competing controls through dominance of continental and hydrothermal sources respectively.
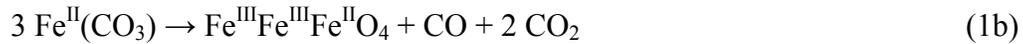
6.2. Iron Oxidation

6.2.1. Clastic Models

The enormous but evenly distributed amounts of iron needed to cover basinal sites of BIF deposition would appear to require the transport of iron its soluble ferrous form. Two exceptions to this requirement exist. The first occurs in recent models of BIF formation that attribute iron deposition to turbiditic flows of hydrothermal muds on the flanks of submarine volcanoes (Krapez *et al.*, 2003; Lascalles, 2007; Pickard *et al.*, 2004; Pecoits *et al.*, 2009). Such models face severe difficulties. For one, they fail to adequately address the mechanism of primary iron oxidation. In contemporary hydrothermal systems, iron exhibits little spontaneous precipitation upon contact with oxygen: on the Eastern Pacific Red Seamount, for instance, ferrous iron in mildly acidic (pH $\approx$ 5) low-temperature fluids that discharge into cold ($\sim$ 2 °C) and

oxygenated (pO_2 = 0.06 atm) bottom-water remains in solution for over 30 years (Alt, 1988). In anoxic Archaean deepwater, such iron oxidation and precipitation would have been even more impeded. Furthermore, a clastic origin fails to account for the paucity of both sedimentary structures and aluminous clastic detritus in canonical BIFs.

A second - and related - hypothesis is that the iron in BIF starts out as a ferrous precipitate, such as siderite, that recrystallizes to magnetite (or haematite, under unusually elevated fO_2) upon metamorphism:

$$Fe^{2+}_{(aq)} + CO_2 + H_2O \rightarrow Fe^{II}(CO_3) + 2\,H^+ \tag{1a}$$

$$3\,Fe^{II}(CO_3) \rightarrow Fe^{III}Fe^{III}Fe^{II}O_4 + CO + 2\,CO_2 \tag{1b}$$

However, siderite decarbonation should precipitate graphite, and commences above ~ 450 ºC under ideal laboratory conditions (French and Rosenberg, 1965; French, 1971). These facts are at odds with the common occurrence of magnetite- and haematite- bearing BIF assemblages barren of carbon at and below upper greenschist facies.

This leaves the controversial question of the mechanism controlling primary oxidation of Fe^{2+} to Fe^{3+}. Four different models have been proposed towards this end, three of which appeal to biology. These are outlined below.

6.2.2. Oxidative Photolysis

Numerous laboratory experiments have shown that the action of sunlight, and particularly ultraviolet (UV) radiation, contributes to Fe^{2+} oxidation (e.g. Cairns-Smith, 1978; Braterman *et al.*, 1983):

$$2\,Fe^{2+}_{(aq)} + 6\,H_2O + h\upsilon \rightarrow 2\,Fe^{III}(OH)_3 + H_2 + 4H^+ \tag{2}$$
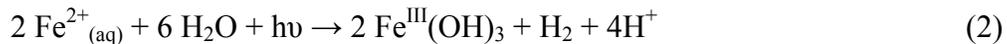
Work by Cockell (2002) attempted to constrain the solar UV flux to Earth through time. Due to limited knowledge of key factors such as the partial pressures of CO_2, N_2 and trace gases, an uncertainty of two orders of magnitude exists for Archaean UV fluxes. However, with most workers agreeing on oxygen levels $<10^{-4}$ present

atmospheric levels (PAL), the low ozone column abundance almost certainly allowed for far higher levels and frequencies of UV radiation during Archaean times (Margulis *et al.*, 1976; Kasting and Donahue, 1980; Kasting, 1987). The transition from intense, high-frequency UV-C (λ = 200 - 280 nm) and UV-B (λ = 280 - 320 nm) radiation to lower intensities and frequencies that accompanied the rise of oxygen provides a potential control on the temporal distribution of BIFs.

It has been argued that laboratory experiments attempting to simulate photochemical oxidation are overly simplistic and not representative of the multi-element solutions found in marine environments. For instance, it was mentioned previously that the Precambrian oceans likely had far higher concentrations of amorphous silica (Siever, 1992). Under such conditions, dissolved silica and iron react readily to form an amorphous iron-silicate gel (Hamade *et al.*, 2000), thereby greatly limiting the precipitative effect of UV radiation. Another drawback of the photochemical model is that the site of iron oxidation is restricted to the air/water interface.

