

## HYDROTHERMAL BACTERIAL BIOMINERALIZATION: POTENTIAL MODERN-DAY ANALOGUES FOR BANDED IRON-FORMATIONS

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**ABSTRACT:** Precambrian banded iron-formations (BIFs) are chemical sediments of hydrothermal origin and consist of Fe-rich minerals with alternating layers of chert. Because microorganisms potentially played a role in their precipitation, the study of bacterial-mineral interactions at modern hydrothermal environments may provide small-scale analogues to those conditions under which they accumulated. Interestingly, microbial populations currently growing at hot springs and deep-sea vents are commonly encrusted in iron and silicate minerals. Iron biomineralization occurs either passively through interaction between the reactive sites of the cell and dissolved cationic iron from the hydrothermal fluid, or actively through chemolithotrophic iron-oxidation by bacteria such as *Gallionella* genera. Amorphous silica precipitates on individual bacteria through hydrogen bonding between hydroxy groups in the extracellular polymers and hydroxyl groups in dissolved silica, with some colonies becoming completely cemented together within a siliceous matrix up to several micrometers thick. Iron-silicates form due to reactions between dissolved silica and cell-bound iron. In these predominantly nonspecific processes, bacterial cells simply catalyze reactions that are rendered possible by the supersaturated conditions created by the sudden physical and chemical changes induced through venting. Diagenetic reactions, some of which are also catalyzed by microorganisms growing in the sediment, can further alter the mineralogy of these primary precipitates, leading to the formation of secondary magnetite and siderite. In this way, all of the main mineralogical components of BIFs can be associated with microbial activity.

### INTRODUCTION

Banded iron-formations (BIFs) are some of the most abundant sedimentary deposits of the Precambrian, with major accumulations having formed during the late Archean (2.7–2.5 Ga) and early Proterozoic (2.5–1.8 Ga) (Isley, 1995). These thin-bedded or laminated rocks contain an anomalously high content of iron, and commonly, layers of chert (James, 1954). Most BIFs have similar bulk compositions and mineral assemblages, although Archean BIFs are not as thick or laterally extensive as their Proterozoic counterparts (Gole and Klein, 1981). Iron and silica contents are typically in the range of 20–35 wt. % and 40–50 wt. %, respectively (James, 1983), while the mineralogy consists of quartz, magnetite, hematite, various carbonates, ferrous iron-silicates, and pyrite; some carbonaceous material is also present (McConchie, 1987; Klein and Beukes, 1992). The banding in BIFs generally comprises alternating layers of Fe-rich minerals with layers of chert (and carbonate) that can be observed at three different scales: macro, meso, and micro (Trendall, 1965; Trendall and Blockley, 1970). Macrobands are coarse alterations of contrasting Fe-oxide facies (magnetite, hematite) and shalc facies (referred to as S-macrobands, with chert, siderite, and iron-silicates) decimeters to tens of meters in thickness; mesobands are centimeter thick units; and microbands usually range from submillimeter to 5 mm (Morris, 1993). The lateral continuity of mesobands is a characteristic feature of some iron-formations, and in the Dales Gorge Member, Hamersley Group BIF, Western Australia, for example, they can be traced for more than 130 km through the basin (Ewers and Morris, 1981).

It is generally accepted that BIFs are chemical precipitates (Morris, 1993), with the iron primarily derived from a

hydrothermal source (Simonson, 1985; Klein and Beukes, 1992; Isley, 1995; Simonson and Hassler, 1996). This model is supported by (i) estimates of higher surface heat flow and rapid hydrothermal cycling rates for the late Archean-early Proterozoic (Turcotte, 1980; Jacobsen and Pimentel-Klose, 1988), (ii) rare earth element (REE) distribution patterns in BIFs (Jacobsen and Pimentel-Klose, 1988; Derry and Jacobsen, 1990; Bau and Möller, 1993), (iii) sulfur and neodymium isotopic compositions of Archean and early Proterozoic iron-formations (Cameron, 1983; Jacobsen and Pimentel-Klose, 1988), and (iv)  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios and  $^{18}\text{O}$  depletion in Archean and early Proterozoic carbonates (Veizer et al., 1982; Beukes et al., 1990). Interestingly, the transition from hydrothermal-dominated ocean chemistry of the Archean to continental-dominated modern seawater was established by approximately 0.7–0.8 Ga, coinciding with the last major BIF deposits of the Rapitan Group, N.W.T., Canada (Klein and Beukes, 1992).

Although the origin of iron in BIFs has been clarified, mechanisms for their deposition are still under debate (see McConchie, 1987 and Morris, 1993, for detailed discussions). Interactions between microorganisms and dissolved ferrous iron and silica in the Precambrian ocean have been suggested as one plausible means for mineral precipitation (Cloud, 1965, 1973; LaBerge, 1973; Baur et al., 1985; Birnbaum and Wireman, 1985; Holm, 1987, 1989; Neelson and Myers, 1990; Widdel et al., 1993; Ehrenreich and Widdel, 1994; Konhauser and Ferris, 1996). Cloud (1965, 1973) originally proposed that primitive oxygen-releasing photosynthetic bacteria, which may have lacked suitably advanced oxygen-mediating enzymes, attached any free  $\text{O}_2$  that was generated to convenient oxygen acceptors in the immediate vicinity of the bacterial population. The abundant ferrous iron in solution at that time would have served as such an acceptor, thereby maintaining the reducing environment necessary for their survival. This process of transferring oxygen

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to nonbiological oxygen acceptors may have later evolved into a source of energy for chemolithotrophic microaerophilic bacteria such as *Gallionella ferruginea*. Holm (1987, 1989) speculated that slow biological oxidation of hydrothermal solutions by these microorganisms, in an ocean with limited free photosynthetic oxygen, was primarily responsible for the precipitation of ferrous to ferric iron over wide ocean basins. Alternatively, the discovery of purple bacteria that couple ferrous iron oxidation to anoxygenic photosynthesis has been suggested as a means for early BIF deposition in the Archean, before free oxygen became available as an oxidant (Widdel et al., 1993; Ehrenreich and Widdel, 1994).

