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Biogenic Fe(III) minerals: From formation to diagenesis and preservation in the rock record

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ABSTRACT

Fe-metabolizing bacteria are intimately linked to the cycling of Fe in modern environments and have likely been key players in the evolution of the Earth's biogeosphere. Fe minerals have also been suggested as a key preservative of cell organic matter in sediments, keeping otherwise labile phases conserved at least on time scales of 100,000 years. The interpretation of a biological influence on the Fe rock record is difficult without a deeper understanding of the mechanisms of biogenic Fe(III) and Fe(II) mineral formation, the character of these minerals, and their diagenesis over short and long time scales. Here, we present the recent advances in the study of abiogenic and biogenic Fe(III) minerals. In particular, we focus on the role of Fe(II)-oxidizing bacteria in the deposition of ancient banded iron formations (BIF). We discuss this work within the framework of the main challenge: separating biogenic from abiogenic processes over deep time. We describe how efforts in isotope geochemistry, biomarker research, mineral analysis and biogeochemistry are helping to establish a window to the past. Finally, we present some new approaches that help investigate the main processes leading to the formation and potential fate of Fe-organic matter aggregates.

Contents

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1. Introduction

Microorganisms are architects of their environment, influencing the lithosphere, hydrosphere, and the atmosphere. As seen on Earth today, bacteria are active cyclers of major elements such as C, Fe, S, and oxygen as well as trace elements like Mo, As and Ni. They synthesize and dissolve minerals (e.g. Konhauser, 2007a), as well as fractionate isotopes. The earliest signs of life are 3.8 billion years old (Rosing et al., 1996), so the chemical evolution of the Earth has therefore been accompanied by the evolution of life and the influence of bacteria (for a review see Ehrlich, 1998). Which microbial populations were present through key biogeochemical transitions and how they altered their environment are still unresolved, forming the impetus behind the two main approaches that dominate studies of early Earth bacterial life. In one approach, ancient rocks are directly investigated for signs of life using methods such as the extraction and analysis of molecular biomarkers, trace metal analysis, and the exploration of isotope fractionations particular to a biological source (e.g., Kaufman and Knoll, 1995; Summons et al., 1999; Canfield et al., 2000; Johnson et al., 2003; Mojzsis et al., 2003; Arnold et al., 2004; Johnson et al., 2004; Brocks et al., 2005; Brocks and Banfield, 2009; Fischer et al., 2009; Czaja et al., 2010). In the other approach, modern analogs are compared to ancient systems and also used to build biogeochemical models (e.g. Meyer-Dombard et al., 2005; Crowe et al., 2008a; Dahl et al., 2010, 2013).

Throughout most of the Precambrian, the global ocean was Fe-rich and O_2-poor (Poulton and Canfield, 2011), which is recorded in significant Fe deposition in marine shales and banded iron formations (BIFs). The specific Fe contents and Fe mineralogy in these sediments help elucidate the evolution of the biogeochemical Fe cycle from before the "Great Oxidation" of the Earth's atmosphere (GOE) at 2.3 to 2.4 billion years ago (Ga) to when oxygen became abundant in the deep ocean (e.g. Kump and Holland, 1992; Canfield et al., 2007, 2008; Raiswell et al., 2011; Planavsky et al., 2012; Och et al., 2013). Indeed, ancient BIFs and Fe-rich shales may harbor evidence of ancient life during the evolution of the biogeosphere, hydrosphere and atmosphere. In particular, experiments carried out with Fe-metabolizing bacteria and analyses of ancient BIFs have helped towards an understanding of biogenic and abiogenic Fe oxide formation as related to BIF deposition. These efforts have led to several proposed BIF formation mechanisms. One suggestion is the abiotic oxidation of Fe(II) through O_2 produced by cyanobacteria. Alternatives involve the direct oxidation of Fe(II) by ancient microorganisms, i.e. microaerophilic Fe(II)-oxidizers using cyanobacterially-produced O_2 as electron acceptor or anoxygenic phototrophic Fe(II)-oxidizers that use light energy to oxidize Fe(II) in the absence of O_2 (Cloud, 1968; Hartman, 1984; Konhauser et al., 2002; Kappler et al., 2005a; Posth et al., 2013a). The main challenges in understanding the biological roots of BIFs are to define the signals produced by organisms and to understand the diagenetic processes which influence biogenic Fe(III) minerals from the point of formation until preservation in the rock (Fig. 1).

One can in principle explore whether complex biogeochemical processes can be traced from laboratory experiments and model systems to ancient Fe-rich rock samples. In some recent studies, this problem has been approached by using modern bacteria (Kappler and Newman, 2004; Kappler et al., 2005a; Konhauser et al., 2007b; Hegler et al., 2008; Posth et al., 2008, 2010). The potential markers, or biosignatures, left behind by Fe(III) mineral forming strains can be investigated by studying their physiology and resulting biomineralization reactions under various environmental and geochemical conditions.

Here, we discuss what is known to date of the precipitation of these biogenic minerals in the water column, the influence of microbial mineral diagenesis during sedimentation and in the sediment, as well as the impact of temperature and pressure over time on the preservation of potential biosignatures. We focus on the case of BIFs as our main example and discuss what is known from the rock record to illustrate the challenge of separating abiotic from biotic processes. We describe the main hypotheses of how microorganisms were involved in the development of ancient Fe-rich deposits, explain how various organisms form Fe(III) (oxyhydr)oxides and how these structures interact with their environment. We finish with a discussion of the short-term cycling of these minerals and recent studies that experimentally test the long-term alteration that biogenic Fe(III) minerals undergo through temperature and pressure.

2. Microbial processes in ancient iron deposits

2.1. The enigma of banded iron formations

Banded iron formations (BIFs) have been studied over the past decades as a source of information on the evolution of the early hydrosphere, atmosphere, lithosphere, and biosphere. BIFs are sedimentary structures consisting of alternating Fe-rich (~20–40% Fe) and Fe-poor, siliceous (40–50% SiO_2) layers. They precipitated primarily throughout the late Archean Eon (2.7–2.5 Ga) and Paleoproterozoic Eon (2.5–1.8 billion years ago), but then reemerged in the Neoproterozoic Eon (~0.7 billion years ago) (Bekker et al., 2004, 2010). Therefore, the time frame in which BIFs appear in the rock record spans the transition from an anoxic Earth to an environment in which cyanobacteria evolved and oxygen concentrations began to rise in the Earth atmosphere and oceans (e.g. Cloud, 1968; Canfield, 1998; Anbar et al., 2007; Farquhar et al., 2011). Despite extensive research of these structures to understand the biogeochemical environment in which they were deposited, it is still unclear how BIFs were formed across geological time.

BIFs are vast deposits of up to 10^5 km^2 in area and contain $>10^{13}$ tons of Fe (Trendall, 2002). They are typically hundreds of meters thick and are the main source of mined Fe ore worldwide. The largest formations are found in the Hamersley range in Australia and the Transvaal Supergroup in South Africa. Other major BIFs include the Krivoy Rog Supergroup, Ukraine (2.2 Ga); Labrador Trough, Canada; Lake Superior Region, USA (2.5–1.6 Ga); Gunflint and Biwabik, North America (2.2–2.0 Ga), Carajás Formation (2.6 Ga) and Urucum Region, Brazil (0.8 Ga). The least metamorphosed BIFs consist of chert, magnetite, hematite, carbonates (siderite, dolomite-ankerite), greenalite, stilpnomelane and riebeckite (Klein, 2005). It is generally agreed that BIF minerals reflect both diagenetic and metamorphic overprinting. The presence of both ferric and ferrous minerals gives BIFs an overall average oxidation state of $Fe^{2.4+}$ (Klein and Beukes, 1992). Ferric hydroxide ($Fe(OH)_3$), greenalite ($(Fe)_3Si_2O_5(OH)_4$), green rusts (general formula: $[Fe^{II}_{(1-x)}Fe^{III}_x(OH)_2]^{x+}\cdot[(x/n)A^{n-}\cdot(m/n)H_2O]^{x-}$) and siderite ($FeCO_3$) were likely the primary minerals (Klein, 2005; Zegeye et al., 2012; Rasmussen et al., 2013).

The characteristic banding of BIFs (Fig. 2A, B) occurs on a wide range of scales, from coarse macrobands (meters in thickness), to mesobands (centimeter-thick units), millimeter, and to submillimeter layers (Trendall and Blockely, 1970). Among the latter is the wide variety of varve-like repetitive laminae, known as microbands. It is still unknown which processes cause this alternating Fe-rich and silica-rich banding. A number of abiotic mechanisms have been put forth for the deposition of the Fe-rich and Si-rich layers in BIFs (e.g. Garrels et al., 1973; Garrels, 1987; Wang et al., 2009), with the most recent describing episodic resedimentation of Fe-silicates alternating with periods without deposition and seafloor silification (Rasmussen et al., 2013). Another mechanism for the deposition of alternating Fe-rich and Si-rich layers combines abiotic and microbial processes. Temperature fluctuations trigger the alternating precipitation of Fe(III) (oxyhydr)oxides-by anoxygenic Fe(II)-oxidizing phototrophic bacteria and silica by abiotic processes, depositing the alternating Fe-rich and Si-rich layers in this proposal (Posth et al., 2008).

BIFs are categorized by their areal extent and volcanic influence as Algoma or Superior type BIFs. Algoma type BIFs are generally small in lateral extent and have a volcanic association (Gross, 1966, 1980;

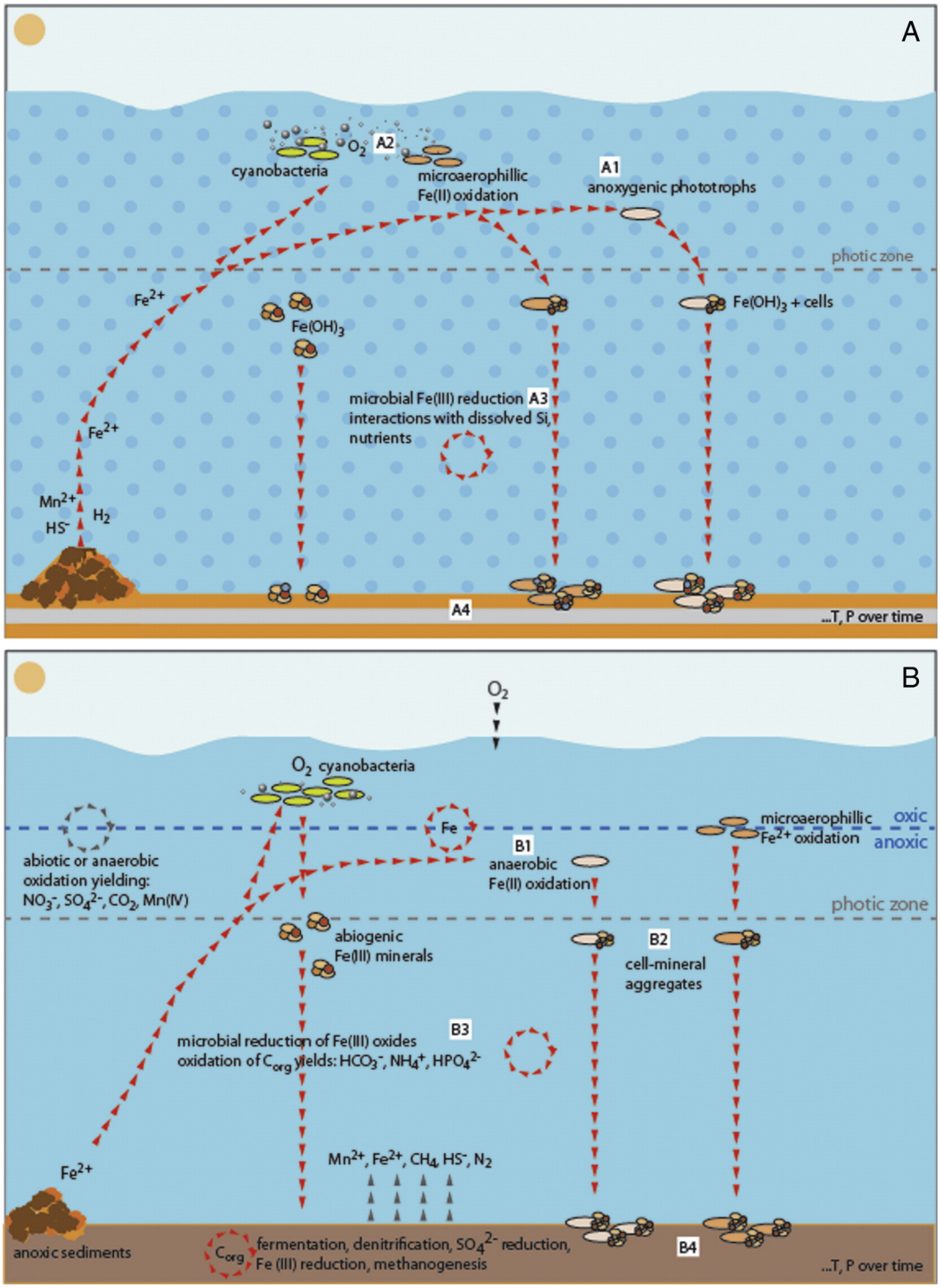

Fig. 1. Conceptual model of biogenic Fe(III) production, Fe(III) mineral precipitation, and short and long term diagenetic processes in early Archean and contemporary settings. (A) Early Archean depositional environments are believed to have been anoxic. Fe(II) is assumed to be sourced from hydrothermal vents (~0.05–0.5 mM Fe(II)) and dissolved silica (●) from the continents (~2 mM). Fe(II)-oxidizing phototrophs thriving in the photic zone, would oxidize dissolved Fe(II) and reduce CO_2 (A1). If present, cyanobacteria would generate isolated oases of oxygen, which abiotically oxidizes Fe(II) to Fe(III). The resulting opposing oxygen- and Fe^{2+}-gradients could also support microaerophilic Fe(II)-oxidizing bacteria (A2). Cell–mineral aggregates are produced in the water column by anoxygenic phototrophs and microaerophilic Fe(II)-oxidizing bacteria and undergo short term diagenesis such as microbial degradation and abiotic alterations, possibly associated with silica (A3). Short term and long term diagenesis of the aggregates takes place within the sediment. These processes both not only influence and are influenced by the biogeochemical environment during formation and deposition, but also determine the markers of life remaining in these formations today (A4). B) Contemporary, stratified systems can harbor anoxygenic Fe(II)-oxidizing phototrophs in anoxic niches with dissolved Fe(II) sourced, from example, from Fe(II)-bearing minerals or Fe(III) reduction in the sediment (B1). Both phototrophic and microaerophillic Fe(II)-oxidizing bacteria precipitate cell–Fe(III)-mineral aggregates (B2). These aggregates may be cycled by microbial and phytoplanktonic processes and may be subject to interaction with other solute species in the water column during sedimentation (B3). At the sediment, the remaining cell–mineral aggregates will undergo sediment diagenesis (B4).

Huston and Logan, 2004; Bekker et al., 2010), while Superior type BIFs found in shelf environments, are vast and without a dominant volcanic influence. They are also distinguished by their Fe oxide composition as hematite or magnetite BIFs (James, 1954). Hematite BIFs have facies consisting principally or entirely of interbedded chert and primary hematite. They can be oolitic, for example, like the Gunflint range.

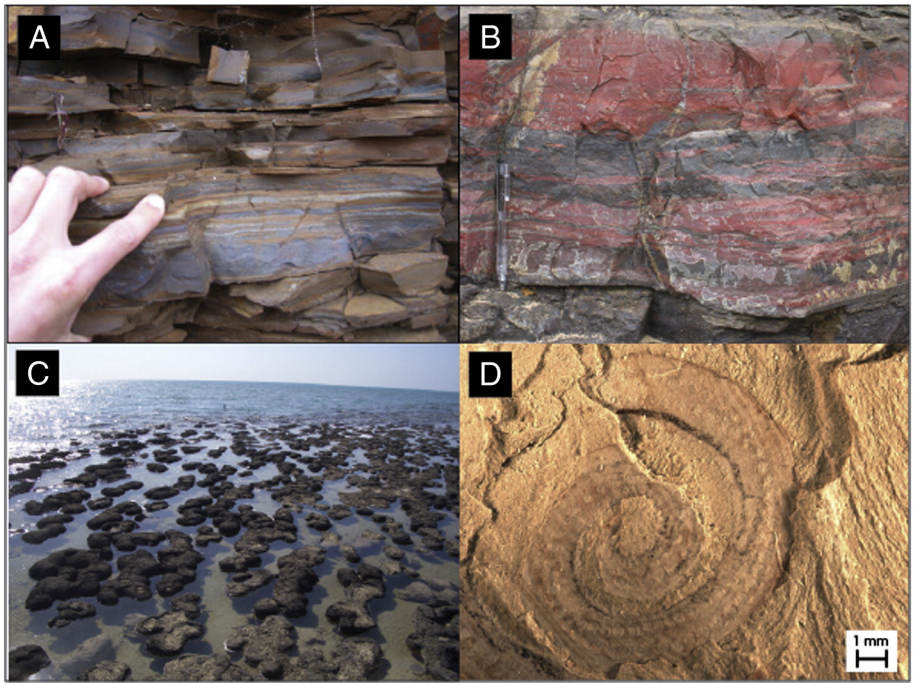

Fig. 2. The potential archive of life in the rock record studied in A) the 3.0 billion year old Gamohaan Hill BIF, South Africa, B) the 3.0 White Mfolozi Gorge BIF, South Africa, C) the Hamelin Pool, Australia stromatolites (photo courtesy of Merle Eickhoff) and D) a fossilized worm from the Chengliang Lagerstätte, Yunnan province, S. China (courtesy of Emma Hammarlund).

Magnetite BIFs consist of magnetite layers which can grade into silicate rock, be mixed with carbonate, or sprinkled with hematite or chert lenses (James, 1954). BIFs can also fall into the category of granular versus nongranular depending on the nature of the silica layers. Granules, are approximately 0.5 mm in diameter, irregular, and can be within a chert matrix. The granules can have a greenalite or magnetite core, but do not have the concentric layering seen in hematitic ooliths. Non-granular BIFs are usually laminated and may chiefly be composed of minnesotaite with magnetite and carbonate in some layers (James, 1954) (for a review, see Posth et al., 2011).

BIF deposition bridges a time of significant atmospheric change (Canfield, 1998; Farquhar et al., 2000; Anbar et al., 2007; Farquhar et al., 2011; Crowe et al., 2013). The ancient oceans of the early Precambrian are also known to have been anoxic and rich in dissolved Fe(II) (0.05–0.5 mM) and silica (~2 mM). For these reasons, BIFs have long offered a geochemical archive of the past, but the framework set by their redox state and mineralogy also can help us interpret their formation mechanism. Nevertheless, whether a single deposition mechanism or a mix of processes resulted in the formation of these Fe deposits over time is still unclear. The large BIFs of the Superior type, such as the Hamersley and the Transvaal formations are believed to have been deposited in semi-restricted, marine basins with minimal wave action on the margins of large cratons (Beukes, 1973; Klein and Beukes, 1992; Morris and Horwitz, 1983; for a review see Klein, 2005). The mineralogy, presence of Fe(III) oxides and redox state of the Fe in BIFs suggest that at least some Fe(II) oxidation mechanism played a role in their formation. However, during the deposition of early BIFs, it is still assumed that the atmosphere and oceans were anoxic. Bulk ocean waters could have supported concentrations of dissolved, reduced Fe(II) between 0.05 and 0.5 mM (Holland, 1973; Morris, 1993). The main source of Fe(II) into BIF depositional basins was most likely hydrothermal (e.g., Jacobsen and Pimental-Klose, 1988; Bau and Möller, 1993; Hamade et al., 2003); however there is still discussion as to the required proximity of the Fe source to the BIF deposition site. Fe(II) was either transported from the deep ocean to the outer continental shelf by upwelling currents (e.g. Holland, 1973; Morris and Horwitz, 1983) or was directly deposited from hydrothermal plumes of mid-ocean ridges, which suggests a link to Algoma-type BIF (Isley, 1995; Isley and Abbot, 1999). Furthermore, there may have been significant inputs from diagenetic remobilization and terrestrial runoff to many depositional basins (Kump and Holland, 1992; Raiswell et al., 2011).