6.2.3. Oxygenic Photosynthesis

The demonstrated presence of sulphate in shallow Archaean ocean(s) has led some (e.g., Ohmoto and Felder, 1987) to speculate that oxidizing conditions existed near the surface of a stratified Archaean ocean. Abiotic mechanisms, such as the photolysis of water vapour followed by the escape of hydrogen to space, are inadequate to explain the amount of oxygen incorporated into Precambrian BIFs, however, and so a biotic source must be sought.

Oxygenic photosynthesis entails the light-driven breakdown of water into oxygen. In this scenario, a soluble oxidant such as O_2 would have attained sufficient concentrations in the upper ocean to allow for indirect iron oxidation and precipitation at the oxic/anoxic boundary, inhibiting Fe^{2+} diffusion into overlying waters:

$$4Fe^{2+}_{(aq)} + O_2 + 10H_2O \rightarrow 4Fe^{III}(OH)_3 + 8H^+$$
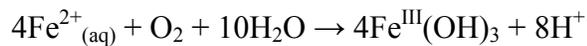
(3)

Plankton growth today is strongly dependent on iron supply as a nutrient. Archaean oxygen-producing microorganisms may likewise have flourished during episodic Fe^{2+} (and nutrient) influx events, thereby coupling episodic iron influx with oxygenic photosynthesis-induced precipitation.

6.2.4. Chemolithoautotrophy

In the presence of free oxygen, oxidation of Fe^{2+} can also be performed by chemolithoautotrophic organisms. This mechanism has the obvious advantage of allowing for sub-photic zone oxidation, on par with empirical evidence:

$$12\ Fe^{2+} + O_2 + 2\ CO_2 + 32\ H_2O \rightarrow 2\ [CH_2O] + 12Fe(OH)_3 + 24\ H^+ \quad (4)$$
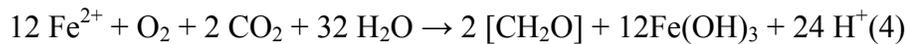
Laboratory experiments with *Gallionella ferruginea*, which makes use of the above pathway, indicate rates of iron oxidation >60 times faster than abiotic reactions (Søgaard *et al.*, 2000). Given the slow rates of abiotic iron oxide precipitation from oxygenated seawater now, chemolithotrophic mechanisms seem much more likely than passive abiotic oxidation after oxygenic photosynthesis to account for the large amounts and widespread areas of Superior BIFs.

6.2.5. Anoxygenic Phototrophy

Biologically mediated primary oxidation of Fe^{2+} to Fe^{3+} in an otherwise anoxic environment provides an appealing solution to the BIF dilemma. In 1994, Ehrenreich and Widdel announced the discovery of a new type of metabolism, involving the anaerobic oxidation of ferrous iron coupled to CO_2 reduction, by two different strains of purple bacteria. Subcultures were grown in defined mineral media of 10 mmol/liter $FeCO_3$.

Both strains were shown to be capable of both hetero- and auto- phototrophy:

$$4Fe^{2+} + CO_2 + 11H_2O \rightarrow CH_2O + 4Fe(OH)_3 + 8H^+ \quad (5)$$
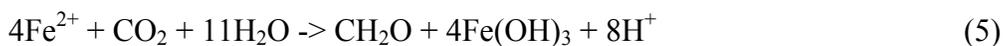
In addition to ferrous iron, strain 'SW2' utilizes $H_2 + CO_2$, monocarboxylic acids, glucose and fructose, while strain 'L7' utilizes $H_2 + CO_2$, acetate, pyruvate, and glucose as substrates for phototrophic growth. Neither strain utilizes free sulphide, but rather grows on black ferrous sulphide (FeS) to yield sulphate (SO_4^{2-}) and ferric iron. The authors noted that in bicarbonate-rich environments at pH ~7, the redox couple $Fe(OH)_3 + HCO_3^- / FeCO_3$ has a redox potential $E_0' = +0.2$ V, with ferrous iron in this case providing a far more favourable electron donor than in Cloud's (1965, 1973) proposed Fe^{3+}/Fe^{2+} redox couple under acidic conditions ($E_0' = +0.77$ V).