Simultaneously, saturation of ocean waters with respect to silica due to the absence of silica-secreting microorganisms (e.g., diatoms, radiolarians) at that time provided ideal conditions for the precipitation of amorphous silica (Siever, 1992). The sudden cooling and pressure drop of hydrothermal effluent after venting on the ocean floor (Williams and Crerar, 1985), evaporation on continental shelves (Morris, 1993), tidal flats and restricted lagoons (Knoll, 1985), and coprecipitation with iron (Ewers, 1983) could each have led to silica supersaturation and precipitation. During diagenesis, these primary silica precipitates subsequently may have undergone a dissolution-reprecipitation pathway with a characteristic sequence of mineralogical transformations progressing from amorphous silica to low-temperature cristobalite to quartz, the phase of lowest entropy and slowest nucleation and growth rates (Williams and Crerar, 1985). A biological role for amorphous silica precipitation has also been considered, since bacteria are known to create favorable geochemical conditions for silicification through their metabolic activities (Birnbaum and Wireman, 1985) and they provide highly reactive surfaces for silica nucleation and mineral growth (Urrutia and Beveridge, 1993). The presence of Precambrian microfossils in carbonaceous cherts (Awramik et al., 1983; Walsh and Lowe, 1985; Schopf and Packer, 1987; Schopf, 1993) and BIFs (Barghoorn and Tyler, 1965; Cloud, 1965; LaBerge, 1973), as well as the presence of silicified stromatolites (Lowe, 1980; Walter et al., 1980) would certainly seem to suggest that microorganisms were, in some manner, inextricably linked to silica precipitation.

Because Precambrian banded iron-formations are chemical sediments of hydrothermal origin, and microorganisms potentially played a role in their precipitation, I propose here that the study of bacterial-mineral interactions at modern hydrothermal environments may provide small-scale analogues to those conditions under which they accumulated. This paper will show (i) that bacteria directly form iron and silicate minerals in modern hydrothermal environments and (ii) that these biomineralization processes correlate well with conditions that may have existed in the Precambrian, resulting in banded iron-formation.

#### HYDROTHERMAL BIOMINERALIZATION

Bacteria are found today throughout the hydrosphere, commonly inhabiting environments that cannot sustain other life forms. At hot springs, photosynthetic cyanobacteria (e.g.,

*Synechococcus* sp.) and filamentous bacteria (e.g., *Chloroflexus* sp.) frequently form well-defined laminated mats adjacent to hydrothermal vents and in their outflow channels (Walter et al., 1972; Walter, 1976; Doemel and Brock, 1977). In Yellowstone National Park, USA, for example, these mats can reach several millimeters in thickness with both *Synechococcus* and *Chloroflexus* cells growing to depths where sufficient light exists, below which anaerobic decomposition by heterotrophic bacteria takes place (Doemel and Brock, 1977; Walter et al., 1992). In some high-sulfide springs, cyanobacterial growth is suppressed, and pure *Chloroflexus* populations are developed via anoxygenic photosynthesis (Castenholz, 1973). In groundwater from geothermal areas, such as those in Iceland, high ferrous iron concentrations encourage the growth of iron-oxidizing bacteria such as *Gallionella ferruginea* (Holm, 1987).

In deep-sea hydrothermal environments, bacterial productivity is highest in the vicinity of warm vents, where reducing fluids mix with downwelling cold, oxygenated seawater (Jannasch and Mottl, 1985). Bacterial communities growing at these sites have concentrations that range from  $10^6$  to  $10^9$  cells per milliliter (Jannasch and Wirsén, 1981). Reduced sulfur compounds appear to represent the major electron donors for aerobic microbial metabolism, although methane-, hydrogen-, iron-, and manganese-oxidizing bacteria are also locally important (Jannasch and Mottl, 1985). Methanogenic, acetogenic, and sulfur-reducing bacteria commonly occupy anoxic niches where  $\text{CO}_2$  and  $\text{H}_2$  are present (Baross et al., 1982; Harmsen et al., 1997).

These mixed bacterial communities interact diversely with their surrounding aqueous environment. Passive interactions occur when microorganisms behave as a solid-phase sorbents for dissolved ions. This behavior stems from bacterial cells having high surface area to volume ratios (Beveridge, 1988) and exceptionally reactive surfaces comprising exposed anionic functional groups (Beveridge and Fyfe, 1985). Once bound to the cells, these metals reduce the activation energy barriers to heterogeneous nucleation by providing sites where additional ions can be sorbed and authigenic minerals are formed (Ferris, 1997; Fortin et al., 1997; Konhauser, 1997, 1998). Conversely, some bacteria actively promote mineral formation by producing metabolic end products (e.g.,  $\text{OH}^-$ ,  $\text{CO}_2$ ,  $\text{H}^+$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{S}$ ) that react with dissolved metal ions, leading to supersaturation (Thompson and Ferris, 1990; Fortin and Beveridge, 1997), or they produce enzyme-mediated changes in redox state (e.g., oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ) (Ghiorse and Ehrlich, 1992). In this regard bacteria catalyze reactions that are kinetically slow, or even thermodynamically unfeasible prior to their intervention, and hence induce mineral growth under potentially unfavorable conditions (Ehrlich, 1996). The biogenically formed minerals have crystal habits and chemical compositions similar to those produced by precipitation from inorganic solutions since they are governed by the same equilibrium principles that control mineralization of their inorganic counterparts.