A number of Fe(II) oxidation mechanisms have been put forth to account for BIF deposition. One possible oxidation mechanism leading to Fe(III) mineral deposition is the effect of ultraviolet radiation (Fig. 3). High levels of UV radiation could have reached the Earth's surface until a protective ozone layer formed with the rise of atmospheric O_2. Dissolved ferrous Fe species, such as Fe^{2+} or $Fe(OH)^{+}$, absorb radiation in the 200–400 nm range, leading to the formation of H_2 gas and dissolved ferric Fe [Eq. (1)], which in turn, hydrolyzes to form ferric hydroxide at circumneutral pH (Cairns-Smith, 1978; Braterman et al., 1983).

$$2Fe^{2+}{}_{(aq)} + 2H^{+} + h\nu \rightarrow 2Fe^{3+}{}_{(aq)} + H_2\uparrow \quad (1)$$

The influence of this oxidation mechanism, however, is less in complex solutions. In solutions, like that of early ocean water, with higher concentrations of dissolved Fe(II), Si and HCO_3^-, ferrous Fe-silicates could be expected to precipitate. The kinetics of this precipitation would render Fe(II) oxidation catalyzed by UVA or UVC negligible (Konhauser et al., 2007).

Another possible oxidation mechanism involves the activities of microorganisms. The possibility that the metabolic activity of planktonic bacteria in the photic zone could have driven the deposition of BIFs was first suggested by Cloud (1965, 1972). Cloud proposed that O_2 production by cyanobacterial photosynthesis could have chemically oxidized dissolved Fe(II) and resulted in ferric oxide precipitation (Eq. (2), Fig. 3).

$$4\,Fe^{2+} + O_2 + 4\,H_2O \rightarrow 2\,Fe_2O_3 + 8\,H^{+} \quad (2)$$

Yet, in the anoxic atmosphere of the early Precambrian, O_2 would have been localized to “oxygen oases” associated with cyanobacterial blooms in coastal settings and possibly within the photic zone (Cloud, 1965, 1972). This hypothesis has since been developed to include a

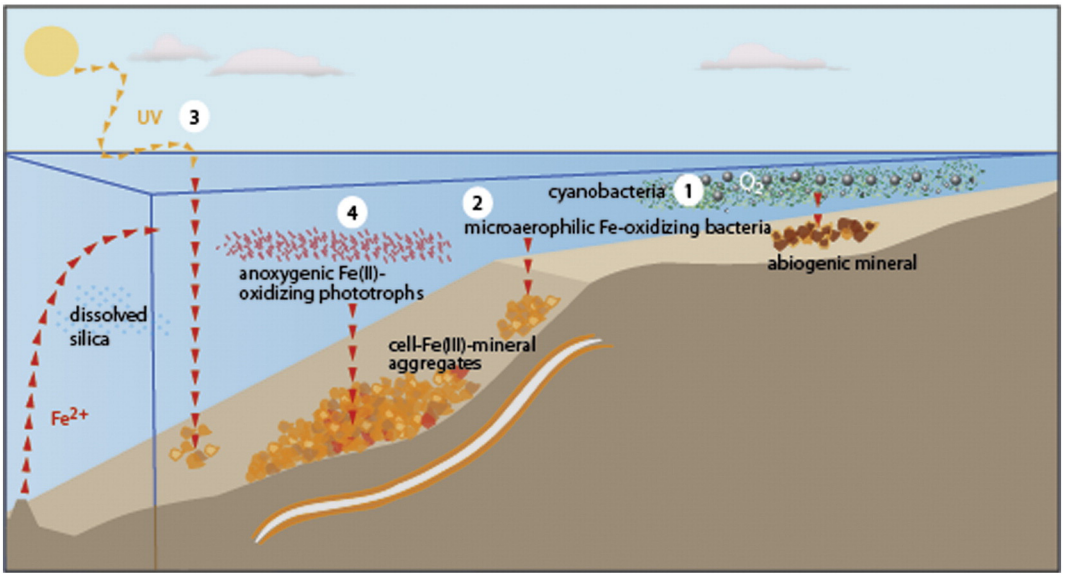

Fig. 3. Proposed depositional mechanisms for Precambrian banded iron formations (BIFs). Dissolved Fe(II), i.e. Fe^{2+}, is believed to be sourced from hydrothermal vents into a water column saturated by dissolved silica. For a water column in which oxygen is present at least in low concentrations, the first theory that invoked microorganisms is based on the production of oxygen by cyanobacteria. This oxygen reacts abiotically with dissolved Fe(II) once released into the water column producing Fe(III) followed by precipitation of abiogenic Fe(III) minerals that are not necessarily associated with biomass (1). In an ocean with at least localized oxygen, microaerophilic Fe(II)-oxidizing bacteria, could also take advantage of opposing oxygen- and Fe^{2+}-gradients and precipitate cell–Fe(III)-mineral aggregates (2). In an anoxic water column, UV light could photooxidize Fe(II) and precipitate abiogenic Fe(III) (oxyhydr)oxides (3) and the direct microbial Fe(II) oxidation via anoxygenic Fe(II)-oxidizing phototrophs also forming cell–Fe(III)-mineral aggregates (4).
From Konhauser et al. (2002), Kappler et al. (2005a) and Posth et al. (2011).

role for microaerophilic Fe(II)-oxidizers utilizing a metabolic niche once oxygen was made available (Holm, 1989) (see also Section 4.2).

2.2. The role of Fe(II)-oxidizing photoautotrophs

In an anoxic setting, the C and Fe cycles could also have been linked via anoxygenic Fe(II)-oxidizing photosynthesis and offer another potential Fe(II) oxidation mechanism for BIFs (Garrels et al., 1973; Hartman, 1984). This metabolism would directly produce biogenic Fe(III) (oxyhydr)oxides, even being able to turnover Fe(II) deeper in the water column by utilizing accessory pigments capable of capturing light not absorbed by oxygenic phototrophs (Konhauser et al., 2002; Kappler et al., 2005a; Fig. 3). These organisms can oxidize Fe(II) to Fe(III) and reduce CO_2 to build biomass (Eq. (3)).

$$4Fe^{2+} + HCO_3^- + 10H_2O \rightarrow 4Fe(OH)_3 + (CH_2O) + 7H^+ \quad (3)$$

There are a number of Fe(II)-oxidizing phototrophic strains, both freshwater and marine, known today (e.g., Ehrenreich and Widdel, 1994; Heising et al., 1999; Straub et al., 1999; Jiao et al., 2005). It is believed that anoxygenic Fe(II)-oxidizing phototrophs were present in the early Archean oceans due to their apparent antiquity (Xiong, 2006) and their utilization of Fe(II), which was an abundant electron donor in the ancient, ferruginous oceans. The isolation of bacteria capable of Fe(II)-oxidizing photosynthesis (Widdel et al., 1993) has made it possible to cultivate and test the constraints of this metabolism in the laboratory. Physiological experiments have been carried out with strains of Fe(II)-oxidizing phototrophs representing green sulfur bacteria, purple sulfur bacteria and purple non-sulfur bacteria. All strains are mesophiles, neutrophiles, and tolerant of a wide range of Fe(II) concentrations and light intensities (Hegler et al., 2008). In addition, the presence of 2 mM dissolved silica, a likely concentration in the Archean ocean (Siever, 1992), does not hinder the oxidation of Fe(II) by these strains (Konhauser et al., 2007; Posth et al., 2008). In fact, when anoxygenic Fe(II)-oxidizing phototrophs were cultivated in a salt solution containing dissolved Fe(II) and silica, temperature fluctuations caused the alternating precipitation of biogenic Fe(III) (oxyhydr)oxides and silica (Posth et al., 2008). These studies showed that in a system inhabited by Fe-metabolizing bacteria, Fe and Si, temperature alone could trigger alternating precipitation of Fe-rich and Si-rich layers typical of BIFs (Posth et al., 2008).

3. Interpreting biogenicity of Fe minerals in the rock record

Ancient sediments are our window into the past. We probe them through analyses of fossils, isotope fingerprints, geochemical composition, molecular biomarkers and mineralogy and hope to obtain an understanding of the coevolution of the planet with life (Fig. 2). The further we probe back in time, the more difficult it becomes to determine the biogenicity of a structure. Diagenetic or metamorphic processes may have influenced the sample and both abiotic and biotic processes can create textures which can be interpreted as biogenic (e.g. Schopf and Packer, 1987; Brasier et al., 2002, 2005; McLoughlin et al., 2008). The interpretation of sedimentary structures in the Proterozoic (2.5 to 0.52 Ga) is guided by some general rules which recommend that biogenic structures be: 1) in rocks of known provenance, 2) in a sequence of established age, 3) indigenous to and, 4) syngenetic with the primary deposited enclosing rock. Finally, the structure must be 5) of assured biological origin (Schopf, 1992; outlined in Schopf, 1993; Brasier et al., 2005). The earliest evidence of life generally agreed upon goes back to approximately 3.8 billion years ago and is based on isotopic evidence for biological carbon fixation followed closely by isotopic evidence for methanogenesis (Mojzsis et al., 1996; Rosing, 1999; Ueno et al., 2006), microbial sulfate reduction (Shen et al., 2001) and possibly sulfur disproportionation (Philippot et al., 2007) at ~3.5 billion years ago.

Organic biomarker analysis of the rock record has also been used to determine biogenicity of ancient sedimentary structures. This approach is based on the signature membrane lipids found in the three domains of life, Bacteria, Archaea, and Eukarya preserved as organic molecules in the sediment. Although a large fraction of biological material is recycled in the sediment or destroyed via diagenetic processes, recalcitrant molecules such as some components of the lipid membrane retain a recognizable similarity to the original molecule and can thus be used to reconstruct the presence of specific classes of organism in ancient

environments even after decomposition and alteration. Reconstruction of a community is still challenging, however, as the preservation of lipids may be selective and may not represent the most abundant organisms.

The study of ancient biomarkers has contributed to our understanding of ancient Fe metabolisms. The presence of 2α-methylhopanes was first believed to be specific only to cyanobacteria (Brocks et al., 1999; Summons et al., 1999) and was thought to increase cell membrane rigidity. Genome sequences, however, showed that a number of facultative and obligate anaerobes possess the genes for hopanoid synthesis. It was soon demonstrated that pure cultures of *Geobacter sulfurreducens* produce a variety of hopanoids which are structurally related to 2α-methylhopane under strictly anoxic conditions (Fischer et al., 2005; Härtner et al., 2005). In addition, the anoxygenic Fe(II)-oxidizing phototroph *Rhodopseudomonas palustris* TIE-1 also generates 2-methylhopanoids under anoxic conditions (Rashby et al., 2007) and C-2 methylation of hopanoids increases when Fe(II) concentrations are elevated in the growth medium (Eickhoff et al., 2013). It is certain that 2-methylhopanoids have a more diverse origin than first anticipated. The influence of Fe concentration on C-2 methylation of the hopanoids, however, suggests that the presence of these biomarkers in the rock record reveals a Fe-rich, anoxic setting at deposition. Anoxygenic photoautotrophs that fix CO_2 by utilizing Fe^{2+} or sulfur compounds as electron donors are considered key organisms responsible for primary production on early Earth (Canfield et al., 2006). The isotopic fractionation of $^{13}C/^{12}C$ in ancient rocks may be indicative of life as the transformation of inorganic carbon (e.g., CO_2 or HCO_3^-) via autotrophic pathways into organic carbon involves the preferential incorporation of the lighter isotope, ^{12}C, into the organic phase. This incorporation of the lighter isotope results in a range of $\delta^{13}C$ from −4‰ to −35‰ in bacteria and a reservoir enriched in the heavier isotope, ^{13}C. Highly negative carbon isotope values of organic matter, for example in sedimentary cherts throughout the Archean Eon (Hayes et al., 1999) and graphite globules in 3.7 billion year old sedimentary rocks from the Isua supracrustal belt ($\delta^{13}C$ of −19‰) (Rosing, 1999), are consistent with fixation by ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCo), and therefore suggestive of a key role for phototrophic and non-phototrophic bacteria utilizing RuBisCo in the deposition of ancient sediments. However, in phototrophic bacteria, it is known that different carbon fixation pathways are utilized (Quandt et al., 1977; Sirevåg et al., 1977) such as the reductive acetyl-CoA, reductive citric acid cycle, Calvin cycle (with key enzyme RuBisCo) as well as the hydroxypropionate pathway. To a certain extent, these pathways have overlapping degrees of carbon fractionation. However, C-isotope studies of lakes and fjords harboring large populations of anoxygenic phototrophs, as well as cultures studies of anoxygenic phototrophs suggest that the bulk C-isotope fractionation reflects the C-fixation pathway utilized by the bacterial community as a whole (Velinsky and Fogel, 1999; Zyakun et al., 2009). The bulk C-isotope fractionation between dissolved organic carbon and particulate organic carbon differed measurably when the reductive citric acid cycle was utilized over the Calvin cycle by the microbial population (Zyakun et al., 2009). Further work linking C-isotope fractionation in the water column and in the sediment of S-rich and Fe-rich systems may offer further insight. In order to understand isotopic fractionation in terms of element cycling and ancient metabolisms of Fe-rich environments, a number of studies focus on Fe isotope fractionation in abiogenic and biogenic Fe minerals either alone or in combination with other relevant isotope systems.

3.1. The Fe-isotope record

The study of Fe isotope systematics in biotic and abiotic environments has been spurred by an interest in transition metals, Fe cycling in Earth history, and the discovery of microbial Fe(III) reduction as a major process in natural environments (e.g., Lovley et al., 1987; Canfield et al., 1993; Coleman et al., 1993; Lovley et al., 1993). Thorough reviews of Fe isotope systematics and applications to both modern and ancient settings have been contributed by Johnson et al. (2008a,b) as well as Dauphas and Rouxel (2006) and Anbar and Rouxel (2007) and are recommended for a full understanding of Fe and other transition metal isotope dynamics.

Understanding of Fe isotopes requires an appreciation of the complex interactions between dissolved Fe phases such as Fe^{2+} and Fe^{3+} aquo-complexes and particulate phases like ferrihydrite, as well as between poorly crystalline Fe(II) minerals and more crystalline phases. Although dissolved and particulate phases do not by themselves create distinct isotope reservoirs, isotope effects between species can occur, and may be overshadowed by kinetic effects during the precipitation of ferric Fe (Bullen et al., 2001) (see Section 4.1 for further discussion of the stages of ferric Fe precipitation). Distinct isotope reservoirs allow for the preservation of isotopic signatures in the rock record (Bullen et al., 2001; Icopini et al., 2004).

Non-redox, abiotic processes occurring in Fe-rich systems, such as mineral precipitation of Fe(III) (oxyhydr)oxides, carbonates and sulfides and dissolution of Fe(III) (oxyhydr)oxides via ligands or siderophores lead to kinetic and equilibrium isotope fractionation (up to 1‰, Anbar et al., 2000). In addition, abiotic Fe(II) oxidation or sorption of $Fe^{2+}{}_{(aq)}$ onto ferric hydroxides has also been found to fractionate Fe (Bullen et al., 2001; Icopini et al., 2004). Of course, the distinction between potential Fe isotope fractionation driven by abiotic Fe(II) oxidation and Fe(III) reduction processes and fractionation due to biological activity of Fe-cycling bacteria is the key to determining the biogenicity of Fe minerals in natural environments.

Cultures of the Fe(III)-reducing bacterium *Shewanella algae* were responsible for a fractionation of Fe of 1-2‰ (Beard et al., 1999; Beard et al., 2003). Anoxygenic Fe(II)-oxidizing photoautotrophic bacteria produce ferric (oxyhydr)oxides enriched in the heavy isotope by −1.5 ± 0.2‰ relative to Fe(II) in pure and enrichment cultures (Croal et al., 2004). This fractionation was independent of the Fe(II) oxidation rate (Croal et al., 2004). As our knowledge of early Earth atmosphere and oceans has evolved, later studies have branched out to cover other Fe(II)-oxidizing strains and environmental conditions. Isotopically heavier Fe(III) (oxyhydr)oxides are also produced by microbially-catalyzed aerobic Fe(II) oxidation at low pH (Balci et al., 2006) and nitrate-reducing Fe(II) oxidation (Kappler et al., 2010). As a comparison, the chemical oxidation of Fe(II) in natural environments (e.g. Bullen et al., 2001) has been found to produce isotopically heavier Fe(III) (oxyhydr)oxides relative to aqueous Fe (~−2‰). These studies showed that enrichment of the heavy isotope is observed for both biotic and abiotic processes and thus does not allow biogenicity to be simply constrained. The rapid electron exchange between aqueous Fe^{2+} and Fe^{3+} during oxidation and during microbial Fe(III) reduction, causes isotopic equilibrium to be reached between reduced and oxidized species and therefore, the Fe isotope fractionation to be independent of whether it is a chemical or biological mechanism.

Fe isotope paleorecords may be found in Fe–Mn crusts for more recent earth history reconstruction, as well as black shales and BIFs for early earth reconstruction (Anbar and Rouxel, 2007). We herein focus on the efforts made to read the Fe isotope record in BIF. The range of $\delta^{56}Fe$ measured in Archean and early Paleoproterozoic BIFs (−2.5 to 1.0 ‰ relative to the bulk Earth) from the Transvaal group, South Africa covers the entire range known for Fe isotopic composition of ancient rocks on Earth. The Fe isotope composition of BIFs does, however, differ from values in igneous rocks and modern marine sediments ($\delta^{56}Fe$ of 0.00 ± 0.05‰). Indeed, the wide range of Fe isotope composition of the major BIF minerals (hematite, magnetite, Fe-carbonate, and pyrite) has been interpreted to reflect kinetic and equilibrium isotope fractionation during formation and transformation of minerals, a variation in the fluid isotope composition from which the minerals precipitated, and the participation of microbial processes (Johnson et al., 2003; Johnson et al., 2004; Johnson and Beard, 2005; Johnson et al., 2013).

The Fe isotope values determined with isolates of anoxygenic Fe(II)-oxidizing phototrophs correlate well with those determined for the

Archean using early Proterozoic banded rocks of the Transvaal Supergroup, South Africa ($^{56}Fe/^{54}Fe$ values in hematite as high as +0.75 to +1.0‰ (Johnson et al., 2003) compared to the Fe from hydrothermal vents (±0‰)). The similarity in values determined from cultures of anoxygenic phototrophs and nitrate-reducing, Fe(II)-oxidizing bacteria to those of Fe(III) (oxyhydr)oxides formed by chemical oxidation makes it difficult to distinguish between biotic and abiotic processes (Bullen et al., 2001; Kappler et al., 2010). However, an emerging study of the water column and sediment of Fe-rich Lake Pavin, France may yield a fresh look at this problem where Fe-isotope profiles from the water column (0.1 to 1200 μM dissolved Fe(II)) reveal an increase in $\delta^{56}Fe$ from −2.14 across the oxic–anoxic boundary to the lake bottom (Busigny et al., personal communication), which the authors suggest is controlled by the partial oxidation of dissolved ferrous iron and linked to water column cycling. Further study at this and similar lakes may reveal more about how Fe isotope fractionation is influenced by microbial processes.

In order to gain further insight about the processes determining the preserved Fe isotope signature, multiple isotope studies on Precambrian BIFs have more recently been undertaken. The comparative analysis of various isotope systems in the same rock transect is helping to investigate how main element cycles are linked by abiotic and biotic processes. For example, a study of the 2.5 billion year old Kuruman Iron Formation (Transvaal Supergroup, South Africa) and the Dales Gorges Member of the Brockman Iron Formation (Hamersley Group, Australia) employed a comparison of the Fe and the Si isotopic signatures across mineral phases to shed light on BIF genesis (Steinhoefel et al., 2010). UV femtosecond laser ablation MC-ICP-MS analyses across Fe-rich and Si-rich layers revealed a uniformity in $\delta^{30}Si$ (−1.3 and −0.8‰ across each core section) (Steinhoefel et al., 2010). A series of studies carried out by Czaja, Johnson, Beard and co-workers in recent years have also taken this approach to clarify the paleorecord with respect to Fe cycling and Earth oxygenation. In these studies, a wide range of $\delta^{56}Fe$ values along with C and O isotope data in South African Transvaal BIFs (2.5–3.0 Ga old Kuruman and Campbellrand) and Australian BIFs (2.5–2.7 Ga Hamersley) were attributed to dissimilatory Fe(III) reduction (Czaja et al., 2010; Heimann et al., 2010). In contrast, the tighter range of $\delta^{56}Fe$ values determined for the 3.7 Ga Isua BIF, both across and within magnetite bands were ascribed to anoxygenic photosynthetic Fe(II)-oxidizing bacteria, irrespective of the higher grade metamorphosis (amphibolite facies) these formations have undergone (Czaja et al., 2013). The authors based this conclusion on a dispersion/reaction model which suggests extremely low O_2 content in the photic zone, consistent with formation by anoxygenic phototrophs (Czaja et al., 2013). This work has lead to an understanding of the evolution of Fe(III) production from an early BIF record dominated by photoferrotrophs to increasing roles for oxygenic phototrophs and dissimilatory Fe (III) reduction in later BIFs.