A number of purple and green bacteria are now known to make use of similar pathways (Widdel *et al.*, 1993; Ehrenreich and Widdel, 1994; Heising and Schink, 1998; Heising *et al.*, 1999). The base of the photic zone in today's oceans lies at a depth of ~120 m, but was probably shallower during less luminous Archaean times. However, the absorbance carotenoids used by anoxygenic iron oxidizers exploit the electromagnetic band between 400 and 500 nm, allowing photosynthesis to greater depths than their aerobic competitors (Kappler *et al.*, 2006). The existence of iron-oxidizing anoxygenic phototrophs thus forms a tempting explanation for the existence of iron-rich bands in BIFs.

6.2.6. Summary of Biological Processes

As pointed out by Walter and Hofmann (1983), the very existence of fine BIF laminations suggests the absence of burrowing megascopic fauna until after ~1.6 Ga. On the other hand, microbiological mechanisms can potentially account for the precipitation of iron out of solution in a variety of environments, ranging from an anoxygenic photic zone to a (locally?) oxygenated sub-photic zone. However, the production of oxygen at depths anticipated for BIF deposition remains enigmatic, and may require a hithero-unexplored interplay within a complex microbial ecosystem.

Importantly, concentrations of nutrients (P) and trace metals (V, Mn, Co, Zn, and Mo) found in iron-rich BIF bands can easily support microbe populations capable

of precipitating Hamersley-scale BIFs – even during periods of maximum iron precipitation (Konhauser *et al.*, 2002).

7.   Conclusion

Banded Iron Formations ('BIFs') are highly controversial chemical precipitates characterized by the presence of alternating layers of iron-rich and amorphous silica-rich layers. This dichotomous compositional layering is usually expressed on several scales at any given outcrop, from fine sub-millimetre-scale varve-like laminae to metre-scale bands. Even on a microscopic scale, the boundary between the ferruginous and siliceous layers is distinctly abrupt.

An understanding of the origin of BIFs provides useful insight into conditions existing on the early lithosphere, hydrosphere and atmosphere. Like all sedimentary rocks, BIFs provide the geologist with information regarding the depositional environment, rate of sediment accumulation, and so forth. However, BIFs have proved particularly tantalizing windows on the early earth due to their possible intimate coupling with oxygen concentration and their narrow temporal-, depositional-, and tectonic- niches in the geological record.

In the context of early earth evolution, it is the possible link to an evolving biosphere that makes BIFs particularly interesting. The highly ordered and regionally continuous alternating layering of BIFs, physiochemical constraints aside, should be hard to achieve in a dead environment constantly striving for entropy maximization (Lorenz D., 2002). Apart from being an essential - and sometimes limiting – nutrient, iron is used as a metabolic agent by numerous microorganisms. Some of these, including specific species of oxygenic- and anoxygenic- photoautotrophs and chemoferrotrophs, lend credence to the theory of BIF-deposition being, at least in part, a microbially mediated process. Direct evidence for microbial activity during Archaean BIF deposition remains elusive. Could an interplay of primitive metabolisms, perhaps operating at different redox- and photic- levels within a stratified ocean, have been at work?

The principal enigma remains the BIF banding visible at virtually all scales. That such periodicity can be attributed solely to variations in iron and/or silica influx, be they of hydrothermal or continental origin, is hardly likely. Even in a stratified ocean, both hydrothermal iron production and continental erosion remain highly chaotic phenomena. Perhaps, then, some hithero uncharacterized electrolyte cycle unique to early oceans controlled the regional banding (Chapter 5).

Table 1: Comparison of typical ironstones with iron formations (after James, 1966)

Characteristic	Ironstones	Iron Formations
Age		
Minimum age	Pliocene	Late Precambrian
Major development	Lower Palaeozoic; Jurassic	2.5-3.0 Ga
Maximum age	Palaeo-Proterozoic (~2.0 Ga)	3760 ± 70 Ma
Thickness of major units	1-50 m	50-600 m
Original aerial extent, max. dimension	< 150 km	> 100 km
Physical character	massive to poorly banded; silicate and oxide-facies oolitic	thinly bedded; layers of haematite, magnetite, siderite, or silicate alternating with chert; chert ~50%
Mineralogy		
goethite	dominant	none
haematite	fairly common	common
magnetite	relatively rare	common
chamosite	dominant primary silicate	absent
glauconite	minor	absent
siderite	common	common
calcite	common	rare
dolomite	common	fairly common
pelletal collophane	relatively abundant	absent
greenalite	none	dominant primary silicate
quartz (chert)	rare	major constituent
pyrite	common	common
Chemistry	high iron	low Al, Na, K and minor elements; much lower P

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