#### *Iron Hydroxides*

In terrestrial hot springs, the presence of iron hydroxide, ir

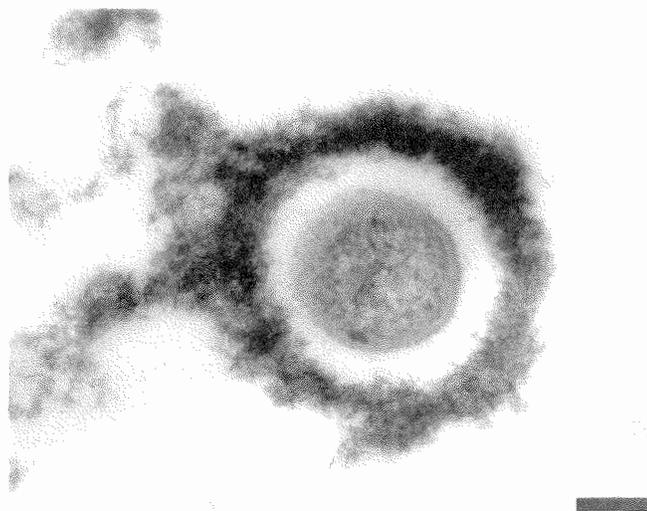


FIG. 1.—Transmission electron micrograph (TEM) of an epilithic bacterial cell from a hot spring effluent channel at Lýsuhóll, Iceland. The bacterial cell is surrounded by a dense, iron-rich capsule consisting of amorphous ferric hydroxide. Scale bar = 140 nm.

association with microbial mats, has been reported from geothermal areas in Iceland (Holm, 1987; Konhauser and Ferris, 1996) and Yellowstone National Park (Ferris et al., 1986). At Húsatóttir, Iceland, samples of Fe(III) precipitate were taken from the bottom of a drilled well (80 m in depth) used to pump low-temperature (12°C) geothermal water (Holm, 1987). Microscopic analysis revealed that the iron precipitate consisted mainly of living cells, stalks, and other remains of *Gallionella ferruginea*. On 1 mg of dry precipitate dispersed in 1 ml of water, the total living cell count of *Gallionella ferruginea* was  $2 \times 10^8$  cells (Holm, 1987). Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) of microbial mats growing in hot spring outflow channels of Lýsuhóll, Iceland, indicated a highly mineralized bacterial community (Konhauser and Ferris, 1996). Individual bacterial cells (Fig. 1) or microcolonies were frequently observed surrounded by an iron-rich capsule (a hydrated polysaccharide material that is naturally anionic and has great potential for scavenging metals). In Lýsuhóll, precipitation of iron phases was not restricted to cells with encapsulating material; the partial and complete encrustation of some bacterial cells by fine-grained (<100 nm in diameter) spheroids composed of amorphous ferric hydroxide were also observed. Other cells underwent intracellular mineralization so that the cytoplasm was completely replaced with amorphous iron hydroxide once the cell had lysed.

In marine hydrothermal environments, Fe-hydroxides are commonly precipitated in the region immediately surrounding the vent, the peripheral sediments, and the hydrothermal plume (Karl et al., 1988; Juniper and Tebo, 1995). Baross and Deming (1985) provided evidence that at an active black smoker from the East Pacific Rise, iron was deposited in significantly greater amounts on rock surfaces covered with microbial mats than on uncolonized rocks. Electron microscopic examination of vestimentiferan tubes at two chimneys on the southern Juan de Fuca Ridge (Fig. 2) revealed diverse unicellular and filamentous bac-

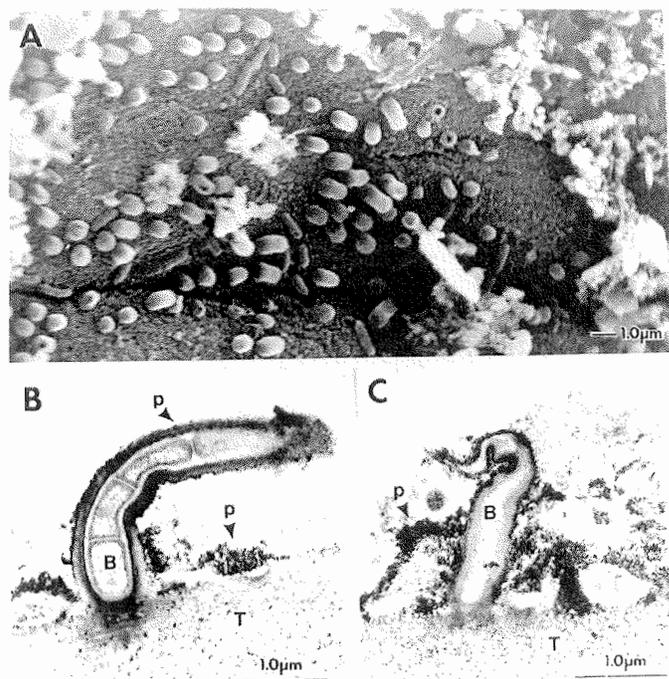


FIG. 2.—Electron micrographs of vestimentiferan tubes from a site of Fe-oxide encrustation on the southern Juan de Fuca Ridge. (A) Scanning electron micrograph (SEM) of the tube surface with light colonization by sheathed bacteria. (B) TEM photo showing Fe particle (p) accumulation on sheath of bacterium (B) attached to the tube surface (T). (C) Extensive Fe particle accumulation in unorganized extracellular slime surrounding the bacterium. Reprinted with permission of the author and CRC Press (Juniper and Tebo, 1995).