3.2. Mineralogy as biosignature

In the absence of remnants of biological origin in the rock record, such as fossils, a signature of life may be found in the identity, structure and assembly of minerals. Specific mineral identity, structure and assembly are known to form as a direct or indirect consequence of microbial metabolism. An example is the magnetite crystal chains precipitated and aligned by magnetotactic bacteria, which are traceable in natural environments (Blakemore, 1975; Gorby et al., 1988). The precipitation of Fe(III) minerals by cells can also create unique structures like the Fe(II)-oxidizing *Gallionella* and *Leptothrix* sp. which form twisted stalks and sheaths of Fe(III) (oxyhydr)oxides (Fig. 4), possibly as a means of avoiding encrustation (e.g., Emerson and Revsbech, 1994a). These casts allow them to be identified in natural samples (Emerson and Revsbech, 1994b). Also in anoxic settings, the metabolism of microorganisms, like anoxygenic Fe(II)-oxidizing phototrophs or nitrate-reducing Fe(II)-oxidizers, can be directly linked to the precipitation of minerals which range in crystallinity from poorly crystalline to crystalline (Kappler and Newman, 2004; Kappler et al., 2005b; Hegler et al., 2008; Miot et al., 2009a). The properties of these minerals, however, are very similar to those of chemically-synthesized minerals when

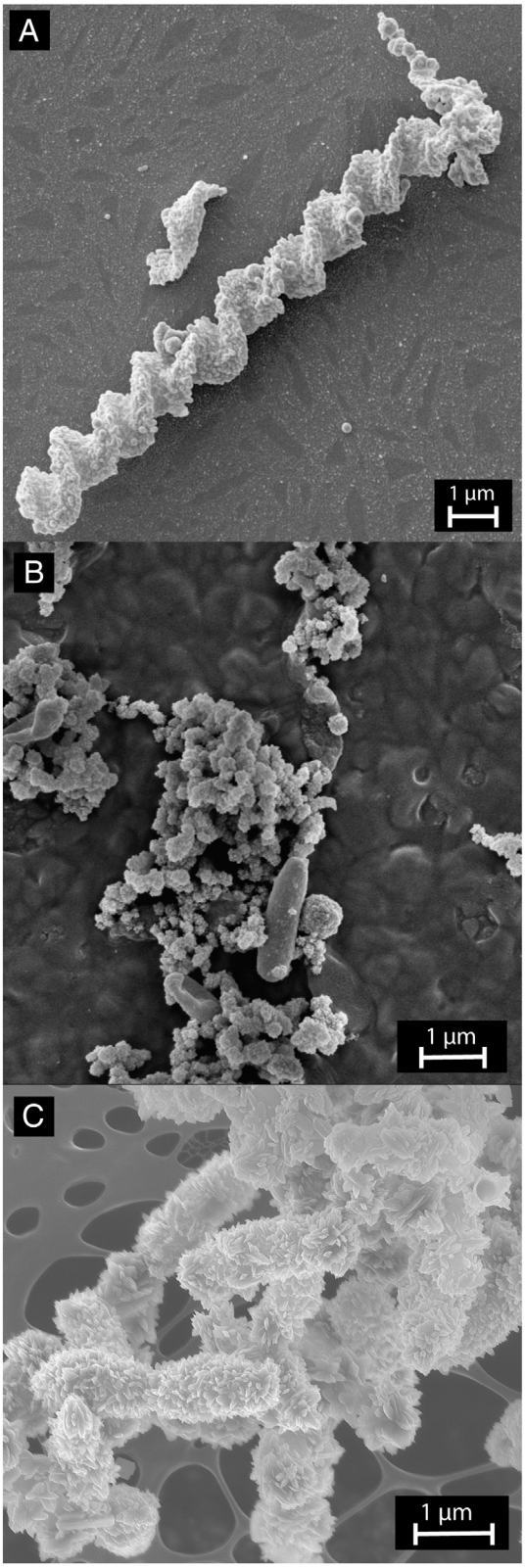

Fig. 4. A) Twisted stalks of organic fibrils typically produced by the microaerophillic-Fe(II)-oxidizing bacteria, *Gallionella* sp. from the Gonzen Mine, Sargans, Switzerland (image taken by Martin Obst). B) The Fe(III) (oxyhydr)oxide ferrihydrite as produced by anoxygenic Fe(II)-oxidizing phototrophic bacteria, *Rhodobacter ferrooxidans* sp. strain SW2, and C) nitrate-reducing, Fe(II)-oxidizing bacteria *Acidovorax* sp. BoFeN1 encrusted by goethite.

analyzed with standard methods, such as X-ray diffraction (XRD). More sophisticated methods, such as Mössbauer spectroscopy, electron microscopic analyses and synchrotron analyses are required to distinguish biotic from abiotic minerals and investigate their transformation through geological timeframes (Miot et al., 2014). Nonetheless, abiotic and biotic minerals can differ, in that biogenic mineral has inherently incorporated and associated organic matter which influences the structure of the minerals over short and long term diagenesis (ex. Kappler et al., 2005a; Posth et al., 2010; Muehe et al., 2013). These interactions are discussed in more detail in the coming sections.

In addition to active biomineralization, bacteria also indirectly foster mineral production by passively offering a template for mineral nucleation or by changing conditions to promote mineral precipitation. Mineral assemblages templated by organic polymers and modifications to mineral surfaces or mineral distribution patterns may also present distinctive biosignatures via the alteration of the mineral by metabolic by-products (Banfield et al., 2001).

4. Formation of biogenic Fe(III) minerals: from Fe(II) to Fe(III) (oxyhydr)oxides

Fe(III) minerals can be formed in aqueous settings both abiotically and biotically and both types of processes can occur simultaneously. The rate of formation, the surrounding physio-chemical environment, and the presence of nucleation sites all influence the structure, size, crystallinity and composition of the minerals formed (e.g. Hansel et al., 2003, 2005). Since the presence and absence of organisms can actively and passively influence formation rate and environment, and offer reactive sites, biogenic and abiogenic minerals can differ from one another due to their formation mechanism. One challenge in understanding biogenic Fe(III) mineral formation is to clarify how Fe(II)-oxidizing bacteria carry out their metabolism and avoid becoming enmeshed in a matrix of insoluble ferric minerals.

4.1. Abiotic formation of Fe(III) (oxyhydr)oxides

The abiotic formation of Fe(III) oxy(hydr)oxides from dissolved Fe(III), i.e. Fe^{3+}, such as ferrihydrite (simplified: $Fe(OH)_3$, suggested for ordered ferrihydrite: $Fe_{10}O_{14}(OH)_2$, Michel et al., 2007) and goethite (α-FeOOH) occurs via direct chemical precipitation by rapid Fe^{3+} hydrolysis followed by nucleation and crystallization. In addition, various Fe(III) (oxyhydr)oxides can be converted into other (oxyhydr)oxides and oxides by dissolution/reprecipitation, dehydration, partial reduction or a solid state transformation (Cornell and Schwertmann, 2003, Fig. 5). The recrystallization rate can be on the scale of minutes–months. The rate and crystallization product are influenced by the solution chemistry, for example the concentration of ions in solution, including not only Fe^{2+} and Fe^{3+}, but also bicarbonate and phosphate (Grundl and Delwiche, 1993; Larese-Casanova et al., 2010; Cismasu et al., 2012).

Free, dissolved, ferrous iron (Fe^{2+}) can be present in anoxic, aqueous settings that are acidic or basic, organic poor or organic rich. With exposure to an oxic atmosphere or other oxidizing agents, ferrous iron will be oxidized and precipitate stepwise first as nanoparticular Fe(III) crystallites and ultimately as a crystalline ferric Fe(III) (oxyhydr)oxide (Fig. 5). The ultimate transformation can be generalized following:

$$Fe^{2+} \xrightarrow{k\ ox} Fe^{3+} \xrightarrow{k\ hyd} Fe(OH)_{n}^{3-n} \xrightarrow{k\ ppt} \text{crystallites}_{nano} \xrightarrow{k\ xtal} \text{crystalline phase}$$

(e.g., goethite) (Grundl and Delwiche, 1993).

The oxidation rate of ferrous iron with oxygen is known to be a function of ferrous iron concentration, hydroxyl concentration (i.e. pH) and O_2 concentration, and at pH > 3 is first order with respect to Fe^{2+} and oxygen partial pressure and second order with respect to $[OH^-]$

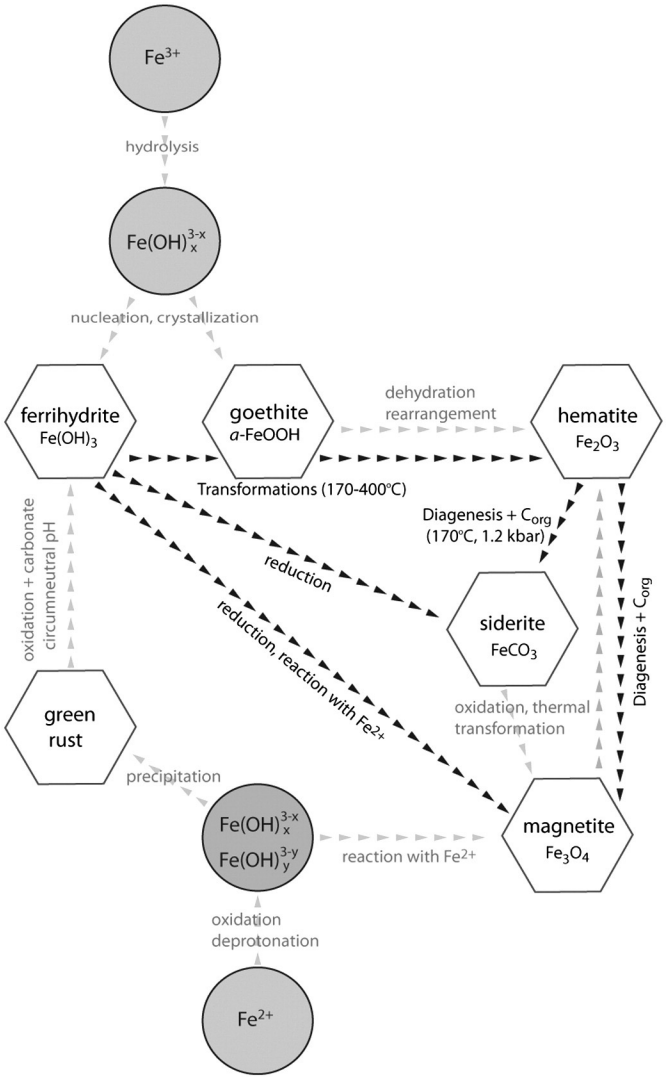

Fig. 5. Abiotic formation and transformation of ferric (oxyhydr)oxides. Adapted from Cornell and Schwertmann (2003).

(Grundl and Delwiche, 1993). The rate of formation of a hydrolyzed metal species is based on the deprotonation of H_2O and is very rapid.

Due to this rapid formation, poorly crystalline Fe(III) (oxyhydr)oxide (ferrihydrite) and the more crystalline Fe(III) (oxyhydr)oxide goethite commonly form. However, ferric Fe mineral precipitation is initiated by the precipitation of small ferric (oxyhydr)oxide polymers, which increase in size to colloidal-sized (oxyhydr)oxide solids, which then form spheres and larger aggregates (Macalady et al., 1990; Yuwono et al., 2010, 2012). These precipitates can be mixed solids with varied composition since SO_4^{2-}, NO_3^-, Cl^-, PO_4^{3-}, ClO_4^-, and organics can also co-precipitate. Depending on the saturation state of the solution, further mineral growth will proceed either as condensation of two or more nuclei, or of monomeric $Fe(OH)^o$ onto an existing nuclei.

Ferrihydrite, in particular, precipitates directly from Fe(III) salt solutions. The Fe(III) salt dissociates and forms the hexa-aquo ion [Eq. (5)].

$$FeCl_3 + 6H_2O \rightarrow Fe(H_2O)_6^{3+} + 3Cl^- \quad (5)$$

(from Cornell and Schwertmann, 2003).

As the electropositive hexa-aquo cation induces H_2O ligands to act as acids, stepwise deprotonation of the six H_2O ligands takes place [Eq. (6)]. The complete hydrolysis results in an Fe(III) oxide or

(oxyhydr)oxide [Eqs. (7), (8)].

$$Fe(H_2O)_6^{3+} \rightarrow Fe(H_2O)_5(OH)^{2+} + H^+ \quad (6)$$

$$Fe(H_2O)_6^{3+} \rightarrow FeOOH + 3H^+ + 4H_2O \quad (7)$$

Cornell and Schwertmann (2003).

$$2Fe(H_2O)_6^{3+} \rightarrow Fe_2O_3 + 6H^+ + 9H_2O \quad (8)$$

Cornell and Schwertmann (2003).

4.2. Formation of Fe(III) minerals by microaerophilic Fe(II)-oxidizing bacteria

Fe-metabolizing bacteria influence the Fe cycle in that they actively utilize Fe(II) as electron donor and initiate the production of Fe(III) (oxyhydr)oxides. Microaerophilic Fe(II)-oxidizing bacteria carry this out by using O_2 as electron acceptor both under acidic (ex. *Thiobacillus ferrooxidans*, *Sulfobacillus acidophilus*) and circumneutral pH conditions (ex. *Gallionella ferruginea*, *Leptothrix ochracea*) (for a review see Kappler and Straub, 2005; Konhauser et al., 2011). At acidic pH, ferrous Fe is stable even in the presence of O_2 (with the exception of highly concentrated HCl solutions, Porsch and Kappler, 2011), so that these bacteria do not compete with O_2 for Fe(II) oxidation. At pH values greater than 2, however, Fe(II) begins to react abiotically with O_2 and precipitates as a Fe(III) solid. Therefore, neutrophilic Fe(II)-oxidizing bacteria must compete with the chemical oxidation of Fe(II) by O_2 if they are to obtain energy from Fe(II) oxidation (Druschel et al., 2008; Schmidt et al., 2010). They grow optimally under microoxic conditions in gradients of oxygen and Fe(II).

Gallionella sp. are bean-shaped organisms that produce twisted stalks encrusted with ferric Fe minerals (Fig. 4). *Leptothrix* sp. form tubular sheaths encrusted in ferric Fe. It has been postulated that the sheaths and stalks allow these strains to avoid encrustation by the ferric minerals (Hanert, 1981, 1992; Hallberg and Ferris, 2004; Chan et al., 2011). These bacteria thrive today in environments at oxic to anoxic interfaces, like Fe seeps, freshwater wetlands, hydrothermal vents and seamounts (e.g., Emerson and Revsbech, 1994b; Emerson and Moyer, 2002). The study of the rates and mechanisms of Fe(II) oxidation by these organisms, especially in the field, is made difficult by additional processes which occur simultaneously in these Fe-rich systems. First, the abiological oxidation of Fe(II) can mask that carried out by the bacteria. Second, Fe(III) (oxyhydr)oxides precipitated on the organic stalks or sheaths autocatalyze further abiotic Fe(II) oxidation even after the bacteria themselves are no longer active. Third, organic ligands present in the microbial mats influence the redox kinetics of the systems (for an overview see Emerson and Weiss, 2004). Furthermore, the microbial processes can influence the abiotic ones, as the abiotic rate of Fe(II) oxidation may be decreased by the presence of the bacteria via the binding of Fe(II) to cell or exopolymer surfaces (Emerson and Weiss, 2004).

4.3. Formation of Fe(III) minerals by Fe(II)-oxidizing phototrophs

Biogenic Fe(III) minerals are also produced by anoxygenic Fe(II)-oxidizing phototrophic bacteria, also referred to as photoferroautotrophs. These organisms do not form sheaths or stalks like the microaerophilic Fe(II)-oxidizing bacteria, but rather produce Fe(III) (oxyhydr)oxides that consist of poorly crystalline ferrihydrite and nanocrystalline goethite (α-FeOOH) (Kappler and Newman, 2004). These minerals become more crystalline over time and have been found to reside mostly on extracellular fibers and sometimes as small patches on the cell surface (Miot et al., 2009a; Miot et al., 2009c). Anoxygenic Fe(II)-oxidizing phototrophs oxidize Fe(II) to Fe(III) and build biomass according to Eq. (3). The location of Fe(II) oxidation in the cell and the molecular mechanism of phototrophic Fe(II) oxidation is still unresolved. As the deposition of poorly soluble Fe(III) oxides in the periplasm or cytoplasm would hinder cell function, it has been proposed that Fe(II) oxidation in anoxygenic Fe(II)-oxidizing bacteria takes place on the cell surface (Ehrenreich and Widdel, 1994). This is one reason why theoretical models for Fe(II) oxidation in anoxygenic phototrophs place a redox-active component in the outer cell membrane with electrons transported through the periplasm to the reaction center in the cell membrane (Yarzábal et al., 2002). This is similar to the model constructed for Fe(II) oxidation in the acidophilic Fe(II)-oxidizing bacteria *Acidithiobacillus ferrooxidans*. Operons responsible for phototrophic Fe(II) oxidation have since been identified in two strains (Croal et al., 2007; Jiao and Newman, 2007). One part of the operon encodes c-type cytochromes in both strains that could function as the Fe(II) oxidoreductase (Croal et al., 2007; Jiao and Newman, 2007). While this research takes us a step closer to understanding Fe(II) oxidation, the cellular location of this process is still unclear and therefore biogenic Fe(III) mineral development in the steps progressing from initial oxidation is still unresolved. Indeed, a mechanism that prevents inter-cellular precipitation of ferric Fe or one that allows its excretion or transport away from the cell is required. Some hypotheses for this transport away from the cell surface are Fe(III) solubilization by complexation and surface charge modification (Sobolev and Roden, 2001; Kappler and Newman, 2004; Schädler et al., 2009; Saini and Chan, 2013). Another possibility is the existence of a low pH microenvironment around the cell which would cause Fe(III) oxide to precipitate away from the cell surface (Hegler et al., 2010). Although it would be expected that the positively charged Fe(III) minerals sorb to the negatively charged cell surface and lead to encrustation, electron-microscopy analysis of the phototrophic Fe(II)-oxidizing *Thiodictyon* sp. strain F4 showed no such encrustation. Using microscopy with a pH-sensitive fluorescent dye it was shown that the pH adjacent to the cell surface of *Thiodictyon* sp. was pH 6.0 with a medium pH of 6.6. Biogeochemical modeling showed that this difference would lower Fe(III) sorption and precipitation rates at the cell surface (Hegler et al., 2010). An investigation of the putative Fe oxidoreductase of *Rhodobacter ferrooxidans*, FoxE, showed pH dependent Fe(II) oxidation by this di-heme, c-type chromosome (Saraiva et al., 2012). The authors postulate that Fe(II) oxidation rate is modulated by adjustment of the heme reduction potential, and which may afford these organisms the control needed to adjust to varied Fe environments and avoid encrustation. Indeed, what is observed is that some cells may have developed means to avoid full encrustation by Fe(III) minerals while others become passive templates for encrustation. The end result is biogenic minerals either consisting completely of Fe mineral surfaces, or biogenic minerals that are aggregates of cells and Fe minerals (Fig. 4). These structures and their implications are discussed further in Section 4.5.

4.4. Formation of Fe(III) minerals by nitrate-reducing, Fe(II)-oxidizing bacteria

The microbial oxidation of Fe(II) in the absence of O_2 and light could occur by using nitrate as an electron acceptor [Eq. (4)]. During mixotrophic growth with acetate, as well as Fe(II) and nitrate as electron acceptor, these bacteria produce Fe(III) that typically forms mineral crusts around the cells (Fig. 4). It was initially suggested (Straub et al., 1996) that these organisms catalyze the oxidation of Fe(II) and couple it directly to the reduction of nitrate according to the following equation:

$$10Fe^{2+} + 2NO_3^- + 24H_2O \rightarrow 10Fe(OH)_3 + N_2 + 18H^+. \quad (9)$$

However, most if not all isolates capable of performing this reaction are mixotrophic, i.e. they need an organic co-substrate to continuously oxidize Fe(II) with nitrate as electron acceptor (Benz et al., 1998).

Abiotic oxidation of Fe(II) driven by reactive NO, NO_2^- and NO_2 formed during nitrate reduction is well documented (Moraghan and Buresh, 1977; Picardal, 2012). In particular, green rust was suggested to be a reactive intermediate in these processes (Pantke et al., 2012). It remains uncertain whether heterotrophic nitrate reduction causes the observed oxidation of Fe(II) (Muehe et al., 2009; Carlson et al., 2012; Picardal, 2012; Chakraborty and Picardal, 2013; Klueglein and Kappler, 2013; Kopf et al., 2013; Klueglein et al., 2014).

Bacteria carrying out nitrate-reducing, Fe(II) oxidation (e.g. *Acidovorax* sp. strain BoFeN1, *Azospira oryzae* strain PS) have been isolated both from brackish and freshwater settings and may indeed drive anaerobic ferrous iron oxidation in the suboxic zones of various aquatic sediments (Straub et al., 1996; Kappler et al., 2005b). Dissolved Fe(II) and FeS, as well as microbially-reduced synthetic goethite, biogenic magnetite, Fe(III) oxide-rich subsoils, and potentially even pyrite are oxidized in the presence of nitrate by such organisms (Straub et al., 1996; Weber et al., 2001; Kappler et al., 2005b; Larese-Casanova et al., 2010; Bosch et al., 2011). In the case of nitrate-dependent pyrite oxidation, however, the role of nitrite as oxidant has not been clarified completely. While chemically precipitated $FeCO_3$ is rapidly oxidized, it was found that biogenic $FeCO_3$ was not readily oxidized by these strains (Weber et al., 2001; Miot et al., 2009b). The authors suggest that the reduced surface area of biogenic $FeCO_3$ in comparison to that of abiogenic $FeCO_3$ hindered microbially-driven Fe(II) oxidation.

As mentioned above, the mechanism of Fe(II) oxidation by nitrate-reducing Fe(II)-oxidizing bacteria is still not fully understood. However, initial microscopic observations of *Acidovorax* sp. strain BoFeN1 showed encrustation of the cells. This encrustation differed from that seen in the anoxygenic Fe(II)-oxidizing phototrophs (e.g. *R. ferrooxidans* sp. strain SW2) (Kappler et al., 2005a; Schädler et al., 2009). This difference is of potential importance for the interpretation of fossils of Fe-bacteria. The nitrate-reducing cells became completely encrusted by the Fe(III) (oxyhydr)oxides over time even preserving protein globules in the periplasm (Miot et al., 2011). This cell encrustation appears to proceed first by rapid precipitation (within minutes) in the periplasm of the cell, and then via the formation of surface-bound globules that were first situated at the cell poles (Miot et al., 2009a). It is possible that Fe(II) oxidation takes place in the periplasm. Dissolved Fe(II) may either diffuse to and be bound at the cell surface or enter via a diffusive uptake or transport mechanism. The oxidation of the Fe(II) could then be carried out by an Fe oxidase protein located in the periplasm or on the cell surface (Schädler et al., 2009). If the oxidation of Fe(II) occurs in the periplasm, either the poorly soluble Fe(III) precipitates in the periplasm or else the microbes have evolved a mechanism by which to transport the poorly soluble Fe(III) out of the cell via an Fe(III) transport system (e.g., Miot et al., 2011). Non-encrusting cells must have a mechanism that transports soluble Fe(III) away from the cell before precipitation can occur, such as the presence of organic ligands which form dissolved Fe(III) complexes (Kappler and Newman, 2004), soluble colloidal Fe(III) species (Sobolev and Roden, 2001) or a low pH microenvironment around the cell itself (Hegler et al., 2010).

4.5. Properties of biogenic Fe(III) (oxyhydr)oxides

Microorganisms can influence the formation of Fe(III) (oxyhydr)oxides through a number of processes, which allow us to differentiate biotic from abiotic minerals. Microorganisms can alter solution chemistry through their metabolisms. They can precipitate Fe(III) (oxyhydr) oxides actively as described above or passively by offering a template for mineral formation. In all cases, biogenic minerals, in contrast to their abiogenic counterparts, can harbor organic carbon in the form of cell matter, either viable or dead (e.g., Ferris, 2005; Mikutta et al., 2008; Posth et al., 2010; Fig. 6). The incorporation of cell material may not be fully stoichiometric as expected from Eq. (3). In the case of anoxygenic Fe(II)-oxidizing phototrophs, a quantification of Fe(III) to organic carbon in the biogenic minerals from pure cultures showed that some cell matter remained suspended and did not settle as part of the biogenic mineral. This unexpected excess of Fe(III) minerals to organic carbon in the precipitate has implications not only for the interaction of the aggregate in the water column, but also for its aging in the sediment (Posth et al., 2010).

Anoxygenic Fe(II)-oxidizing phototrophs form aggregates of cells and Fe(III) minerals, which form a net-like structure (Fig. 6B, Posth et al., 2010). The aggregates appear bulbous or ragged in shape with an average size of 10–40 μm and density between 2.0 and 2.4 g/cm^3. With increasing Fe(II) concentration in solution, the cell fraction of the biogenic minerals increases and the density decreases. As a comparison, particle sizes at the marine, Fe-rich Loihi Seamount where microaerophilic Fe(II)-oxidizing bacteria are in the nm range (3.5–4.6 nm; Toner et al., 2012). A reduced particle size results in lower sedimentation rates and increased reaction time in the water column.

The mineralogy of the biogenic ferric Fe phase depends on the rate of Fe(II) oxidation, solution chemistry and the presence of preexisting minerals (Kappler et al., 2005b; Senko et al., 2005; Larese-Casanova et al., 2010; Posth et al., 2010; Dippon et al., 2012). For example, intermediate, mixed valence phases, such as green rust, have been observed in microbial Fe(II)-oxidizing cultures and in particular have been identified in cultures of the nitrate-dependent, Fe(II)-oxidizing *Acidovorax* sp. BoFeN1 (Pantke et al., 2012). In experiments with *Acidovorax* sp. BoFeN1 transferred from an Fe-free culture medium (only acetate) to medium containing dissolved Fe(II), poorly-crystalline Fe(III) (oxyhydr)oxide ferrihydrite was identified with XRD. The cells were

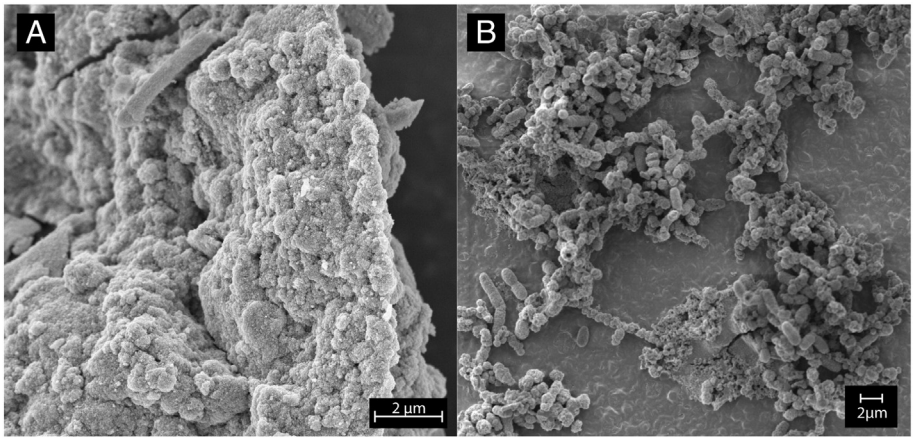

Fig. 6. Scanning electron micrographs of abiogenic and biogenic Fe(III) minerals: (A) chemically synthesized Fe(III) (oxyhydr)oxide 2-line ferrihydrite and (B) cell–Fe(III)-mineral aggregate networks formed by the anoxygenic phototrophic Fe(II)-oxidizer *Rhodobacter ferrooxidans* sp. strain SW2.

covered with irregularly shaped plates and needles. When this strain was transferred from a culture medium containing acetate and Fe minerals, crystalline Fe(III) (oxyhydr)oxide goethite was identified with XRD (Kappler et al., 2005b), the Fe minerals having functioned as a template for (oxyhydr)oxide precipitation. When mineral nucleation sites were present in *Acidovorax* sp. BoFeN1 cultures, mineral precipitation of the same underlying mineral phase, e.g. magnetite, was triggered (Dippon et al., 2012). The mineralogical outcome is also a result of the co-precipitation of ions and organic substances with the Fe(III) (oxyhydr)oxides which may disrupt mineral identity and crystallinity. Initial Fe(III) (oxyhydr)oxide nucleation is influenced by sorption of ions and organic molecules and full crystal development can be prevented (for a review, see Cornell and Schwertmann, 2003). Larese-Casanova et al. (2010) speculate that these co-precipitation processes occur during Fe(III) precipitation outside of the cell and are the best explanation of the Fe(III) mineralogy in the presence of carbonate, phosphate, and organic matter, such as humic substances.

Senko et al. (2005) show that Fe(II) oxidation rate is also important in Fe(III) mineral formation in cultures of nitrate-reducing, Fe(II)-oxidizing bacteria (FW33AN); as the Fe(II) oxidation rate decreased, a stronger goethite signal was identified by XRD and a larger proportion of the Fe(III) was crystalline. However, the Fe(II) oxidation rate is controlled largely by the aqueous environment in complex solutions. In cultures of *Acidovorax* sp. BoFeN1, increased phosphate concentrations yielded a lower Fe(II) oxidation rate. BoFeN1 likely had difficulty accessing the Fe(II) that was caught up in the solid Fe(II)-phosphate phase formed in this medium but unidentifiable using either Mössbauer spectroscopy or XRD (Larese-Casanova et al., 2010). Phosphate species have also been observed to alter Fe(III) crystallinity during Fe(II) oxidation (Châtellier et al., 2004) and Fe(III) precipitation (Thibault et al., 2009) and may influence the metabolism of nitrate-reducing Fe(II)-oxidizing bacteria (Senko et al., 2005). In experiments with anoxygenic Fe(II)-oxidizing phototrophs, it was observed that goethite formed in cultures grown with dissolved Fe(II) in the presence of low phosphate concentrations. In contrast, with high phosphate concentrations and poorly crystalline Fe(II) minerals (Fe(II)-phosphates) initially present, poorly ordered ferrihydrite (or Fe(III) phosphate) was formed (Miot et al., 2009a; Hohmann et al., 2010; Posth et al., 2010; Cosmidis et al., 2014).

Interestingly, in contrast to phosphate, concentrations of humic acid (Pohokee Peat Humic Acids (PPHA)) and carbonate in solution were found not to significantly influence Fe(II) oxidation rates (Larese-Casanova et al., 2010). Generally, humic acids weakly complex aqueous Fe(II) and in these experiments, the DOC:Fe(II) ratios were likely too low to see any effect. However, species such as aqueous $Fe(CO_3)_2^{2-}$ can be quickly taken up and oxidized and therefore do not affect bacterial oxidation. However, humic acids and carbonate did affect the product formed. With increasing carbonate or PPHA concentration, goethite was seen to form at the expense of lepidocrocite (Larese-Casanova et al., 2010).

The presence of silica in solution also influences the mineralogy of biogenic Fe minerals. Phototrophic Fe(II)-oxidizing bacteria continued to oxidize Fe(II) in the presence of up to 2 mM dissolved silica (the concentration estimated for the Archean ocean, modern values ~70 μM) (Konhauser et al., 2007; Posth et al., 2008). Silica coating of biogenic and abiogenic minerals is known to hinder its transformation over time. Indeed, low order ferrihydrite coated by silica is shown to resist alteration via chemical oxidation by oxygen as well as diagenesis up to 400 °C (Toner et al., 2012). Similarly, the stabilization of biogenic 2-line ferrihydrite by both PO_4^{3-} and Si in the micromolar range was also seen in growth experiments with *Ralstonia* sp. as well as with mine waters and is interpreted as the result of the formation of colloidal Fe oxides (Swanner et al., 2011).

Solution pH was also found to have an immense effect on the resulting mineralogy in cultures of nitrate-dependent, Fe(II)-oxidizing bacteria (Larese-Casanova et al., 2010). At pH 7, lepidocrocite and a small amount of goethite were formed. Slightly acidic conditions resulted in the formation of lepidocrocite and no goethite, which is consistent with studies carried out in abiotic systems (Cornell and Schwertmann, 2003) and may also be on the result of the higher fraction of carbonic acid at lower pH and its lowered affinity for Fe(III) (oxyhydr)oxide surfaces. Slightly basic conditions resulted in the production of goethite at the expense of lepidocrocite. Here, a blue-green intermediate phase, identified as green rust, was also observed during the first 3 hours; this then turned orange yellow (Pantke et al., 2012).

4.5.1. Bacterial exopolymers: function and significance as biosignatures

The interface between the cell and its environment is at the cell surface and the properties of this surface are of the utmost importance to the microorganism's survival (reviewed in Beveridge, 1988; Beveridge and Graham, 1991). Cells interact with their environment via the production of organic polymers not only to scavenge nutrients, but also to induce the crystallization of mineral phases that could otherwise encrust the cell (Chan et al., 2004; Chan et al., 2011). Aside from offering a template for ferric oxide nucleation, bacterial surfaces and exopolymers offer binding sites for metal sorption of anions (Fortin and Ferris, 1998; Ferris, 2005). For example, in samples from hydrothermal vents along the Juan de Fuca Ridge, mineralogical analysis identified 2-line ferrihydrite and poorly-ordered goethite associated with structures resembling *L. ochracea* and *G. ferruginea* (Kennedy et al., 2003a, b), as well as an abundance of Fe, O, C, N, Ca, Si and P detected via X-ray photoelectron spectroscopy (XPS) (Kennedy et al., 2003b). This association between ferrihydrite and organic matter was even found to stabilize the Fe mineral at higher temperatures (Toner et al., 2009a,b).

Both in the lab and in natural settings with marine and freshwater strains, polymers produced by bacteria are identified as acidic polysaccharides with carboxyl functional groups (Phoenix et al., 2002; Chan et al., 2009). These polysaccharide strands produced by bacteria in Fe-rich environments contain and template poorly crystalline Fe (oxyhydr)oxides (defined as ß-FeOOH, i.e. akaganeite, and ferrihydrite), providing a mechanism to keep mineral precipitation away from the cell (Chan et al., 2004). Indeed, the carboxyl functional groups are spatially correlated with the Fe(III) (oxyhydr)oxide distribution (Chan et al., 2009). The pH near the cell can be reduced by 1) oxidation of Fe(II) coupled to the reduction of oxygen, 2) the precipitation of ferric Fe as Fe(III) (oxyhydr)oxide or 3) the localization of ferrous Fe sorption onto Fe(III) (oxyhydr)oxide surfaces (Chan et al., 2004). Decreasing the pH outside the cell increases the proton motive force and prevents the Fe from precipitating onto the cell. Interestingly, the Fe(III) (oxyhydr)oxides forming along the fibrils are recrystallized and can result in oriented crystals with high aspect ratios. The impact of the polymers on the templated mineral was found to become more pronounced as the crystals aged (Chan et al., 2009). The crystal growth, mineral phase identity, and reactivity are greatly influenced by the polysaccharide fibrils, and filaments in siliceous rocks are often considered potential fossils of Fe(II)-oxidizing bacteria. However, only recently have observations of stalk growth in the modern marine Fe(II)-oxidizing strain *Mariprofundus ferrooxydans* using light, X-ray and electron microscopy granted a correlation between ancient and modern samples. Using time-lapse light microscopy, Chan et al. (2011) observed these *M. ferrooxydans* excreting stalks during growth. Furthermore, the Fe(III)-rich stalks consist of several fibrils where mineral growth occurs at a slower rate than in the areas surrounding the core so that larger crystals are found within and on the fibrils (Chan et al., 2011). Chan et al. (2011) suggest that structures with extracellular Fe bound to organic molecules can be useful biosignatures. The resilience of these structures in ancient rocks still needs to be determined.

5. Cell–mineral aggregates in the water column

Cell–mineral aggregates produced by Fe-metabolizing bacteria in the water column are likely key vehicles for organic matter and Fe flux

in Fe-rich, anoxic settings. For example, in Lake Matano, Indonesia, 90% of the allochthonous organic matter in the epilimnion has been found to be primarily oxidized via Fe(III) reduction between 100 and 200 m depth (Crowe et al., 2008b). By extrapolation, if Fe-metabolizing bacteria like anoxygenic Fe(II)-oxidizing phototrophs were key players in the deposition of BIF in the Precambrian, then precipitating cell–mineral aggregates were important points of reaction in these ancient basins. As they settled through the water column, they were certainly a source for bacterial turnover and nutrient scavenging. An estimation of their residence time can indicate interaction with ions, metals and other microorganisms before reaching the basin floor. Using Stokes' Law, the sedimentation rate of cell–mineral aggregates produced by anoxygenic Fe(II)-oxidizing phototrophs was shown to be influenced by its lighter cell organic matter component. The cell component of the biogenic minerals lowers the total particle density from ~4.0 g/cm^3 for ferrihydrite to ~2.4 g/cm^3 for cell–Fe(III) mineral aggregates (as a comparison water at 25 °C is 0.9970 g/cm^3) (Posth et al., 2010). As well as particle density, the properties of the aqueous environment can also influence the sedimentation rate; the higher fluid viscosity and density of seawater result in a slightly decreased sedimentation rate compared to a freshwater system. Using these parameters, a cell-ferric Fe mineral aggregate produced by anoxygenic phototrophs would theoretically reside for approximately 1–1.2 day(s) in a 100 m water column (Posth et al., 2010). The relative similarity of particle sedimentation rates for freshwater and saltwater was confirmed in studies of lake and marine snow, where the settling velocity of lake snow was reported to be fairly similar to marine snow (Grossart and Simon, 1993).

Work carried out at Lake Matano in recent years, however, also grants us insights into mineral formation processes in the water column (Crowe et al., 2008a,b; Zegeye et al., 2012). These authors demonstrated the presence of carbonated green rust, a mixed-valence Fe mineral, in the water column of Lake Matano (Zegeye et al., 2012). As discussed in Sections 3 and 4, green rust is likely one of the primary BIF minerals and has been identified in Fe-metabolizing cultures. The work of Crowe, Poulton and co-workers at Lake Matano demonstrates the importance of green-rust for our understanding of Fe mineralogy in ancient oceans and modern O_2-poor settings. It also opens up the exciting possibility for the study of this mineral in complex, natural settings. Due to its structure, mixed valence state and sorption capacity, it is expected that green rust in the water column would have a significantly different reactivity than poorly-crystalline ferrihydrite and would therefore impact microbial cycling and diagenesis. Green rust is a challenging mineral to work with and our understanding of its role in biogeochemical settings is still nascent.

5.1. Sorption to and co-precipitation by cell–mineral aggregates

Metals, ions and nutrients can sorb to Fe(III) (oxyhydr)oxides and be sequestered until being released through changes in the geochemical setting or microbial activity. Biogenic minerals have a cell component that consists of exopolysaccharides, organic metabolites, microbial exudates and cell detritus. They also differ from abiogenic minerals in terms of their lower crystallinity and overall smaller crystal size (Châtellier et al., 2001, 2004). Due to the average overall negative charge of bacterial surfaces (Beveridge, 1988; Beveridge and Graham, 1991) as opposed to the positive charge of the mineral surface, biogenic minerals can sorb cations and metals from solution (Tadanier et al., 2005). A lower sorption capacity of biogenic Fe(III) minerals may also result from the lower surface area and decreased number of sorption sites (biogenic = ~158 m^2 g/l (Kappler et al., 2005b), abiogenic granulated iron hydroxide(GEH®) = ~278 m^2 g/l (Kleinert et al., 2011)). Differences in mineralogy between biogenic and abiogenic minerals may also influence functional group density; for example, ferrihydrite has a higher number of functional groups (16.8 μmol sites per m^2) than goethite (5.73 μmol sites per m^2) (Dzombak and Morel, 1990), which provides oxyanions in solution with more binding sites on the mineral (Cornell and Schwertmann, 2003). The negatively-charged organic compounds present in biogenic minerals may also compete with anions in solution for sorption sites (Posth et al., 2010). The organic component can alter the surface charge of the biogenic mineral (point of zero charge, pzc ~ 4.4 (Hegler et al., 2010)), as compared to that of abiogenic minerals (pzc ~7–8 for ferrihydrite and goethite). The presence of the redox-active organic component of biogenic minerals may even stimulate microbial turnover and affect the release of sorbed oxyanions, like arsenate (O'Loughlin, 2008; O'Loughlin et al., 2008, 2010; Kleinert et al., 2011) or cause the formation of cell–mineral–anion colloids that increase transport of these components (Sharma et al., 2010).