teria colonizing the tube surfaces where they accumulated iron hydroxide (as Fe-rich spheres 6–8  $\mu\text{m}$  in diameter) around their sheaths (Tunnicliffe and Fontaine, 1987). These spheres were shown to eventually coalesce to form a continuous crust in both vertical and horizontal dimensions. The sequence of formation suggests that iron was initially adsorbed to reactive organic sites on the cells, but that further iron accumulation may have resulted autocatalytically (Tunnicliffe and Fontaine, 1987). Extensive deposits of biogenic ferric hydroxide have also been described from the surface sediments of the ancient caldera of Santorini, Aegean Sea. Hanert (1973) and Holm (1987) both found Fe-encrusted stalks of *Gallionella ferruginea* occurring in such masses that the activity and importance of this bacterium in iron sedimentation was unquestionable. In deep hydrothermal areas, iron hydroxides were found to form on bacterial filaments growing in mud deposits at the Larson and Red Seamounts, near 21°N, East Pacific Rise (Alt, 1986, 1988) and on the Loihi Seamount, Hawaii (Karl et al., 1988, 1989). Because the mud consisted essentially of bacterial filaments, and the hydrothermal waters in which these deposits formed were slightly acidic (pH 5 to 6) and low in dissolved  $\text{O}_2$  (spontaneous oxidation of ferrous to ferric iron would be very slow under these conditions), biologically catalyzed precipitation was clearly favored over abiotic oxidation processes (Juniper and Tebo, 1995).

The microbial precipitation of ferric hydroxide (e.g., ferrihydrite) can occur both passively and actively. In the first instance, the oxidation and hydrolysis of cell-bound ferrous iron or the binding of ferric species [e.g.,  $\text{Fe}(\text{OH})^{2+}$ ,  $\text{Fe}(\text{OH})_2^+$ ] and

cationic colloidal species [e.g.,  $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})_5(\text{OH})^{2+}$ ] to negatively charged polymers (MacRae and Edwards, 1972; Ferris et al., 1989) can result in ferric iron deposition. Alternatively, ferrous iron transported into an oxygenated environment spontaneously reacts with dissolved oxygen (at circumneutral pH) to precipitate rapidly as ferric hydroxide on available nucleation sites. Bacteria passively act as such sites, and over a short period of time the microbial mats can become completely encrusted in amorphous iron as abiological surface catalysis accelerates the rate of mineral precipitation (Ghiorse, 1984). It has even been suggested that under circumneutral pH any bacterium that produces acidic, extracellular polymers will nonspecifically adsorb positively charged Fe-hydroxides (Ghiorse, 1984). This is due to the point of zero charge (pH where the mineral has zero charge) of amorphous Fe-hydroxides (e.g., ferrihydrite) being in the range of 5.3 to 7.5 for natural samples (Schwertmann and Fechter, 1982), which thereby allows reactive organic sites to scavenge ferric iron from the surrounding waters. The growth of iron-depositing microbial populations in environments where they are constantly covered in amorphous iron hydroxide suggests that these sites must also provide the bacteria with favorable growth conditions. Quite possibly the continual supply of iron, as well as the trace metals and anions that adsorb or coprecipitate directly onto iron hydroxides (German et al., 1991), may serve as an ideal nutrient source in close proximity to the cells.

The active process by which iron hydroxides form stems from the metabolism of Fe(II)-oxidizing bacteria that derive energy from the biological oxidation of Fe(II) to Fe(III) for the fixation of carbon from carbon dioxide dissolved in water (Ehrlich, 1990). At neutral pH, Fe(II) oxidation by *Gallionella* genera occurs under partially reduced conditions of 0.1–1 mg of  $\text{O}_2$  per liter (Ehrlich, 1990). The existence of these microaerophilic bacteria relies on their oxidizing efficiency relative to abiotic oxidation at low-oxygen fugacity. Because very little energy is generated in the oxidation of ferrous to ferric iron, these microaerophilic bacteria must oxidize large quantities of iron to grow (Lees et al., 1969). Consequently, even a small number of bacteria can be responsible for precipitating vast amounts of iron (Brock et al., 1984). Ferrous iron has also been observed to undergo microbial oxidation under anoxygenic conditions. Widdel et al. (1993) and Ehrenreich and Widdel (1994) have described purple, nonsulfur bacteria that combined ferrous iron oxidation with  $\text{CO}_2$  fixation for cellular material, with light as the energy source. Ferrous iron oxidation took place on the outer membrane so that the insoluble ferric hydroxide remained outside of the cell (Ehrenreich and Widdel, 1994). Straub et al. (1996) also demonstrated that the biological oxidation of ferrous iron, in the absence of oxygen, was possible by light-independent, chemotrophic activity with nitrate as the electron acceptor.

Once the primary iron hydroxides are precipitated and incorporated into the sediment, several diagenetic reactions can subsequently alter their mineralogies, textures, and structures. The transformation of ferric hydroxide into hematite takes place through internal aggregation and rearrangement (Cornell et al., 1987), and in marine sediments, its formation is favored under

high temperatures and low organic matter content (Schwertmann and Fitzpatrick, 1992). However, the observed presence of a mixed ferric hydroxide/hematite assemblage on bacterial cells, in present-day biofilms, suggests that this process may also occur rapidly at surface conditions (Ferris et al., 1989; Sawicki et al., 1995). Dissimilatory Fe(III)-reducing bacteria have been shown to produce magnetite under anaerobic conditions, as a by-product during the oxidation of organic compounds coupled with the reduction of poorly crystalline, Fe(III) oxide (Lovley, 1991). For example, in hydrothermal sediments located 25 km from the East Pacific Rise, authigenic magnetite was recovered at the redoxline between Fe-oxidizing to Fe-reducing conditions (Karlin et al., 1987). The formation of siderite in marine sediments has also been shown to result from the ability of bacteria (e.g., *Desulfovibrio* sp.) to release ferrous iron, via bacterial Fe(III)-reduction, into waters with excess seawater bicarbonate (Coleman et al., 1993). In deep sediment from Santorini, beneath the iron hydroxide layers, siderite was identified as a by-product of microbial diagenesis (Holm, 1987).