The influence of biogenic minerals, however, is not restricted to sorption processes. Biogenic minerals produced during Fe(II) oxidation effectively remove arsenic (As(III) and As(V)) from solution via coprecipitation as well as through sorption (Fuller et al., 1993; Roberts et al., 2004; Zouboulis and Katsoyiannis, 2005; Hohmann et al., 2010). Yet, compared to sorption to abiogenic Fe(III) (oxyhydr)oxides, the maximum loading to biogenic minerals during co-precipitation is approx. 5 times lower (Kleinert et al., 2011). These differences in the capture of anions and metals by sorption to biogenic minerals as opposed to coprecipitation with these minerals are most likely based on the continuous exposure of the anions to surface sites as the minerals are formed. The anions and metals are able to sorb to small crystal surfaces and be embedded in the mineral via the processes of sorption, inclusion and occlusion before the larger aggregate is formed (Fuller et al., 1993; Kleinert et al., 2011).

6. Cell–mineral aggregates in the sediment (short-term diagenesis)

6.1. Microbial cycling of organic matter in modern sediments

Most organic carbon is recycled in the water column and in the unconsolidated sediment, which makes these cell–mineral aggregates highly reactive during precipitation, sedimentation and the early stages of sediment diagenesis. Below the surface of modern sediments, organic matter is mineralized via fermentation, denitrification, methanogenesis, Fe(III) and Mn(IV)-reducing bacteria, and sulfate-reducing bacteria. Indeed, in modern coastal waters more than 50% of all organic matter in the sediment is oxidized to CO_2 by anaerobic sulfate-reducing bacteria with the rest being oxidized by aerobic organisms (Jørgensen, 1977, 1982). The largest fraction of biomass in aqueous settings is degraded through the joint activity of a variety of microorganisms containing a variety of exoenzymes, which cut the large biomolecules like lipids, carbohydrates and proteins, into smaller molecules, like sugars and amino acids.

The oxidation of organic matter in marine sediments will produce solutes such as HCO_3^-, NH_4^+, HPO_4^{2-}, and depending on the oxidant being reduced can also release Mn^{2+}, Fe^{2+}, HS^- and CH_4 (Fig. 1). On a vertical scale, sediments classically display a sequence of oxidants from O_2, to NO_3^-, Mn(IV), Fe(III), SO_4^{2-} reduction and methanogenesis at depth (Aller et al., 1986). In areas with a fixed organic carbon input from primary production and high sediment reworking (i.e., wave action, bioturbation), reductants can become limited while oxidants are recharged resulting in sediments that remain suboxic rather than becoming anoxic (Aller et al., 1986).

In both freshwater and marine settings, the lability and preservation of sedimentary organic matter are influenced by its association with mineral surfaces. The stabilization of easily degradable organic components, such as amino acids and simple sugars, can be facilitated by sorption to these minerals (Keil et al., 1994). Furthermore, the efficiency of carbon burial in marine waters is correlated with exposure of organic particles to oxygen (Hartnett et al., 1998). A recent study surveying various marine depositional environments points to the association of Fe minerals and organic carbon, even normally labile organic phases, as the mechanism that binds 21.5 ± 8.6% of the organic carbon in

sediment and could be responsible for the preservation of 19–45 × 10^{15} g of organic carbon globally (Lalonde et al., 2012).

In Fe-rich environments, such as many freshwater sediments, or Archean ocean sediments with low S, the biotic or abiotic oxidation of dissolved Fe(II) leads to Fe(III) (oxyhydr)oxide production. These poorly crystalline Fe phases can remain stable for years when dried or stabilized by organic matter, but in aqueous suspension transform into hematite (via dehydration), goethite, and lepidocrocite (through Fe(II) catalyzed transformation), depending on pH and solution chemistry (Cornell and Schwertmann, 2003; Toner et al., 2009a,b). A recent study on the Loihi Seamount has shown, however, that a poorly crystalline silica coating on low-range ordered (natural) ferrihydrite can stabilize the Fe(III) (oxyhydr)oxide over time against oxidation and diagenetic alteration (Toner et al., 2012, see also Section 4.5). Dependent upon the solution chemistry and presence of nucleation sites, biogenic Fe(III) minerals (poorly crystalline ferric (oxyhydr)oxides) precipitated by bacteria such as the anoxygenic phototroph *R. ferrooxidans* strain SW2 also convert to the more crystalline goethite and lepidocrocite after approximately one month (Kappler and Newman, 2004). This transition is potentially stimulated by the presence of small amounts of remaining Fe(II) in solution or by slow, microbially catalyzed Fe(III) reduction (Hansel et al., 2003; Kappler and Newman, 2004). These biotic and abiotic Fe(III) mineral phases are important electron acceptors for not only abiotic, but also biotic processes. Abiogenic and particularly biogenic Fe(III) hydroxides in anoxic settings can be readily reduced by Fe(III)-reducing bacteria (Straub et al., 1998; Langley et al., 2009). This has been demonstrated in Fe-rich and Fe-poor marine environments (Canfield, 1989). In Fe-rich settings, in which HS^- has largely been utilized or precipitated as Fe-sulfide, Fe(III) reduction driven by sediment turnover can form mineral phases like siderite (Fe(II)-carbonate), vivianite (Fe(II)-phosphate) and chamosite (phyllosilicate) (Aller et al., 1986).

In conceptual models of processes in BIF depositional basins, the deposition of biomass is linked to microbial Fe(III) reduction in the sediment. This will lead to the formation not only of dissolved Fe(II) and Fe(II) mineral phases, but also to new biomass of Fe(III)-reducers (Konhauser et al., 2005). This biomass production is heightened by the proliferation of anaerobic respiring and fermenting bacteria. Recent work on marine sediments suggests that such biomass may remain labile for longer periods of time than first believed (~100,000 years) (Lomstein et al., 2012), particularly in Fe-rich settings (Lalonde et al., 2012). It is therefore important to consider, that biomass/necromass which arrives to or is produced at the sediment, may remain available to turnover and only slowly decrease with time.

6.2. Microbial cycling of organic matter in ancient sediments

The turnover of both organic matter and Fe(III) minerals studied in the few anoxic, Fe-rich environments on Earth today helps draw conclusions about processes in ancient BIF sedimentary basins. A clue to the dominant processes in these ancient settings is the average oxidation state of iron, $Fe^{2.4+}$, in Precambrian BIF. This may be explained by the simultaneous settling of Fe(III) and Fe(II). However, the partial microbial reduction of Fe(III) to Fe(II) may also explain this mixed oxidation state.

The C-isotope record is studied in order to gain insight to the cycling of organic matter in the past. One major challenge in interpreting the ancient C-isotope record, however, is in understanding diagenetic or light metamorphic processes that may occur to the primary mineral. Light carbon isotope compositions measured in carbonaceous inclusions of apatite grains taken from the 3.8 billion year old Isua supracrustal belt have been interpreted as indicative of early life (Mojzsis et al., 1996). Yet, the validity of such an interpretation has been questioned due to the uncertainty in constraining the primary nature of the minerals in such a setting (i.e., Van Zuilen et al., 2002; Lepland et al., 2005) and demonstrates the difficulty of distinguishing abiotic from biotic processes in the early Archean record.

Determination of the C-isotope signature in siderite-rich transects ($\delta^{13}C$ ~ −10‰, Steinhoefel et al., 2010) gives values in the range $\delta^{13}C = -14$ to −3‰ previously determined in samples from the Transvaal (Beukes and Klein, 1990; Beukes et al., 1990; Kaufman, 1996; Fischer et al., 2009) and suggests a mixed inorganic and dissolved organic carbon source (Steinhoefel et al., 2010). Furthermore, while carbonates with significant negative $\delta^{13}C$ values have been interpreted as the result of diagenetic organic matter degradation accompanied by Fe(III) reduction, the heterogeneities in transects of BIF can also be explained by diagenesis linked to abiotic and biotic processes (Johnson et al., 2003; Steinhoefel et al., 2010; Planavsky et al., 2012).

In the sediment, the organic carbon associated with bacterial remnants (either of Fe(II)-oxidizing planktonic bacteria or alternative metabolisms) would offer a reductant for the short-term diagenetic transformation of deposited Fe(III) and could produce siderite ($FeCO_3$) and magnetite (Fe_3O_4). The presence and structure of magnetite in these sediments suggest a secondary origin. For example, magnetite is present as disseminated grains within but disrupting sedimentary laminae, in laminated beds that truncate sedimentary layering, as layer-discordant veins, and as cleavage fill (Ewers and Morris, 1981; Krapež et al., 2003). The antiquity of such an anaerobic Fe(III) respiratory pathway is supported by 1) the capacity of extant hyperthermophilic bacteria and archaea that branch deeply in the universal phylogenetic tree to reduce Fe(III) (Vargas et al., 1998), 2) the highly negative $\delta^{56}Fe$ values found in magnetite-rich BIF samples as old as 2.9 Ga (Johnson et al., 2003; Yamaguchi et al., 2005) and 3) the comparable negative iron isotope fractionations observed in experimental culture with dissimilatory Fe(III)-reducing bacteria (O'Loughlin et al., 2010). Yet, the efficacy of a microbial role in BIF deposition and diagenesis is tested by the low content of organic carbon in ancient BIF (<0.5%, Gole and Klein, 1981). Coupling the oxidation of organic matter to the reduction of Fe(III) minerals in these sediments would explain the abundance of light carbon isotopic signatures associated with the interlayered carbonate minerals (Perry et al., 1973; Walker, 1984; Baur et al., 1985). It may also explain the low content of organic carbon.

In oxic to sub-oxic settings, the turnover of organic matter produced by aerobic microbial Fe(II) oxidation would diminish the deposition of detritus and biomass. Abiotic Fe(II) oxidation via cyanobacterial oxygen without the precipitation of the cyanobacterial biomass could lead to an excess of Fe(III) relative to organic carbon in settling biogenic particles and a shift in Fe:C ratio in the deposits (Konhauser et al., 2005). In the anoxic setting of the BIF basin, any fermentation products in the shallow sediments would have been oxidized by some anaerobic respiratory process (Rothman et al., 2003). To date the evidence still suggests that nitrate, sulfate and Mn(IV) were unavailable or available only in very low concentrations as major precipitate components in the depositional basin. At ~2.75 Ga, minimal nitrate and sulfate (~200 μM, Habicht et al., 2002) would be available due to trace O_2 concentrations and perhaps be limited to restricted sulfate-rich environments (Ewers and Morris, 1981; O'Loughlin et al., 2010; Canfield et al., 2000; Habicht et al., 2002; Strauss, 2003). Around 2.3 Ga, the sedimentary sulfide record shows the presence of >1 mM sulfate (Canfield, 1998; Canfield et al., 2000). The presence of MnO_2 was likely insignificant as the concentration of Mn(II) released in hydrothermal effluent is up to 5 times lower than that of Fe(II) (Campbell et al., 1988) and there are presently no known anoxygenic phototrophic Mn(II)-oxidizing bacteria that would support the potential importance of this pathway. However, it is known that ferric (oxyhydr)oxides in a BIF depositional basin, as well as the partially reduced phases found in BIF such as magnetite could have supported a microbial process coupling the oxidation of organic carbon to the reduction of ferric Fe (Nealson and Myers, 1990; Johnson et al., 2008a,b; Wu et al., 2009). Indeed, it has been estimated that 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 (Konhauser et al., 2005).

Yet, BIF deposition by anoxygenic phototrophs could also lead to a reduced amount of carbon in the sediment due to the composition of the aggregates they produce. Characterization of the biogenic minerals produced by model anoxygenic Fe(II)-oxidizing phototrophs shows that the precipitated cell–mineral aggregates have a stoichiometric excess of Fe(III) to carbon; some cells were not associated with Fe(III) minerals and remained in solution (Posth et al., 2010). In order to better estimate in which form, if any, biogenic Fe(III) minerals remain resilient in the rock record, the diagenetic processes in the water column and in the sediment can be investigated. In particular, the diagenesis of biogenic minerals may grant some new information as to how these minerals may transform over geological time.

7. Testing diagenesis over geological time — linking the present to the past

The organic carbon present in the sediment as a result of microbial activity helps drive mineral transformations under temperature and pressure conditions over geological time and may be preserved in some way. Current research in early Earth biogeochemistry and astrobiology aims to understand the forms in which cell organic matter is preserved over geological time. Understanding how these biosignatures are formed and how they can be interpreted could grant insight into the evolution of microorganisms on Earth. Knowing what to look for in extraterrestrial samples will help us better understand the conditions necessary for life and how it has perhaps proliferated on other planets. The search for life on Mars by "following the water" or "following the energy" is carried out using remote and rover-assisted geochemical methods (e.g., Squyres et al., 2009). On Earth, this search for the origin and evolution of life from a biogeochemical standpoint is largely carried out by fossil, isotope and biomarker studies in the laboratory, not only using field samples (see Section 2), but also using molecular biological approaches to reach back into the phylogeny of microbial life. The advantage of studying field samples on model environments resembling early Earth (e.g., Lake Matano, Lake Cadagno) or Mars analogs (e.g. Rio Tinto) is that they offer the possibility to study biogeochemical processes easily and in situ (Fernandez-Remolar et al., 2005; Crowe et al., 2008a; Canfield et al., 2010; Gomez et al., 2011). The key to interpretation of early Earth, or indeed Mars analog environments, however, is finding a means to bridge between what is seen today and the original environment. During the course of time, sedimentary structures undergo diagenetic changes due to the influence of temperature and pressure. It is extremely challenging to determine what assortment of transformation processes took place. Our knowledge of mineral transformation processes and particularly the influence of biology on these changes are still lacking. As a result, our view of the primary mineral and of the original precipitating environment is obscure (Han, 1966; Dimroth and Chauvel, 1973; Perry et al., 1973; Han, 1978; Walker, 1984; Klein, 2005). Yet, ancient sedimentary structures offer us one of the best archives of early Earth conditions and early life. Determining which primary materials were first deposited to make up the ancient sedimentary structures we study today is therefore one of the largest challenges of ancient Earth research as it would allow us to read the archive sedimentary structures offer us. Of utmost importance in these studies is parsing which end-products are truly biotic in origin and which can also result from abiotic processes. To this end, an integration of approaches, such as that of a recent study combining microscopic, mineralogical and biomolecular analytics (Preston et al., 2011) provides a promising future approach.

Understanding the transformation of both biotic and abiotic Fe(III) (oxyhydr)oxides is a key to linking the present with the past. Over long time periods, temperature and pressure influence sedimentary mineral assemblages. Ferrihydrite is known to dehydrate to hematite when exposed to heat or mechanical stress following [Eq. (10)]

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O \quad (10)$$

(Cornell and Schwertmann, 2003).

In the presence of organic carbon, as would be the case for cell–mineral aggregates formed by anoxygenic phototrophs or other Fe(II)-oxidizing bacteria (e.g. microaerophiles), ferric hydroxide ($Fe(OH)_3$) can be (partially) reduced and theoretically yield siderite ($FeCO_3$), magnetite (Fe_3O_4) and elemental C. Potentially water (H_2O), methane (CH_4) and possibly hydrogen (H_2) are released via a series of dehydration and coupled redox reactions. Biomass is oxidized and Fe(III) reduced with electrons stemming from the biomass (represented by CH_2O; see generalized, non-balanced Eq. (11)):

$$Fe(OH)_3 \text{ or } Fe_2O_3 + CH_2O \rightarrow Fe^{III}{}_2O_3, Fe^{II}CO_3, Fe^{II}Fe^{III}{}_2O_4, CH_4, C, H_2, H_2O. \quad (11)$$

It is the formation of magnetite, however, that is particularly interesting in terms of BIF deposition. BIF samples from the 2.48 Ga Dales Gorge Member of the Brockman Iron Formation, Western Australia (Pickard, 2002; Pecoits et al., 2009) may contain new signatures of microbial activity; 1) magnetite crystals that are analogous to modern biogenic magnetite in crystallochemistry, 2) (Ca, Sr) apatite nanoparticles intergrown with magnetite, and 3) the presence of Fe(III) acetate salt in both BIF and in association with magnetite formed in Fe(III)-reducing bacteria cultures (Li et al., 2011).

The biological role in magnetite formation in deposits exposed to long periods of temperature and pressure diagenesis is not simple to constrain. Golden et al. (2001) elegantly demonstrated how the diagenetic alternation of Fe(III) minerals can form the zonation of Mg–Fe–Ca carbonates, magnetite, and Fe sulfides in the Martian meteorite ALH84001 via simple, inorganic processes. This group went on to show that thermally decomposed magnetite also has a unique, and inorganic, crystal habit. Again with the Martian meteorite in mind, McCollom and Seewald (2003) thermally treated siderite in the presence of water vapor to form magnetite and found the abiotic synthesis of organic compounds such as alkylated and hydroxylated aromatic compounds. In order to avoid the over-interpretation of magnetite presence in BIF samples, experiments reacting ferrihydrite with organic matter under controlled conditions may help constrain which mineral transformations are feasible (Posth et al., 2013b).

The formation of magnetite from ferrihydrite and organic matter has been suggested to occur through three main pathways which have received experimental support (Frost et al., 2007; Pecoits et al., 2009); 1) organic carbon could partially reduce ferrihydrite or hematite, 2) the oxidation of dissolved Fe(II) or Fe(II) minerals, like siderite, could also drive magnetite production and possibly produce methane in the process (French, 1971) and 3) a ferrous iron source like siderite reacting with hematite could also yield magnetite (French, 1971; Miyano, 1987).

$$12Fe(OH)_3 + CH_2O \rightarrow 4Fe_3O_4 + CO_2 + 19H_2O \quad (12)$$

$$6Fe_2O_3 + CH_2O \rightarrow 4Fe_3O_4 + CO_2 + H_2O \quad (13)$$

$$12FeCO_3 + 2H_2O \rightarrow 4Fe_3O_4 + 11CO_2 + CH_4 \quad \text{(or)} \quad (14)$$

$$FeCO_3 + Fe_2O_3 \rightarrow Fe_3O_4 + CO_2 \quad (15)$$

The Fe^{2+} from hydrothermal sources or stemming from microbial Fe(III) reduction has also been proposed as the driver for a non-redox

reaction between Fe(III) minerals and Fe^{2+} which produces magnetite (Ohmoto, 2003).

$$2Fe(OH)_3 + Fe^{2+} \rightarrow Fe_3O_4 + 2H_2O + 2H^+ \quad (16)$$

$$Fe_2O_3 + Fe^{2+} + H_2O \rightarrow Fe_3O_4 + 2H^+ \quad (17)$$

Recently, it was experimentally shown that ferrihydrite or a mixture of ferrihydrite and various amounts of glucose incubated at elevated temperatures and pressure both in the presence or absence of Si could yield minerals found in BIFs (Posth et al., 2013b; Köhler et al., 2013. Chemically-synthesized ferrihydrite ($Fe^{III}(OH)_3$) alone was transformed to hematite via dehydration, but mixtures of ferrihydrite (Fe(III) minerals) and glucose (proxy for biomass) treated under the same temperature and pressure conditions) yielded not just hematite ($Fe^{III}{}_2O_3$), but magnetite ($Fe^{II}Fe^{III}{}_2O_4$), and siderite ($Fe^{II}CO_3$) (Köhler et al., 2013; Posth et al., 2013b) that look very similar to magnetite and siderite structures that are present in BIFs (Köhler et al., 2013; Li et al., 2013). This demonstrates what could be a key difference in Fe mineral transformation between abiotic and biotic systems and suggests that the presence of biomass in the BIF depositional basin sediment was important for these transformations (e.g. Walker, 1984; Johnson et al., 2003; Konhauser et al., 2005; Johnson et al., 2008a,b). Interestingly, the amount of biomass present plays a key role in the product of mineral transformation; the presence of a cell biomass proxy in low amounts resulted in the production of hematite and small amounts of magnetite and siderite. When the amount of initial biomass proxy was increased, magnetite and siderite were formed in high amounts and hematite was not detectable (Posth et al., 2013b).

8. Conclusions

We have summarized here our current knowledge of biogenic Fe(III) (oxyhydr)oxide minerals produced by Fe(II)-oxidizing phototrophic bacteria as compared to microaerophilic Fe(II)-oxidizing, nitrate-reducing Fe(II)-oxidizing and abiotic Fe(II) oxidation processes from production to precipitation and finally to sedimentation, burial and preservation. These processes are relevant for the reconstruction of early biogeochemical systems on Earth, such as Precambrian BIF, as well as for the search for life on Fe-rich planets, like Mars. Nevertheless, much is still unclear about biogenic minerals and specifically their fate in aqueous systems.

The complexity of biogeochemical systems makes tracking and identifying the relevant biological processes in ancient rock particularly challenging. The cycling of minerals and organic matter by microorganisms involves a myriad of reactions and imprints on the biogeochemical record. The main approaches to reconstructing ancient life are either to search for signatures in rocks, like isotope fingerprints, biomarkers or fossils, or to reconstruct ancient processes based on modern analogs. At the very heart of the issue is the question as to how microbial organic matter can be preserved. As biomineralization also offers a means of either preserving organic compounds or creating “templates” of an organic component, one way to link information that can be extracted from isotope, trace metal, biomarker and fossil studies with observations made in analog systems is to understand the processes of short-term (microbial) and long term (temperature and pressure) diagenesis. A proper interpretation of life in the ancient rock record is in many ways hindered by limited knowledge of the processes and influences on biogenic minerals from the point of formation until incorporation in the rock. Studies on microbial turnover of biogenic Fe(III) minerals, the influence of temperature and pressure on these minerals, carbon and Fe isotope fractionation, the resilience of molecular biomarkers and the preservation of fossils may help estimate the extent of the biological footprint for astrobiology and early Earth studies.

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References

Aller, R.C., Mackin, J.E., Cox Jr., R.T., 1986. Diagenesis of Fe and S in Amazon inner shelf muds: apparent dominance of Fe reduction and implications for the genesis of ironstones. Cont. Shelf Res. 6, 263–289.
Anbar, A.D., Rouxel, O., 2007. Metal stable isotopes in paleoceanography. Annu. Rev. Earth Planet. Sci. 35, 717–746.
Anbar, A.D., Roe, J.E., Barling, J., Nealson, K.H., 2000. Nonbiological fractionation of iron isotopes. Science 288, 126–128.
Anbar, A.D., Duan, Y., Lyons, T.W., Arnold, G.L., Kendall, B., Creaser, R.A., Kaufman, A.J., Gordon, G.W., Scott, C., Garvin, J., Buick, R., 2007. A whiff of oxygen before the great oxidation event? Science 317, 1903–1906.
Arnold, G.L., Anbar, A.D., Barling, J., Lyons, T.W., 2004. Molybdenum isotope evidence for widespread anoxia in mid-Proterozoic oceans. Science 304, 87–90.
Balci, N., Bullen, T.D., Witte-Lien, K., Shanks, W.C., Motelica, M., Mandernack, K.W., 2006. Iron isotope fractionation during microbially stimulated Fe(II) oxidation and Fe(III) precipitation. Geochim. Cosmochim. Acta 70, 622–639.
Banfield, J.F., Moreau, J.W., Chan, C.S., Welch, S.A., Little, B., 2001. Mineralogical biosignatures and the search for life on Mars. Astrobiology 1, 447–465.
Bau, M., Möller, P., 1993. Rare Earth element systematics of the chemically precipitated component in Early Precambrian iron-formations and the evolution of the terrestrial atmosphere–hydrosphere–lithosphere system. Geochim. Cosmochim. Acta 57, 2239–2249.
Baur, M.E., Hayes, J.M., Studley, S.A., Walter, M.R., 1985. Millimeter-scale variations of stable isotope abundances in carbonates from banded iron-formations in the Hamersley Group of Western Australia. Econ. Geol. 80, 270–282.
Beard, B.L., Johnson, C.M., Cox, L., Sun, H., Nealson, K.H., Aguilar, C., 1999. Iron isotope biosignatures. Science 285, 1889–1892.
Beard, B.L., Johnson, C.M., Skulan, J.L., Nealson, K.H., Cox, L., Sun, H., 2003. Application of Fe isotopes to tracing the geochemical and biological cycling of Fe. Chem. Geol. 195, 87–117.
Bekker, A., Holland, H.D., Wang, P.-L., Rumble III, D., Stein, H.J., Hannah, J.L., Coetzee, L.L., Beukes, N.J., 2004. Dating the rise of atmospheric oxygen. Nature 427, 117–120.
Bekker, A., Slack, J.F., Planavsky, N., Krapez, B., Hofmann, A., Konhauser, K.O., Rouxel, O.J., 2010. Iron formation: the sedimentary product of a complex interplay among mantle, tectonic, oceanic, and biospheric processes. Econ. Geol. 105, 467–508.
Benz, M., Brune, A., Schink, B., 1998. Anaerobic and aerobic oxidation of ferrous iron at neutral pH by chemoheterotrophic nitrate-reducing bacteria. Arch. Microbiol. 169, 159–165.
Beukes, N.J., 1973. Precambrian iron-formations of southern Africa. Econ. Geol. 68, 960–1004.
Beukes, N.J., Klein, C., 1990. Geochemistry and sedimentology of a facies transition – from microbanded to granular iron-formation – in the early Proterozoic Transvaal Supergroup, South Africa. Precambrian Res. 47, 99–139.
Beukes, N.J., Klein, C., Kaufman, A.J., Hayes, J.M., 1990. Carbonate petrography, kerogen distribution, and carbon and oxygen isotope variations in an Early Proterozoic transition from limestone to iron-formation deposition, Transvaal Supergroup, South Africa. Econ. Geol. 85, 663–690.
Beveridge, T.J., 1988. The bacterial surface — general considerations towards design and function. Can. J. Microbiol. 34, 363–372.
Beveridge, T.J., Graham, L.L., 1991. Surface layers of bacteria. Microbiol. Rev. 55, 684–705.
Blakemore, R., 1975. Magnetotactic bacteria. Science 190, 377–379.
Bosch, J., Lee, K.-Y., Jordan, G., Kim, K.W., Meckenstock, R.U., 2011. Anaerobic, nitrate-dependent oxidation of pyrite nanoparticles by *Thiobacillus denitrificans*. Environ. Sci. Technol. 46, 2095–2101.
Brasier, M.D., Green, O.R., Jephcoat, A.P., Kleppe, A.K., van Kranendonk, M.J., Lindsay, J.F., Steele, A., Grassineau, N.V., 2002. Questioning the evidence for Earth's oldest fossils. Nature 416, 76–81.
Brasier, M.D., Green, P.R., Lindsay, J.F., McLoughlin, N., Steele, A., Stoakes, C., 2005. Critical testing of Earth's oldest putative fossil assemblage from the ~3.5 Ga Apex chert, Chinaman Creek, Western Australia. Precambrian Res. 140, 55–105.
Braterman, P.S., Cairns-Smith, A.G., Sloper, R.W., 1983. Photo-oxidation of hydrated Fe^{2+} — significance for banded iron formations. Nature 303, 163–164.
Brocks, J.J., Banfield, J., 2009. Unravelling ancient microbial history with community proteogenomics and lipid geochemistry. Nat. Rev. Microbiol. 7, 601–609.
Brocks, J.J., Logan, G.A., Buick, R., Summons, R.E., 1999. Archean molecular fossils and the early rise of eukaryotes. Science 285, 1033–1036.

Brocks, J.J., Love, G.D., Summons, R.E., Knoll, A.H., Logan, G.A., Bowden, S.A., 2005. Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea. Nature 437, 866–870.
Bullen, T.D., White, A.F., Childs, C.W., Vivit, D.V., Schulz, M.S., 2001. Demonstration of significant abiotic iron isotope fractionation in nature. Geology 29, 699–702.
Cairns-Smith, A.G., 1978. Precambrian solution photochemistry, inverse segregation, and banded iron formations. Nature 276, 807–808.
Campbell, A.C., Palmer, M.R., Klinkhammer, G.P., Bowers, T.S., Edmond, J.M., Lawrence, J.R., Casey, J.F., Thompson, G., Humphris, S., Rona, P., Karson, J.A., 1988. Chemistry of hot springs on the mid-Atlantic Ridge. Nature 335, 514–519.
Canfield, D.E., 1989. Reactive iron in marine sediments. Geochim. Cosmochim. Acta 53, 619–632.
Canfield, D.E., 1998. A new model for Proterozoic ocean chemistry. Nature 396, 450–453.
Canfield, D.E., Thamdrup, B., Hansen, J.W., 1993. The anaerobic degradation of organic matter in Danish coastal sediments: iron reduction, manganese reduction, and sulfate reduction. Geochim. Cosmochim. Acta 57, 3867–3883.
Canfield, D.E., Habicht, K.S., Thamdrup, B., 2000. The Archean sulfur cycle and the early history of atmospheric oxygen. Science 288, 658–661.
Canfield, D.E., Rosing, M.T., Bjerrum, C., 2006. Early anaerobic metabolisms. Phil. Trans. Roy. Soc. B 361, 1819–1836.
Canfield, D.E., Poulton, S.W., Narbonne, G.M., 2007. Late-Neoproterozoic deep-ocean oxygenation and the rise of animal life. Science 315, 92–95.
Canfield, D.E., Poulton, S.W., Knoll, A.H., Narbonne, G.M., Ross, G., Goldberg, T., Strauss, H., 2008. Ferruginous conditions dominated later Neoproterozoic deep-water chemistry. Science 321, 949–952.
Canfield, D.E., Farquhar, J., Zerkle, A.L., 2010. High isotope fractionations during sulfate reduction in a low-sulfate euxinic ocean analog. Geology 38, 415–418.
Carlson, H.K., Clark, I.C., Melnyk, R.A., Coates, J.D., 2012. Towards a mechanistic understanding of anaerobic nitrate-dependent iron oxidation: balancing electron uptake and detoxification. Front. Microbiol. 3, 57. http://dx.doi.org/10.3389/fmicb.2012.00057.
Chakraborty, A., Picardal, F., 2013. Induction of nitrate-dependent Fe(II) oxidation by Fe(II) in *Dechloromonas* sp. strain UWNR4 and *Acidovorax* sp. strain 2AN. Appl. Environ. Microbiol. 79, 748–752.
Chan, C.S., Stasio, G.D., Welch, S.A., Girasole, M., Frazer, B.H., Nesterova, M.V., Fakra, S., Banfield, J.F., 2004. Microbial polysaccharides template assembly of nanocrystal fibers. Science 303, 1656–1658.
Chan, C.S., Fakra, S.C., Edwards, D.C., Emerson, D., Banfield, J.F., 2009. Iron oxyhydroxide mineralization on microbial extracellular polysaccharides. Geochim. Cosmochim. Acta 73, 3807–3818.
Chan, C.S., Fakra, S.C., Emerson, D., Fleming, E.J., Edwards, K.J., 2011. Lithotrophic iron-oxidizing bacteria produce organic stalks to control mineral growth: implications for biosignature formation. ISME J. 5, 717–727.
Châtellier, X., Fortin, D., West, M., Leppard, G., Ferris, F., 2001. Effect of the presence of bacterial surfaces during the synthesis of Fe oxides by oxidation of ferrous ions. Eur. J. Mineral. 13, 705.
Châtellier, X., West, M., Rose, J., Fortin, D., Leppard, G., Ferris, F., 2004. Characterization of iron-oxides formed by oxidation of ferrous ions in the presence of various bacterial species and inorganic ligands. Geomicrobiol J. 21, 99–112.
Cismasu, A.C., Michel, F.M., Stebbins, J.F., Levard, C., Brown, G.E., 2012. Properties of impurity-bearing ferrihydrite I. Effects of Al content and precipitation rate on the structure of 2-line ferrihydrite. Geochim. Cosmochim. Acta 92, 275–291.
Cloud, P.E., 1965. Significance of the Gunflint (Precambrian) microflora. Science 148, 27–35.
Cloud, P., 1968. Atmospheric and hydrospheric evolution on the primitive Earth. Science 160, 729–736.
Cloud, P., 1972. A working model of the primitive Earth. Am. J. Sci. 272, 537–548.
Coleman, M.L., Hedrick, D.B., Lovley, D.R., White, D.C., Pye, K., 1993. Reduction of Fe(III) in sediments by sulfate-reducing bacteria. Nature 361, 436–438.
Cornell, R., Schwertmann, U., 2003. The Iron Oxides: Structures, Properties, Reactions, Occurrences and Uses, 2nd ed. Wiley-VCH, Weinheim.
Cosmidis, J., Benzerara, K., Morin, G., Busigny, V., Lebeau, O., Jézéquel, D., Noël, V., Dublet, G., Othmane, G., 2014. Biomineralization of iron-phosphates in the water column of Lake Pavin (Massif Central, France). Geochim. Cosmochim. Acta 126, 78–96.
Croal, L.R., Johnson, C.M., Beard, B.L., Newman, D.K., 2004. Iron isotope fractionation by Fe(II)-oxidizing photoautotrophic bacteria. Geochim. Cosmochim. Acta 68, 1227–1242.
Croal, L.R., Jiao, Y., Newman, D.K., 2007. The *fox* Operon from *Rhodobacter* strain SW2 promotes phototrophic Fe(II) oxidation in *Rhodobacter capsulatus* SB1003. J. Bacteriol. 189, 1774–1782.
Crowe, S.A., Jones, C.A., Katsev, S., Magen, C., O'Neill, A.H., Sturm, A., Canfield, D.E., Haffner, G.D., Mucci, A., Sundby, B., Fowle, D.A., 2008a. Photoferrotrophs thrive in an Archean ocean analogue. Proc. Natl. Acad. Sci. U. S. A. 105, 15938–15943.
Crowe, S.A., O'Neill, A.H., Katsev, S., Hehanussa, P., Haffner, G.D., Sundby, B., Mucci, A., Fowle, D.A., 2008b. The biogeochemistry of tropical lakes: a case study from Lake Matano, Indonesia. Limnol. Oceanogr. 53, 319–331.
Crowe, S.A., Dossing, L.N., Beukes, N.J., Bau, M., Kruger, S.J., Frei, R., Canfield, D.E., 2013. Atmospheric oxygenation three billion years ago. Nature 501, 535–538.
Czaja, A.D., Johnson, C.M., Beard, B.L., Eigenbrode, J.L., Freeman, K.H., Yamaguchi, K.E., 2010. Iron and carbon isotope evidence for ecosystem and environmental diversity in the ~2.7 to 2.5 Ga Hamersley Province, Western Australia. Earth Planet. Sci. Lett. 292, 170–180.
Czaja, A.D., Johnson, C.M., Beard, B.L., Roden, E.E., Li, W., Moorbath, S., 2013. Biological Fe oxidation controlled deposition of banded iron formation in the *ca.* 3770 Ma Isua Supracrustal Belt (West Greenland). Earth Planet. Sci. Lett. 363, 192–203.
Dahl, T.W., Anbar, A.D., Gordon, G.W., Rosing, M.T., Frei, R., Canfield, D.E., 2010. The behavior of molybdenum and its isotopes across the chemocline and in the sediments of sulfidic Lake Cadagno, Switzerland. Geochim. Cosmochim. Acta 74, 144–163.
Dahl, T.W., Chappaz, A., Fitts, J.P., Lyons, T.W., 2013. Molybdenum reduction in a sulfidic lake: evidence from X-ray absorption fine-structure spectroscopy and implications for the Mo paleoproxy. Geochim. Cosmochim. Acta 103, 213–231.
Dauphas, N., Rouxel, O., 2006. Mass spectrometry and natural variations of iron isotopes. Mass Spectrom. Rev. 25, 515–550.
Dimroth, E., Chauvel, J.J., 1973. Petrography of the Sokoman Iron Formation in part of the central Labrador Trough, Quebec, Canada. Geol. Soc. Am. Bull. 84, 111–134.
Dippon, U., Pantke, C., Porsch, K., Larese-Casanova, P., Kappler, A., 2012. Potential function of added minerals as nucleation sites and effect of humic substances on mineral formation by the nitrate-reducing Fe(II)-oxidizing strain *Acidovorax* sp. BoFeN1. Environ. Sci. Technol. 46, 6556–6565.
Druschel, G.K., Emerson, D., Sutka, R., Suchecki, P., Luther III, G.W., 2008. Low-oxygen and chemical kinetic constraints on the geochemical niche of neutrophilic iron(II) oxidizing microorganisms. Geochim. Cosmochim. Acta 72, 3358–3370.
Dzombak, D.A., Morel, F.M.M., 1990. Surface Complexation Modeling: Hydrous Ferric Oxide. Wiley, New York.
Ehrenreich, A., Widdel, F., 1994. Anaerobic oxidation of ferrous iron by purple bacteria, a new type of phototrophic metabolism. Appl. Environ. Microbiol. 60, 4517–4526.
Ehrlich, H.L., 1998. Geomicrobiology: its significance for geology. Earth-Sci. Rev. 45, 45–60.
Eickhoff, M., Birgel, D., Talbot, H.M., Peckmann, J., Kappler, A., 2013. Oxidation of Fe(II) leads to increased C-2 methylation of pentacyclic triterpenoids in the anoxygenic phototrophic bacterium *Rhodopseudomonas palustris* strain TIE-1. Geobiology 11, 268–278.
Emerson, D., Moyer, C.L., 2002. Neutrophilic Fe-oxidizing bacteria are abundant at the Loihi Seamount hydrothermal vents and play a major role in Fe oxide deposition. Appl. Environ. Microbiol. 68, 3085–3093.
Emerson, D., Revsbech, N.P., 1994a. Investigation of an iron-oxidizing microbial mat community located near Aarhus, Denmark: laboratory studies. Appl. Environ. Microbiol. 60, 4032–4038.
Emerson, D., Revsbech, N.P., 1994b. Investigation of an iron-oxidizing microbial mat community located near Aarhus, Denmark: field studies. Appl. Environ. Microbiol. 60, 4022–4031.
Emerson, D., Weiss, J.V., 2004. Bacterial iron oxidation in circumneutral freshwater habitats: findings from the field and the laboratory. Geomicrobiol J. 21, 405–414.
Ewers, W.E., Morris, R.C., 1981. Studies of the Dales Gorge Member of the Brockman Iron Formation, Western Australia. Econ. Geol. 76, 1929–1953.
Farquhar, J., Bao, H.M., Thiemens, M., 2000. Atmospheric influence of Earth's earliest sulfur cycle. Science 289, 756–758.
Farquhar, J., Zerkle, A.L., Bekker, A., 2011. Geological constraints on the origin of oxygenic photosynthesis. Photosynth. Res. 107, 11–36.
Fernandez-Remolar, D.C., Morris, R.V., Gruener, J.E., Amils, R., Knoll, A.H., 2005. The Rio Tinto Basin, Spain: mineralogy, sedimentary geobiology, and implications for interpretation of outcrop rocks at Meridiani Planum, Mars. Earth Planet. Sci. Lett. 240, 149–167.
Ferris, F.G., 2005. Biogeochemical properties of bacteriogenic iron oxides. Geomicrobiol J. 22, 79–85.
Fischer, W.W., Summons, R.E., Pearson, A., 2005. Targeted genomic detection of biosynthetic pathways: anaerobic production of hopanoid biomarkers by a common sedimentary microbe. Geobiology 3, 33–40.
Fischer, W.W., Schroeder, S., Lacassie, J.P., Beukes, N.J., Goldberg, T., Strauss, H., Horstmann, U.E., Schrag, D.P., Knoll, A.H., 2009. Isotopic constraints on the late Archean carbon cycle from the Transvaal Supergroup along the western margin of the Kaapvaal Craton, South Africa. Precambrian Res. 169, 15–27.
Fortin, D., Ferris, F.G., 1998. Precipitation of iron, silica, and sulfate on bacterial cell surfaces. Geomicrobiol J. 15, 309–324.
French, B.M., 1971. Stability relations of siderite ($FeCO_3$) in system Fe–C–O. Am. J. Sci. 271, 37–78.
Frost, C.D., von Blanckenburg, F., Schoenberg, R., Frost, B.R., Swapp, S.M., 2007. Preservation of Fe isotope heterogeneities during diagenesis and metamorphism of banded iron formation. Contrib. Mineral. Petrol. 153, 211–235.
Fuller, C.C., Davis, J.A., Waychunas, G.A., 1993. Surface chemistry of ferrihydrite: part 2. Kinetics of arsenate adsorption and coprecipitation. Geochim. Cosmochim. Acta 57, 2271–2282.
Garrels, R.M., 1987. A model for the deposition of the microbanded Precambrian iron formations. Am. J. Sci. 287, 81–105.
Garrels, R.M., Perry Jr., E.A., MacKenzie, F.T., 1973. Genesis of Precambrian iron formations and the development of atmospheric oxygen. Econ. Geol. 68, 1173–1179.
Golden, D.C., Ming, D.W., Schwandt, C.S., Lauer, H.V., Socki, R.A., Morris, R.V., Lofgren, G.E., McKay, G.A., 2001. A simple inorganic process for formation of carbonates, magnetite, and sulfides in Martian meteorite ALH84001. Am. Mineral. 86, 370–375.
Gole, M.J., Klein, C., 1981. Banded iron formations through much of Precambrian time. J. Geol. 89, 169–183.
Gomez, F., Walter, N., Amils, R., Rull, F., Klingelhofer, A.K., Kviderova, J., Sarrazin, P., Foing, B., Behar, A., Fleischer, I., Parro, V., Garcia-Villadangos, M., Blake, D., Ramos, J.D.M., Direito, S., Mahapatra, P., Stam, C., Venkateswaran, K., Voytek, M., 2011. Multidisciplinary integrated field campaign to an acidic Martian Earth analogue with astrobiological interest: Rio Tinto. Int. J. Astrobiol. 10, 291–305.
Gorby, Y.A., Beveridge, T.J., Blakemore, R.P., 1988. Characterization of the bacterial magnetosome membrane. J. Bacteriol. 170, 834–841.
Gross, G.A., 1966. Principal types of iron-formation and derived ores. Can. Min. Metall. Bull. 59, 150–153.
Gross, G.A., 1980. A classification of iron formations based in depositional environments. Can. Mineral. 18, 215–222.