### *Amorphous Silica*

The close association of microorganisms with amorphous silica has been reported from a variety of hot springs, including Yellowstone National Park (Walter et al., 1972; Walter, 1976; Ferris et al., 1986; Hinman and Lindstrom, 1996); Taupo Volcanic Zone, New Zealand (Jones et al., 1997a, b); Kenya Rift (Jones and Renaut, 1996); El Tatio, Chile (Jones and Renaut, 1997); and Geysir, Iceland (Schultze-Lam et al., 1995; Konhauser and Ferris, 1996). The role of microorganisms in silica precipitation at hot springs generally has been considered a passive process (Walter et al., 1972), in that rapid cooling at ambient air temperatures, evaporation and/or steam loss, and a change in pH of the hydrothermal waters following discharge can all induce silicification of growing cells (Fournier, 1985). However, several recent studies using electron microscopy have shown that microorganisms provide favorable nucleation sites that serve as templates for silicification. In sediments from Yellowstone, Ferris et al. (1986) observed individual bacterial cells preserved in successive stages of amorphous silica encrustation; some cells were thoroughly embedded in a mineralized matrix. In New Zealand, bacterial filaments were similarly encrusted by amorphous silica (Jones et al., 1997a, b). That microorganisms catalyze silica precipitation was confirmed through analyses of microbial mats growing around a hot spring vent in Geysir, Iceland, where filamentous phototrophic bacteria resembling *Chloroflexus aurantiacus*, and the unicellular cyanobacterium *Synechococcus* sp., underwent rapid silicification (Schultze-Lam et al., 1995; Konhauser and Ferris, 1996). The mineralization associated with the cells occurred as spheroidal grains (200–500 nm in diameter) both extracellularly on the sheaths of living bacteria and intracellularly within the cytoplasm presumably after the cells had lysed. In many filaments, the silica crystallites appeared to have coalesced such that individual precipitates were no longer distinguishable (Fig. 3); entire colonies sometimes became cemented together in a

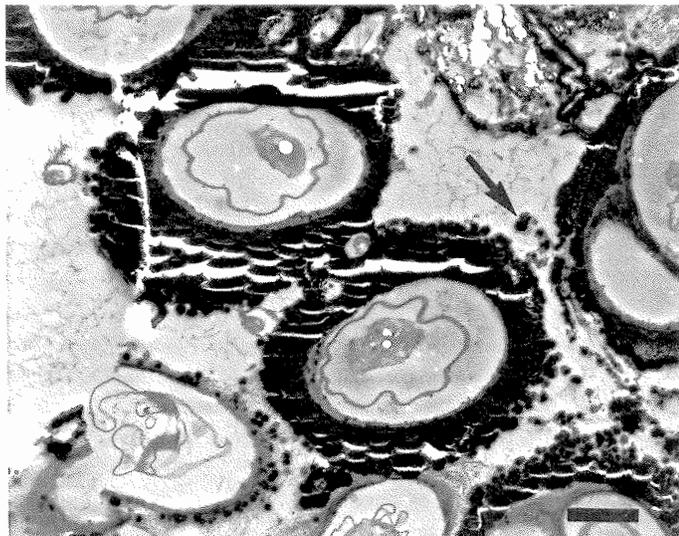


FIG. 3.—TEM image of a colony of filamentous bacteria (from Geysir, Iceland) with epicellular amorphous silica on outer sheath surfaces. Note the presence of a few discernible spheres on the outer edges on the mineralized matrix (arrow). Scale bar = 1.1  $\mu\text{m}$ .

siliceous matrix several micrometers thick (Konhauser and Ferris, 1996). Eventually only the sheath and cell wall of the original organic framework remained recognizable. Thus, it appears that silicification begins when the microorganisms are living (i.e., they serve as nucleation sites) and continues for some time after their death. In the latter stages of silicification, the development of amorphous silica cement between silicified microbial filaments is presumably abiogenic (Jones et al., 1997a). Silicification has also been shown to occur in thermal springs in the Kenya Rift where water temperatures reach above 30°C, temperatures too high to support cyanobacteria and most bacteria. Instead, hyperthermophilic bacteria were shown to survive in this extreme environment, preferentially fixing silica onto secreted microbial mucus (Jones and Renaut, 1996).

In a hydrothermal venting site with talus piles on the wall of a graben at 21°30'S, East Pacific Rise, hot water mixes with seawater in the talus piles producing sulfide and amorphous silica deposits (Juniper and Fouquet, 1988). Upon magnification, the silica crust revealed a filamentous microtexture in which individual filaments were cemented together. Figure 4 shows a section of such a filament heavily coated in concentric layers of deposited silica, with the hollow space likely representing the original bacterial cell (Juniper and Fouquet, 1988).

Based on findings attained from studies on the silicification of wood (Leo and Barghoorn, 1976; Sigleo, 1978), the association of silica with microbial surfaces is probably established by hydrogen bonding of the hydroxyl groups in silicic acid  $[\text{Si}(\text{OH})_4]$  to available hydroxy groups of the bacterial sheath (Ferris et al., 1988). Continued reaction of the bound silica with more silicic acid, from the surrounding waters, results in polymerization and eventual dehydration, which leads to the formation of silica crystallites (Iler, 1980). Results from artificial ossification studies on microorganisms have confirmed that bacteria can be completely silicified (Oehler and Schopf, 1971; Francis et al., 1978; Westall et al., 1995), with the preferential

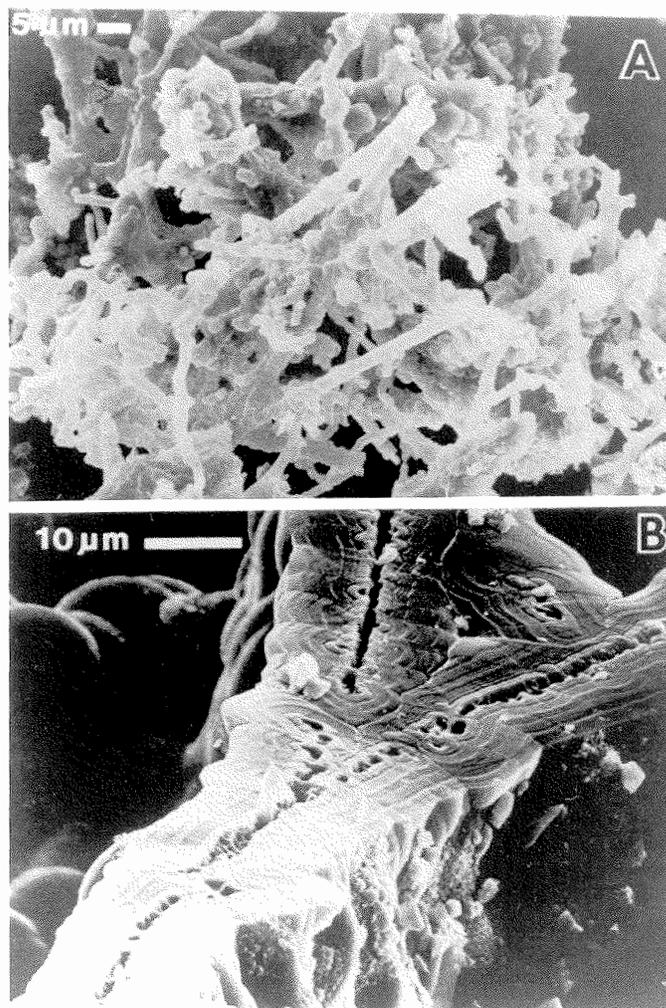


FIG. 4.—(A) Low-magnification SEM photo showing filamentous microtexture of hydrothermal deposits (from 21°30'S, East Pacific Rise). (B) Section of a filament heavily coated in silica. The hollow internal space likely represents the original filament that was covered in concentric layers of deposited silica. Reprinted with permission of the author and *Canadian Mineralogist* (Juniper and Fouquet, 1988).

preservation of cell walls and sheaths (Oehler, 1976). Ferris et al. (1988) have also shown the rapid development of silica crystallites on cellular debris following cell lysis. Evidently, lysed microorganisms continue to serve as templates for silica deposition, with cellular degradation enhancing the mineralization process by increasing the availability of functional groups capable of forming hydrogen bonds with dissolved silica (Knoll, 1985; Ferris et al., 1988). General features of increasing silicification with time include thickening of silica crusts around the bacteria, increasing crystallization of the silica from loose aggregates into dense spheres, and eventually the formation of a mammillated external crust (Westall et al., 1995). Interestingly, pretreatment of cells with iron appeared to denature their autolytic enzymes, thus maintaining intact organic residues during silicification (Ferris et al., 1988).

### Iron Silicates

Bacterial cells, associated with granular and spheroidal crystallites composed exclusively of iron and silica, have been examined from acidic hot spring sediments from Yellowstone National Park, USA (Ferris et al., 1986) and from mats growing in hot spring outflow channels, Krisuvik, Iceland (Konhauser and Ferris, 1996). In the Yellowstone samples, both intact and lysed cells were mineralized, with grains typically smaller than 100 nm (Ferris et al., 1986); one cell that appeared to have undergone an extended episode of iron-silica growth and compaction had an interlocking mosaic that completely encrusted the microorganism. In Krisuvik, bacterial cells were associated with diverse mineral assemblages (Konhauser and Ferris, 1996). In some cells several spheroidal grains (~200 nm) were shown to be embedded in dense Fe-rich capsular material. In other cells from the same sample site, larger amorphous precipitates (~500 nm), consisting of iron and silica in approximately equal proportions, were evident directly on the cell wall (Fig. 5).

Iron-silica deposits have also been identified from various deep-sea hydrothermal sites. One active site at the Philosopher Vent on Explorer Ridge in the northwest Pacific had iron-silica deposits forming with a filamentous morphology (Juniper and Fouquet, 1988). The resemblance of these filaments to those produced by microorganisms, along with the presence of organic carbon (1.3%) and filamentous bacteria (from one vent sample), suggested that bacteria provided substrata for mineral nucleation. Transmitted light microscopy of these iron-silica deposits further identified intense iron accumulation on the filaments, upon which silica precipitated (Fig. 6). Extensive accumulation of microbial-mineral flocs (dominated by iron and silica oxides) were also observed in association with abundant diffuse venting in new lava flows and around less extensive, new venting on older basalt in the CoAxial Segment of the Juan de Fuca Ridge (Juniper et al., 1995). The presence of filaments (resembling *Leptothrix* sp.) in nontronite deposits (Fe-rich smectite) from seamounts in the East Pacific Rise (Alt, 1988),

and the distinct microtube-like morphology in nontronite deposits from white smoker chimneys in the Galapagos Rift and Mariana Trough (Köhler et al., 1994), also suggest that bacteria are directly involved in catalyzing clay mineral formation.

The precipitation of iron-silicate phases closely follows the two-step mineralization process originally described by Beveridge and Murray (1976), in that iron is initially bound to anionic cellular sites, after which dissolved silica is added to the growing mineral via hydrogen bonding between hydroxyl groups. The Fe-rich sites on the cell surface presumably serve as precursors to the more complex surface precipitates, with the iron-silicates using some fraction of the precursor surface as a template for their own growth, in effect circumventing the need for direct nucleation (Steefel and Van Cappellen, 1990). This sequence of reactions appears to correspond with previous theories of hydrothermal nontronite formation that suggested these clays formed either by sorption of silica onto Fe-oxyhydroxides or directly through precipitation from hydrothermal fluids (Köhler et al., 1994).