Grossart, H.-P., Simon, M., 1993. Limnetic macroscopic organic aggregates (lake snow): occurence, characteristics, and microbial dynamics in Lake Constance. Limnol. Oceanogr. 38, 532–546.

Grundl, T., Delwiche, J., 1993. Kinetics of ferric oxyhydroxide precipitation. J. Contam. Hydrol. 14, 71–97.

Habicht, K.S., Canfield, D.E., 1996. Sulphur isotope fractionation in modern microbial mats and the evolution of the sulphur cycle. Nature 382, 342–343.

Habicht, K.S., Gade, M., Thamdrup, B., Berg, P., Canfield, D.E., 2002. Calibration of sulfate levels in the Archean Ocean. Science 298, 2372–2374.

Hallberg, R., Ferris, F.G., 2004. Biomineralization by *Gallionella*. Geomicrobiol J. 21, 325–330.

Hamade, T., Konhauser, K.O., Raiswell, R., Morris, R.C., Goldsmith, S., 2003. Using Ge/Si ratios to decouple iron and silica fluxes in Precambrian banded iron formations. Geology 31, 35–38.

Han, T.-M., 1966. Textural relations of hematite and magnetite in some Precambrian metamorphosed oxide iron-formations. Econ. Geol. 61, 1306–1310.

Han, T.-M., 1978. Microstructures of magnetite as guides to its origin in some Precambrian iron formations. Fortschr. Mineral. 56, 105–142.

Hanert, H.H., 1981. The genus *Gallionella*. In: Starr, M.P., Stolp, H., Trüper, H.G., Balows, A., Schlegel, H.G. (Eds.), The Prokaryotes. Springer, Berlin, pp. 509–515.

Hanert, H.H., 1992. The genus *Gallionella*, In: Balows, A., Trüeper, H.G., Dworkin, M., Harder, W., Schliefer, K.H. (Eds.), 2nd ed. The Prokaryotes, vol. 4. Springer, New York, pp. 4082–4088.

Hansel, C.M., Benner, S.G., Neiss, J., Dohnalkova, A., Kukkadapu, R.K., Fendorf, S., 2003. Secondary mineralization pathways induced by dissimilatory iron reduction of ferrihydrite under advective flow. Geochim. Cosmochim. Acta 67, 2977–2992.

Hansel, C.M., Benner, S.G., Fendorf, S., 2005. Competing Fe(II)-induced mineralization pathways of ferrihydrite. Environ. Sci. Technol. 39, 7147–7153.

Hartman, H., 1984. The evolution of photosynthesis and microbial mats: a speculation on banded iron formations. In: Cohen, Y., Castenholz, R.W., Halvorson, H.O. (Eds.), Microbial Mats, Stromatolites. Alan R Liss, New York, pp. 451–453.

Härtner, T., Straub, K.L., Kannenberg, E., 2005. Occurrence of hopanoid lipids in anaerobic *Geobacter* species. FEMS Microbiol. Lett. 243, 59–64.

Hartnett, H.E., Keil, R.G., Hedges, J.I., Devol, A.H., 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. Nature 391, 572–575.

Hayes, J.M., Strauss, H., Kaufman, A.J., 1999. The abundance of C-13 in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma. Chem. Geol. 161, 103–125.

Hegler, F., Posth, N.R., Jiang, J., Kappler, A., 2008. Physiology of phototrophic iron(II)-oxidizing bacteria — implications for modern and ancient environments. FEMS Microbiol. Ecol. 66, 250–260.

Hegler, F., Schmidt, C., Schwarz, H., Kappler, A., 2010. Does a low-pH microenvironment around phototrophic FeII-oxidizing bacteria prevent cell encrustation by FeIII minerals? FEMS Microbiol. Ecol. 74, 592–600.

Heimann, A., Johnson, C.M., Beard, B.L., Valley, J.W., Roden, E.E., Spicuzza, M.J., Beukes, N.J., 2010. Fe, C, and O isotope compositions of banded iron formation carbonates demonstrate a major role for dissimilatory iron reduction in ~2.5 Ga marine environments. Earth Planet. Sci. Lett. 294, 8–18.

Heising, S., Richter, L., Wolfgang, L., Schink, B., 1999. *Chlorobium ferrooxidans* sp. nov., a phototrophic green sulfur bacterium that oxidizes ferrous iron in coculture with a *Geospirillum* sp. strain. Arch. Microbiol. 172, 116–124.

Hohmann, C., Winkler, E., Morin, G., Kappler, A., 2010. Anaerobic Fe(II)-oxidizing bacteria show As resistance and coprecipitate As during Fe(III) mineral precipitation. Environ. Sci. Technol. 44, 94–101.

Holland, H.D., 1973. The oceans: a possible source of iron in iron-formations. Econ. Geol. 68, 1169–1172.

Holm, N.G., 1989. The $^{13}C/^{12}C$ ratios of siderite and organic matter of a modern metalliferous hydrothermal sediment and their implications for banded iron formations. Chem. Geol. 77, 41–45.

Huston, D.L., Logan, G.A., 2004. Barite, BIFs and bugs: evidence for the evolution of the Earth's early hydrosphere. Earth Planet. Sci. Lett. 220, 41–55.

Icopini, G.A., Anbar, A.D., Ruebush, S.S., Tien, M., Brantley, S.L., 2004. Iron isotope fractionation during microbial reduction of iron: the importance of adsorption. Geology 32, 205–208.

Isley, A.E., 1995. Hydrothermal plumes and the delivery of iron to banded iron formations. J. Geol. 103, 169–185.

Isley, A.E., Abbot, D.H., 1999. Plume-related mafic volcanism and the deposition of banded iron formation. J. Geophys. Res. 104, 15461–15477.

Jacobsen, S.B., Pimental-Klose, M.R., 1988. A Nd isotopic study of the Hamersley and Michipicoten banded iron formations: the source of REE and Fe in Archean oceans. Earth Planet. Sci. Lett. 87, 29–44.

James, H.L., 1954. Sedimentary facies of iron-formation. Econ. Geol. 49, 236–294.

Jiao, Y., Newman, D.K., 2007. The *pio* operon is essential for phototrophic Fe(II) oxidation in *Rhodopseudomonas palustris* TIE-1. J. Bacteriol. 189, 1765–1773.

Jiao, Y., Kappler, A., Croal, L.R., Newman, D.K., 2005. Isolation and characterization of a genetically tractable photoautotrophic Fe(II)-oxidizing bacterium, *Rhodopseudomonas palustris* strain TIE-1. Appl. Environ. Microbiol. 71, 4487–4496.

Johnson, C.M., Beard, B.L., 2005. Biogeochemical cycling of iron isotopes. Science 309, 1025–1027.

Johnson, C.M., Beard, B.L., Beukes, N.J., Klein, C., O'Leary, J.M., 2003. Ancient geochemical cycling in the Earth as inferred from Fe isotope studies of banded iron formations from the Transvaal craton. Contrib. Mineral. Petrol. 144, 523–547.

Johnson, C.M., Beard, B.L., Roden, E.E., Newman, D.K., Nealson, K.H., 2004. Isotopic constraints on biogeochemical cycling of Fe. Rev. Mineral. Geochem. 55, 359–408.

Johnson, C.M., Beard, B.L., Roden, E.E., 2008a. The iron isotope fingerprints of redox and biogeochemical cycling in the modern and ancient Earth. Annu. Rev. Earth Planet. Sci. 36, 457–493.

Johnson, C.M., Beard, B.L., Klein, C., Beukes, N.J., Roden, E.E., 2008b. Iron isotopes constrain biologic and abiologic processes in banded iron formation genesis. Geochim. Cosmochim. Acta 72, 151–169.

Johnson, C.M., Ludois, J.M., Beard, B.L., Beukes, N.J., Heimann, A., 2013. Iron formation carbonates: paleoceanographic proxy or recorder of microbial diagenesis? Geology 41, 1147–1150.

Jørgensen, B.B., 1977. The sulfur cycle of a coastal marine sediment (Limfjorden, Denmark). Limnol. Oceanogr. 22, 814–832.

Jørgensen, B.B., 1982. Mineralization of organic matter in the sea bed — the role of sulphate reduction. Nature 296, 643–645.

Kappler, A., Newman, D.K., 2004. Formation of Fe(III) minerals by Fe(II) oxidizing photoautotrophic bacteria. Geochim. Cosmochim. Acta 68, 1217–1226.

Kappler, A., Straub, K.L., 2005. Geomicrobiological cycling of iron. Rev. Mineral. Geochem. 59, 85–108.

Kappler, A., Pasquero, C., Konhauser, K.O., Newman, D.K., 2005a. Deposition of banded iron formations by anoxygenic phototrophic Fe(II)-oxidizing bacteria. Geology 33, 865–868.

Kappler, A., Schink, B., Newman, D.K., 2005b. Fe(III) mineral formation and cell encrustation by the nitrate-dependent Fe(II) oxidizer strain BoFeN1. Geobiology 3, 235–245.

Kappler, A., Johnson, C.M., Crosby, H.A., Beard, B.L., Newman, D.K., 2010. Evidence for equilibrium iron isotope fractionation by nitrate-reducing iron(II)-oxidizing bacteria. Geochim. Cosmochim. Acta 74, 2826–2842.

Kaufman, A.J., 1996. Geochemical and mineralogic effects of contact metamorphism on banded iron-formation: an example from the Transvaal Basin, South Africa. Precambrian Res. 79, 171–194.

Kaufman, A.J., Knoll, A.H., 1995. Neoproterozoic variations in the C-isotopic composition of seawater: stratigraphic and biogeochemical implications. Precambrian Res. 73, 27–49.

Keil, R.G., Montlucon, D.B., Prahl, F.G., Hedges, J.I., 1994. Sorptive preservation of labile organic matter in marine sediments. Nature 370, 549–552.

Kennedy, C.B., Scott, S.D., Ferris, F.G., 2003a. Ultrastructure and potential sub-seafloor evidence of bacteriogenic iron oxides from Axial Volcano, Juan de Fuca Ridge, northeast Pacific Ocean. FEMS Microbiol. Ecol. 43, 247–254.

Kennedy, C.B., Martinez, R.E., Scott, S.D., Ferris, F.G., 2003b. Surface chemistry and reactivity of bacteriogenic iron oxides from Axial Volcano, Juan de Fuca Ridge, North-East Pacific Ocean. Geobiology 1, 59–69.

Klein, C., 2005. Some Precambrian banded iron formations (BIFs) from around the world: their age, geologic setting, mineralogy, metamorphism, geochemistry, and origin. Am. Mineral. 90, 1473–1499.

Klein, C., Beukes, N.J., 1992. Time distribution, stratigraphy, sedimentologic setting, and geochemistry of Precambrian iron-formations. In: Schopf, J.W., Klein, C. (Eds.), The Proterozoic Biosphere: A Multidisciplinary Study. Cambridge University Press, Cambridge, U.K.

Kleinert, S., Muehe, E.M., Posth, N.R., Dippon, U., Daus, B., Kappler, A., 2011. Biogenic Fe(III) minerals lower the efficiency of iron-mineral-based commercial filter systems for arsenic removal. Environ. Sci. Technol. 45, 7533–7541.

Klueglein, N., Kappler, A., 2013. Abiotic oxidation of Fe(II) by reactive nitrogen species in cultures of the nitrate-reducing Fe(II)-oxidizer *Acidovorax* sp. BoFeN1 — questioning the existence of enzymatic Fe(II) oxidation. Geobiology 11, 180–190.

Klueglein, N., Zeitvogel, F., Stierhof, Y.D., Floetenmeyer, M., Konhauser, K.O., Kappler, A., Obst, M., 2014. Potential role of nitrite for abiotic Fe(II) oxidation and cell encrustation during nitrate reduction by denitrifying bacteria. Appl. Environ. Microbiol. 80, 1051–1061.

Köhler, I., Konhauser, K.O., Papineau, D., Bekker, A., Kappler, A., 2013. Biological carbon precursor to diagenetic siderite with spherical structures in iron formations. Nat. Commun. 4, 1741. http://dx.doi.org/10.1038/ncomms2770.

Konhauser, K.O., 2007. Introduction to Geomicrobiology. Blackwell Publishing, Malden, MA, USA.

Konhauser, K., Hamade, T., Raiswell, R., Morris, R.C., Ferris, F.G., Southam, G., Canfield, D.E., 2002. Could bacteria have formed the Precambrian banded iron formations? Geology 30, 1079–1082.

Konhauser, K., Newman, D.K., Kappler, A., 2005. The potential significance of microbial Fe(III) reduction during deposition of Precambrian banded iron formations. Geobiology 3, 167–177.

Konhauser, K.O., Amskold, L., Lalonde, S.V., Posth, N.R., Kappler, A., Anbar, A., 2007. Decoupling photochemical Fe(II) oxidation from shallow-water BIF deposition. Earth Planet. Sci. Lett. 258, 87–100.

Konhauser, K.O., Kappler, A., Roden, E.E., 2011. Iron in microbial metabolism. Elements 7, 89–93.

Kopf, S.H., Henny, C., Newman, D.K., 2013. Ligand-enhanced abiotic iron oxidation and the effects of chemical vs. biological iron cycling in anoxic environments. Environ. Sci. Technol. 47, 2602–2611.

Krapež, B., Barley, M.E., Pickard, A.L., 2003. Hydrothermal and resedimented origins of the precursor sediments to banded iron formation: sedimentological evidence from the early Paleoproterozoic Brockman Supersequence of Western Australia. Sedimentology 50, 979–1011.

Kump, L.R., Holland, H.D., 1992. Iron in Precambrian rocks — implications for the global oxygen budget of the ancient Earth. Geochim. Cosmochim. Acta 56, 3217–3223.

Lalonde, K., Mucci, A., Ouellet, A., Gelinas, Y., 2012. Preservation of organic matter in sediments promoted by iron. Nature 483, 198–200.

Langley, S., Gault, A., Ibrahim, A., Renaud, R., Fortin, D., Clark, I., Ferris, F.G., 2009. A comparison of the rates of Fe(III) reduction in synthetic and bacteriogenic iron oxides by *Shewanella putrefaciens* CN32. Geomicrobiol J. 26, 57–70.