Experimental work has also confirmed the ability of bacterial cells to form iron-silicate minerals. Silicate anion binding to bacteria was enhanced when the cell walls were preloaded with Fe(III), indicating that the metal participated in a cationic bridging mechanism for silicate binding to the bacterial surface through the formation of ternary complexes (e.g., wall-metal-silicate) (Urrutia and Beveridge, 1993, 1994). Growth of the precipitates then continued until complex silicate structures were formed.

### DISCUSSION

There are three similarities between present-day hydrothermal systems and Precambrian oceans that support this paper's contention that modern bacterial biomineralization may provide small-scale analogues to the conditions under which BIFs were

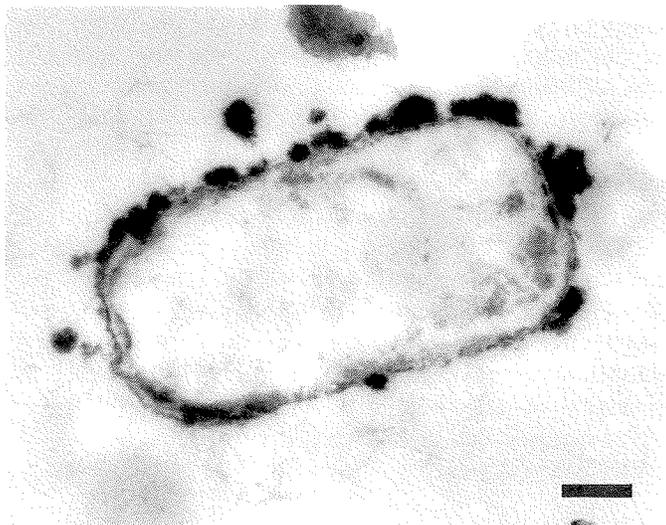


FIG. 5.—TEM image of a bacterial cell from Krisuvik, Iceland, with amorphous iron-silicate grains on the outer cell wall. Scale bar = 200 nm.

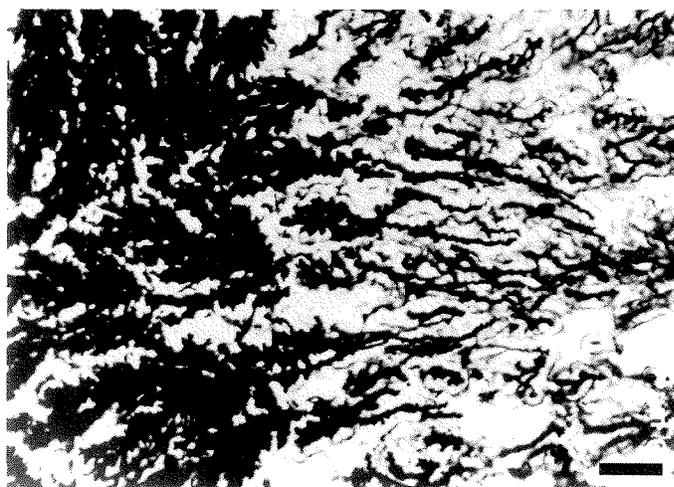


FIG. 6.—Transmitted light microscopy image of the filament-mineral association in iron-silica deposits in a chimney fragment from 12°50'N, East Pacific Rise. The transition from iron-rich (dark) to silica-rich (light) over a distance of 2 mm is shown. Scale bar = 2 μm. Reprinted with permission of the author and *Canadian Mineralogist* (Juniper and Fouquet, 1988).

deposited. First, modern deep-sea vents and hot springs are characterized by the release of warm to hot reducing solutions with high elemental concentrations (Corliss et al., 1979; Henley, 1984). For example, effluent collected from vents along the Mid-Atlantic Ridge and the East Pacific Rise contained dissolved silica and iron (averaging between the two sites) approximately 1,100 ppm and 100 ppm, respectively (Campbell et al., 1988). These values are approximately 1,000 times and 50,000 times greater than concentrations for silica and iron, respectively, in background marine waters (Drever, 1988). Similarly, hot spring effluents (from a variety of sites globally) have dissolved silica concentrations typically exceeding 200 ppm, with some geothermal wells having up to 1,100 ppm (Henley, 1984), while iron concentrations range from 0.8 ppm (Lýsuhóll, Iceland) (Konhauser and Ferris, 1996) to 2.4 ppm (Mammoth Springs, Yellowstone) (Fournier, 1989). The combination of high dissolved iron and silica are unique to hydrothermal systems, and are analogous to conditions in much of the Precambrian, when ocean chemistry was controlled by the interaction of warm seawater with the basaltic oceanic crust (Veizer et al., 1982). In the Archean and early Proterozoic, hydrothermal effluent was transported from the deep sea into the oxic surface waters by unusual geostrophic or wind-driven upwelling (Lowe, 1994) or directly by hydrothermal plumes generated at mid-ocean ridge crests with substantially shallower depths than present (Isley, 1995). This led to surface seawater with high metal concentrations, perhaps up to 250 ppm iron (Veizer, 1983), and silica concentrations close to or at saturation (~120 ppm) with respect to amorphous silica (Siever, 1992).