Larese-Casanova, P., Haderlein, S.B., Kappler, A., 2010. Biomineralization of lepidocrocite and goethite by nitrate-reducing Fe(II)-oxidizing bacteria: effect of pH, bicarbonate, phosphate, and humic acids. Geochim. Cosmochim. Acta 74, 3721–3734.
Lepland, A., van Zuilen, M.A., Arrhenius, G., Whitehouse, M.J., Fedo, C.M., 2005. Questioning the evidence for Earth's earliest life — Akilia revisited. Geology 33, 77–79.
Li, Y.L., Konhauser, K.O., Cole, D.R., Phelps, T.J., 2011. Mineral ecophysiological data provide growing evidence for microbial activity in banded-iron formations. Geology 39, 707–710.
Li, Y.L., Konhauser, K.O., Kappler, A., Hao, X.L., 2013. Experimental low-grade alteration of biogenic magnetite indicates microbial involvement in generation of banded iron formations. Earth Planet. Sci. Lett. 361, 229–237.
Lomstein, B.A., Langerhuus, A.T., D'Hondt, S., Jørgensen, B.B., Spivack, A.J., 2012. Endospore abundance, microbial growth and necromass turnover in deep sub-seafloor sediment. Nature 484, 101–104.
Lovley, D.R., Stolz, J.F., Nord, G.L., Phillips, E.J.P., 1987. Anaerobic production of magnetite by a dissimilatory iron-reducing microorganism. Nature 330, 252–254.
Lovley, D.R., Giovannoni, S.J., White, D.C., Champine, J.E., Phillips, E.J.P., Gorby, Y.A., Goodwin, S., 1993. *Geobacter metallireducens* gen. nov. sp. nov. A microorganism capable of coupling the complete oxidation of organic compounds to the reduction of iron and other metals. Arch. Microbiol. 159, 336–344.
Macalady, D.L., Langmuir, D., Grundl, T., Elzerman, A., 1990. Use of model-generated Fe^{3+} ion activities to compute Eh and ferric oxyhydroxide solubilities in anaerobic systems. ACS Symp. Ser. 416, 350–367.
McCollom, T.M., Seewald, J.S., 2003. Experimental constraints on the hydrothermal reactivity of organic acids and acid anions: I. Formic acid and formate. Geochim. Cosmochim. Acta 67, 3625–3644.
McLoughlin, N., Wilson, L.A., Brasier, M.D., 2008. Growth of synthetic stromatolites and wrinkle structures in the absence of microbes — implications for the early fossil record. Geobiology 6, 95–105.
Meyer-Dombard, D.R., Shock, E.L., Amend, J.P., 2005. Archaeal and bacterial communities in geochemically diverse hot springs of Yellowstone National Park, USA. Geobiology 3, 211–227.
Michel, F.M., Ehm, L., Antao, S.M., Lee, P.L., Chupas, P.J., Liu, G., Strongin, D.R., Schoonen, M.A.A., Phillips, B.L., Parise, J.B., 2007. The structure of ferrihydrite, a nanocrystalline material. Science 316, 1726–1729.
Mikutta, C., Mikutta, R., Bonneville, S., Wagner, F., Voegelin, A., Christl, I., Kretzschmar, R., 2008. Synthetic coprecipitates of exopolysaccharides and ferrihydrite. Part I: characterization. Geochim. Cosmochim. Acta 72, 1111–1127.
Miot, J., Benzerara, K., Morin, G., Kappler, A., Bernard, S., Obst, M., Férard, C., Skouri-Panet, F., Guigner, J.-M., Posth, N.R., Galvez, M., Brown Jr., G.E., Guyot, F., 2009a. Iron biomineralization by anaerobic neutrophilic iron-oxidizing bacteria. Geochim. Cosmochim. Acta 73, 696–711.
Miot, J., Benzerara, K., Obst, M., Kappler, A., Hegler, F., Schädler, S., Bouchez, C., Guyot, F., Morin, G., 2009b. Extracellular iron biomineralization by photoautotrophic iron-oxidizing bacteria. Appl. Environ. Microbiol. 75, 5586–5591.
Miot, J., Benzerara, K., Morin, G., Bernard, S., Beyssac, O., Larquet, E., Kappler, A., Guyot, F., 2009c. Transformation of vivianite by anaerobic nitrate-reducing iron-oxidizing bacteria. Geobiology 7, 373–384.
Miot, J., Maclellan, K., Benzerara, K., Boisset, N., 2011. Preservation of protein globules and peptidoglycan in the mineralized cell wall of nitrate-reducing, iron(II)-oxidizing bacteria: a cryo-electron microscopy study. Geobiology 9, 459–470.
Miot, J., Benzerara, K., Kappler, A., 2014. Investigating microbe/mineral interactions: recent advances in X-ray and electron microscopies and redox-sensitive methods. Annu. Rev. Earth Planet. Sci. (in press).
Miyano, T., 1987. Diagenetic to low-grade metamorphic conditions of Precambrian iron-formations. In: Appel, P.W.U., LaBerge, G.L. (Eds.), Precambrian Iron Formations. Theophrastus Publications, Athens, Greece, pp. 155–186.
Mojzsis, S.J., Arrhenius, G., McKeegan, K.D., Harrison, T.M., Nutman, A.P., Friend, C.R.L., 1996. Evidence for life on Earth before 3800 million years ago. Nature 384, 55–59.
Mojzsis, S.J., Coath, C.D., Greenwood, J.P., McKeegan, K.D., Harrison, T.M., 2003. Mass-independent isotope effects in Archean (2.5 to 3.8 Ga) sedimentary sulfides determined by ion microprobe analysis. Geochim. Cosmochim. Acta 67, 1635–1658.
Moraghan, J.T., Buresh, R.J., 1977. Chemical reduction of nitrite and nitrous oxide by ferrous iron. Soil Sci. Soc. Am. J. 41, 47–50.
Morris, R.C., 1993. Genetic modeling for banded iron-formation of the Hamersley Group, Pilbara Craton, Western Australia. Precambrian Res. 60, 243–286.
Morris, R.C., Horwitz, R.C., 1983. The origin of the iron-formation-rich Hamersley Group of Western Australia — deposition on a platform. Precambrian Res. 21, 273–297.
Muehe, E.M., Gerhardt, S., Schink, B., Kappler, A., 2009. Ecophysiology and the energetic benefit of mixotrophic Fe(II) oxidation by various strains of nitrate-reducing bacteria. FEMS Microbiol. Ecol. 70, 335–343.
Muehe, M., Scheer, L., Daus, B., Kappler, A., 2013. Fate of arsenic during microbial reduction of biogenic vs. abiogenic As–Fe(III)-mineral co-precipitates. Environ. Sci. Technol. 47, 8297–8307.
Nealson, K.H., Myers, C.R., 1990. Iron reduction by bacteria: a potential role in the genesis of banded iron formations. Am. J. Sci. 290-A, 35–45.
O'Loughlin, E.J., 2008. Effects of electron transfer mediators on the bioreduction of lepidocrocite (γ-FeOOH) by *Shewanella putrefaciens* CN32. Environ. Sci. Technol. 42, 6876–6882.
O'Loughlin, E.J., Gorski, C.A., Scherer, M.M., Boyanov, M.I., Kemner, K.M., 2010. Effects of oxyanions, natural organic matter, and bacterial cell numbers on the bioreduction of lepidocrocite (γ-FeOOH) and the formation of secondary mineralization products. Environ. Sci. Technol. 44, 4570–4576.
Och, L.M., Shields-Zhou, G.A., Poulton, S.W., Manning, C., Thirlwall, M.F., Li, D., Chen, X., Ling, H.F., Osborn, T., Cremonese, L., 2013. Redox changes in Early Cambrian black shales at Xiaotan Section, Yunnan Province, South China. Precambrian Res. 225, 166–189.
Ohmoto, H., 2003. Nonredox transformations of magnetite–hematite in hydrothermal systems. Econ. Geol. 98, 157–161.
Pantke, C., Obst, M., Benzerara, K., Morin, G., Ona-Nguema, G., Dippon, U., Kappler, A., 2012. Green rust formation during Fe(II) oxidation by the nitrate-reducing *Acidovorax* sp. strain BoFeN1. Environ. Sci. Technol. 46, 1439–1446.
Pecoits, E., Posth, N.R., Konhauser, K.O., Kappler, A., 2009. Petrography and trace element geochemistry of Dales Gorge banded iron formation: paragenetic sequence, source and implications for the Palaeo-ocean chemistry. Precambrian Res. 172, 163–187.
Perry, E.C., Tan, F.C., Morey, G.B., 1973. Geology and stable isotope geochemistry of the Biwabik Iron Formation, northern Minnesota. Econ. Geol. 68, 1110–1125.
Philippot, P., van Zuilen, M., Lepot, K., Thomazo, C., Farquhar, J., van Kranendonk, M.J., 2007. Early Archaean microorganisms preferred elemental sulfur, not sulfate. Science 317, 1534–1537.
Phoenix, V.R., Martinez, R.E., Konhauser, K.O., Ferris, F.G., 2002. Characterization and implications of the cell surface reactivity of *Calothrix* sp strain KC97. Appl. Environ. Microbiol. 68, 4827–4834.
Picardal, F., 2012. Abiotic and microbial interactions during anaerobic transformations of Fe(II) and NO_x. Front. Microbiol. 3, 112. http://dx.doi.org/10.3389/fmicb.2012.00112.
Pickard, A.L., 2002. SHRIMP U–Pb zircon ages of tuffaceous mudrocks in the Brockman Iron Formation of the Hamersley Range, Western Australia. Aust. J. Earth Sci. 49, 491–507.
Planavsky, N., Rouxel, O.J., Bekker, A., Hofmann, A., Little, C.T.S., Lyons, T.W., 2012. Iron isotope composition of some Archean and Proterozoic iron formations. Geochim. Cosmochim. Acta 80, 158–169.
Porsch, K., Kappler, A., 2011. Fe(II) oxidation by molecular O_2 in HCl and its implication for Fe mineral extraction procedures. Environ. Chem. 8, 190–197.
Posth, N.R., Hegler, F., Konhauser, K.O., Kappler, A., 2008. Alternating Si and Fe deposition caused by temperature fluctuations in Precambrian oceans. Nat. Geosci. 1, 703–708.
Posth, N.R., Huelin, S., Konhauser, K.O., Kappler, A., 2010. Size, density and composition of cell–mineral aggregates formed during anoxygenic phototrophic Fe(II) oxidation: impact on modern and ancient environments. Geochim. Cosmochim. Acta 74, 3476–3493.
Posth, N.R., Konhauser, K.O., Kappler, A., 2011. Banded iron formations. In: Reitner, J., Thiel, V. (Eds.), Encyclopedia of Geobiology. Springer Verlag, pp. 92–103.
Posth, N.R., Konhauser, K.O., Kappler, A., 2013a. Microbiological processes in banded iron formation diagenesis. Sedimentology 60, 1733–1754.
Posth, N.R., Koehler, I., Swanner, E.D., Schroeder, C., Wellmann, E., Binder, B., Konhauser, K.O., Neumann, U., Berthold, C., Nowak, M., Kappler, A., 2013b. Simulating Precambrian banded iron formation diagenesis. Chem. Geol. 362, 66–73.
Poulton, S.W., Canfield, D.E., 2011. Ferruginous conditions: a dominant feature of the ocean through Earth's history. Elements 7, 107–112.
Preston, L.J., Shuster, J., Fernandez-Remolar, D., Banerjee, N.R., Osinski, G.R., Southam, G., 2011. The preservation and degradation of filamentous bacteria and biomolecules within iron oxide deposits at Rio Tinto, Spain. Geobiology 9, 233–249.
Quandt, L., Gottschalk, G., Ziegler, H., Stichler, W., 1977. Isotope discrimination by photosynthetic bacteria. FEMS Microbiol. Lett. 1, 125–128.
Raiswell, R., Reinhard, C.T., Derkowski, A., Owens, J., Bottrell, S.H., Anbar, A.D., Lyons, T.W., 2011. Formation of syngenetic and early diagenetic iron minerals in the late Archean Mt. McRae Shale, Hamersley Basin, Australia: new insights on the patterns, controls and paleoenvironmental implications of authigenic mineral formation. Geochim. Cosmochim. Acta 75, 1072–1087.
Rashby, S.E., Sessions, A.L., Summons, R.E., Newman, D.K., 2007. Biosynthesis of 2-methylbacteriohopanepolyols by an anoxygenic phototroph. Proc. Natl. Acad. Sci. U. S. A. 104, 15099–15104.
Rasmussen, B., Meier, D.B., Krapež, B., Muhlin, J.R., 2013. Iron silicate microgranules as precursor sediments to 2.5-billion-year-old banded iron formations. Geology 41, 435–438.
Roberts, L., Hug, S., Ruettimann, T., Billah, M., Khan, A., Rahman, M., 2004. Arsenic removal with iron(II) and iron(III) in waters with high silicate and phosphate concentrations. Environ. Sci. Technol. 38, 307–315.
Rosing, M.T., 1999. ^{13}C-depleted carbon microparticles in >3700-Ma sea-floor sedimentary rocks from West Greenland. Science 283, 674–676.
Rosing, M.T., Rose, N.M., Bridgewater, D., Thomsen, H.S., 1996. Earliest part of Earth's stratigraphic record: a reappraisal of the >3.7 Ga Isua (Greenland) supracrustal sequence. Geology 24, 43–46.
Rothman, D.H., Hayes, J.M., Summons, R.E., 2003. Dynamics of the Neoproterozoic carbon cycle. Proc. Natl. Acad. Sci. U. S. A. 100, 8124–8129.
Saini, G., Chan, C.S., 2013. Near-neutral surface charge and hydrophilicity prevent mineral encrustation of Fe-oxidizing micro-organisms. Geobiology 11, 191–200.
Saraiva, I.H., Newman, D.K., Louro, R.O., 2012. Functional characterization of the FoxE iron oxidoreductase from the photoferrotroph *Rhodobacter ferrooxidans* SW2. J. Biol. Chem. 287, 25541–25548.
Schädler, S., Burkhardt, C., Hegler, F., Straub, K.L., Miot, J., Benzerara, K., Kappler, A., 2009. Formation of cell–iron–mineral aggregates by phototrophic and nitrate-reducing anaerobic Fe(II)-oxidizing bacteria. Geomicrobiol J. 26, 93–103.
Schmidt, C., Behrens, S., Kappler, A., 2010. Ecosystem functioning from a geomicrobiological perspective — a conceptual framework for biogeochemical iron cycling. Environ. Chem. 7, 399–405.
Schopf, J.W., 1992. Evolution of the Proterozoic biosphere: benchmarks, tempo and mode. In: Schopf, J.W., Klein, C. (Eds.), The Proterozoic Biosphere. Cambridge University Press, New York, pp. 25–39.
Schopf, J.W., 1993. Microfossils of the Early Archean Apex chert: new evidence of the antiquity of life. Science 260, 640–646.

Schopf, J.W., Packer, B.M., 1987. Early Archean (3.3-billion to 3.5-billion-year-old) microfossils from Warrawoona Group, Australia. Science 237, 70–73.
Senko, J.M., Dewers, T.A., Krumholz, L.R., 2005. Effect of oxidation rate and Fe(II) state on microbial nitrate-dependent Fe(III) mineral formation. Appl. Environ. Microbiol. 71, 7172–7177.
Sharma, P., Ofner, J., Kappler, A., 2010. Formation of binary and ternary colloids and dissolved complexes of organic matter, Fe and As. Environ. Sci. Technol. 44, 4479–4485.
Shen, Y., Buick, R., Canfield, D.E., 2001. Isotopic evidence for microbial sulphate reduction in the early Archaean era. Nature 410, 77–81.
Siever, R., 1992. The silica cycle in the Precambrian. Geochim. Cosmochim. Acta 56, 3265–3272.
Sirevåg, R., Buchanan, B.B., Berry, J.A., Troughton, J.H., 1977. Mechanisms of CO_2 fixation in bacterial photosynthesis studied by the carbon isotope fractionation technique. Arch. Microbiol. 112, 35–38.
Sobolev, D., Roden, E.E., 2001. Suboxic deposition of ferric iron by bacteria in opposing gradients of Fe(II) and oxygen at circumneutral pH. Appl. Environ. Microbiol. 67, 1328–1334.
Squyres, S.W., Knoll, A.H., Arvidson, R.E., Ashley, J.W., Bell, J.F., Calvin, W.M., Christensen, P.R., Clark, B.C., Cohen, B.A., de Souza, P.A., Edgar, L., Farrand, W.H., Fleischer, I., Gellert, R., Golombek, M.P., Grant, J., Grotzinger, J., Hayes, A., Herkenhoff, K.E., Johnson, J.R., Jolliff, B., Klingelhöfer, G., Knudson, A., Li, R., McCoy, T.J., McLennan, S. M., Ming, D.W., Mittlefehldt, D.W., Morris, R.V., Rice, J.W., Schröder, C., Sullivan, R.J., Yen, A., Yingst, R.A., 2009. Exploration of Victoria Crater by the Mars Rover Opportunity. Science 324, 1058–1061.
Steinhoefel, G., von Blanckenburg, F., Horn, I., Konhauser, K.O., Beukes, N.J., Gutzmer, J., 2010. Deciphering formation processes of banded iron formations from the Transvaal and the Hamersley successions by combined Si and Fe isotope analysis using UV femtosecond laser ablation. Geochim. Cosmochim. Acta 74, 2677–2696.
Straub, K.L., Benz, M., Schink, B., Widdel, F., 1996. Anaerobic, nitrate-dependent microbial oxidation of ferrous iron. Appl. Environ. Microbiol. 62, 1458–1460.
Straub, K.L., Hanzlik, M., Buchholz-Cleven, B.E.E., 1998. The use of biologically produced ferrihydrite for the isolation of novel iron-reducing bacteria. Syst. Appl. Microbiol. 21, 442–449.
Straub, K.L., Rainey, F.R., Widdel, F., 1999. *Rhodovulum iodosum* sp. nov. and *Rhodovulum robiginosum* sp. nov., two new marine phototrophic ferrous-iron-oxidizing purple bacteria. Int. J. Syst. Bacteriol. 49, 729–735.
Strauss, H., 2003. Sulphur isotopes and the early Archean sulphur cycle. Precambrian Res. 126, 349–361.
Summons, R.E., Jahnke, L.L., Hope, J.M., Logan, G.A., 1999. 2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis. Nature 400, 554–557.
Swanner, E.D., Nell, R.M., Templeton, A.S., 2011. *Ralstonia* species mediate Fe-oxidation in circumneutral, metal-rich subsurface fluids of Henderson Mine, CO. Chem. Geol. 284, 339–350.
Tadanier, C.J., Schreiber, M.E., Roller, J.W., 2005. Arsenic mobilization through microbially mediated deflocculation of ferrihydrite. Environ. Sci. Technol. 39, 3061–3068.
Thibault, P.J., Rancourt, D.G., Evans, R.J., Dutrizac, J.E., 2009. Mineralogical confirmation of a near-P:Fe = 1:2 limiting stoichiometric ratio in colloidal P-bearing ferrihydrite-like hydrous ferric oxide. Geochim. Cosmochim. Acta 73, 364–376.
Toner, B.M., Fakra, S.C., Manganini, S.J., Santelli, C.M., Marcus, M.A., Moffett, J.W., Rouxel, O., German, C.R., Edwards, K.J., 2009a. Preservation of iron(II) by carbon-rich matrices in a hydrothermal plume. Nat. Geosci. 2, 197–201.
Toner, B.M., Santelli, C.M., Marcus, M.A., Wirth, R., Chan, C.S., McCollom, T., Bach, W., Edwards, K.J., 2009b. Biogenic iron oxyhydroxide formation at mid-ocean ridge hydrothermal vents: Juan de Fuca Ridge. Geochim. Cosmochim. Acta 73, 388–403.
Toner, B.M., Berquó, T.S., Michel, F.M., Sorensen, J.V., Templeton, A.S., Edwards, K.J., 2012. Mineralogy of iron microbial mats from Loihi Seamount. Front. Microbiol. 3, 118. http://dx.doi.org/10.3389/fmicb.2012.00118.
Trendall, A.F., 2002. The significance of iron-formation in the Precambrian stratigraphic record. Int. Assoc. Sedimentol. Spec. Publ. 3, 33–66.
Trendall, A.F., Blockely, J.G., 1970. The iron formations of the Precambrian Hamersley Group, Western Australia with special reference to the associated crocidolite. West. Austr. Geol. Surv. Bull. 119.
Ueno, Y., Yamada, K., Yoshida, N., Maruyama, S., Isozaki, Y., 2006. Evidence from fluid inclusions for microbial methanogenesis in the early Archaean era. Nature 440, 516–519.
Van Zuilen, M.A., Lepland, A., Arrhenius, G., 2002. Reassessing the evidence for the earliest traces of life. Nature 418, 627–630.
Vargas, M., Kashefi, K., Blunt-Harris, E.L., Lovely, D.R., 1998. Microbiological evidence for Fe(III) reduction on early Earth. Nature 395, 65–67.
Velinsky, D.J., Fogel, M.L., 1999. Cycling of dissolved and particulate nitrogen and carbon in the Framvaren Fjord, Norway: stable isotopic variations. Mar. Chem. 67, 161–180.
Walker, J.C.G., 1984. Suboxic diagenesis in banded iron formations. Nature 309, 340–342.
Wang, Y.F., Xu, H.F., Merino, E., Konishi, H., 2009. Generation of banded iron formations by internal dynamics and leaching of oceanic crust. Nat. Geosci. 2, 781–784.
Weber, K.A., Picardal, F.W., Roden, E.E., 2001. Microbially catalyzed nitrate-dependent oxidation of biogenic solid-phase Fe(II) compounds. Environ. Sci. Technol. 35, 1644–1650.
Widdel, F., Schnell, S., Heising, S., Ehrenreich, A., Assmus, B., Schink, B., 1993. Ferrous iron oxidation by anoxygenic phototrophic bacteria. Nature 362, 834–836.
Wu, L., Beard, B.L., Roden, E.E., Johnson, C.M., 2009. Influence of pH and dissolved Si on Fe isotope fractionation during dissimilatory microbial reduction of hematite. Geochim. Cosmochim. Acta 73, 5584–5599.
Xiong, J., 2006. Photosynthesis: what color was its origin? Genome Biol. 7, 245.1–245.5.
Yamaguchi, K.E., Johnson, C.M., Beard, B.L., Ohmoto, H., 2005. Biogeochemical cycling of iron in the Archean Paleoproterozoic Earth: constraints from iron isotope variations in sedimentary rocks from the Kaapvaal and Pilbara Cratons. Chem. Geol. 218, 135–169.
Yarzábal, A., Brasseur, G., Ratouchniak, J., Lund, K., Lemesle-Meunier, D., DeMoss, J.A., Bonnefoy, V., 2002. The high-molecular-weight cytochrome *c* Cyc2 of *Acidithiobacillus ferrooxidans* is an outer membrane protein. J. Bacteriol. 184, 313–317.
Yuwono, V.M., Burrows, N.D., Soltis, J.A., Penn, R.L., 2010. Oriented aggregation: formation and transformation of mesocrystal intermediates revealed. J. Am. Chem. Soc. 132, 2163–2165.
Yuwono, V.M., Burrows, N.D., Soltis, J.A., Do, T.A., Penn, R.L., 2012. Aggregation of ferrihydrite nanoparticles in aqueous systems. Faraday Discuss. 159, 235–245.
Zegeye, A., Bonneville, S., Benning, L.G., Sturm, A., Fowle, D.A., Jones, C., Canfield, D.E., Ruby, C., MacLean, L.C., Nomosatryo, S., Crowe, S.A., Poulton, S.W., 2012. Green rust formation controls nutrient availability in a ferruginous water column. Geology 40, 599–602.
Zouboulis, A., Katsoyiannis, I., 2005. Recent advances in the bioremediation of arsenic-contaminated groundwaters. Environ. Int. 31, 213–219.
Zyakun, A.M., Lunina, O.N., Prusakova, T.S., Pimenov, N.V., Ivanov, M.V., 2009. Fractionation of stable carbon isotopes by photoautotrophically growing anoxygenic purple and green sulfur bacteria. Microbiology 78, 757–768.