Secondly, a consortium of microorganisms are currently present in hot springs and deep-sea vents, some of which resemble those found as Precambrian microfossils, including cyanobacteria, anoxygenic phototrophic bacteria, and iron-depositing bacteria. There are several morphological lines of evidence that suggest that cyanobacteria existed at 3.5 Ga (Awramik, 1992), including the presence, in rocks from the Warrawoona Group (~3.5 Ga), of trichome-like filaments (Awramik et al., 1983); microfossils with widths greater than most filamentous bacteria (Schopf, 1993); and coccoïd forms enclosed in a wall-like structure (Schopf and Packer, 1987). The existence of stromatolites (presumed to have formed in shallow, near-shore marine settings) further implies the presence of cyanobacteria, since the microorganisms that formed them were phototactic, photoautotrophic, and produced mucus sheaths, all attributes found in present-day cyanobacteria (Awramik, 1992). In addition to cyanobacteria, mats formed by sulfide-dependent, phototrophic bacteria (e.g., *Chloroflexus* sp.), and possibly sulfur-oxidizing bacteria such as *Beggiatoa* sp., may also have been locally abundant in the Precambrian (Doemel and Brock, 1977; Walter et al., 1972, 1992). Lastly, the presence of thread-like structures in chert from the Gunflint Iron Formation, Ontario (aged ~ 2.0 Ga) that resemble filamentous iron-depositing bacteria such as *Crenothrix* sp., *Sphaerotilus* sp., and *Leptothrix* sp., additionally suggests the presence of bacteria that were involved in the oxidation of ferrous to ferric iron (Barghoorn and Tyler, 1965; Cloud, 1965).

The resemblance of a wide consortia of early Precambrian

microorganisms to those existing today is not surprising. During that period in Earth's history, when major BIFs were accumulating, microorganisms were already flourishing, with nearly all prokaryotic phyla having by that time evolved and diversified (Awramik, 1992). This view is supported by the presence of fossilized microbial remains, stromatolites, chemical fossils, and biogenic minerals reported from early Archean rocks (Lowe, 1980; Awramik et al., 1983; Hayes et al., 1983; Ohmoto et al., 1993), some at least 3.8 Ga (Mojzsis et al., 1996). In fact, the construction of stromatolites by 3.5 Ga implies that these microbes were morphologically well-developed by that time (Awramik, 1992; McNamara and Awramik, 1992).

The third similarity reflects the common occurrence of iron and silicate minerals around modern hydrothermal vents and their presence as primary mineralized constituents of BIFs. Iron hydroxides and amorphous silica are the predominant mineral phases that precipitate around low-temperature, sulfide-deficient, deep-sea vents, where they can form centimeter-thick layers (by diffuse venting through underlying basalts or sulfides), oxide muds, and chimney structures (Juniper and Tebo, 1995). At hot springs, iron and silicate biominerals are also observed, sometimes displaying crude microbanding (K.O. Konhauser, in prep., 2000) reminiscent of the very finely laminated iron-chert beds in, for example, the Hamersley BIF (Morris, 1993).

As discussed above, bacteria contribute to the precipitation of authigenic minerals in modern hydrothermal systems. Herein lies the premise of this paper. If microorganisms are present today in hydrothermal environments, and if they precipitate iron and silicate minerals, then it seems reasonable to argue that Precambrian bacterial populations, also growing in hydrothermal waters, could have formed similar biominerals, i.e., the primary minerals in BIFs. I speculate that previous models for BIF deposition (discussed below) have underestimated the role of microorganisms in the deposition of BIFs. In this new hypothesis, bacteria, growing in the Precambrian oceans, may have served as nucleation sites that catalyzed primary iron and silica mineralization.

In the early Precambrian, biological activity was probably limited to the flat margins of the microcontinents, where microorganisms grew as benthic mats or in the open ocean above areas of dynamic upwelling of deep, nutrient-rich waters or hydrothermal plumes (Lowe, 1994). The planktonic microorganisms presumably flourished when ferrous iron and nutrients were available, allowing them to form iron hydroxides, but they declined in numbers (no mineralization period) when these components became depleted (Cloud, 1973; Baur et al., 1985). It is unclear what proportion of the ferric iron was initially produced in the Archean via photochemical processes (Cairns-Smith, 1978; Braterman et al., 1983; François, 1986), anoxygenic photosynthesis (Widdel et al., 1993; Ehrenreich and Widdel, 1994), photodissociation of water vapor in the atmosphere, generating free oxygen to react with ferrous iron (Walker et al., 1983), or oxygenic photosynthesis (Cloud, 1965, and many others). In a large part it will depend on when cyanobacteria came into existence. If they existed as early as 3.5 Ga (Awramik, 1992), then these microorganisms would certainly have had a major impact on the initial production of oxygen

(Cloud, 1965, 1973). Because the initial O<sub>2</sub> partial pressures may have been extremely low (Walker et al., 1983), bacteria would not have been able to gain energy from oxidation of Fe(II) to Fe(III) with O<sub>2</sub> as an electron acceptor, using instead energy sources such as sunlight to oxidize Fe (Ehrlich, 1990). As O<sub>2</sub> partial pressures increased beyond some threshold concentration, oxidation by microaerophilic bacteria such as *Gallionella* sp. would have become possible and perhaps even favored (under low pO<sub>2</sub>) compared to inorganic oxidation of Fe(II) (Holm, 1987).

The end result of any of these modes of biomineralization would be the precipitation of ferric hydroxide in the water column, its sedimentation, and the systematic accumulation of iron-rich sediment on the ocean floor (Walker et al., 1983). Along with ferric iron, the remains of the microorganism would be deposited. This is suggested by the common presence of spheroidal structures in BIFs, which have been interpreted as relict microfossils (Cloud and Licari, 1968; LaBerge, 1973). Once deposited, the ferric hydroxide eventually would have consolidated as (i) hematite, where oxidizing conditions were maintained in the sediment or organic material was limited; (ii) as magnetite, where partial Fe-reduction occurred in the sediments by microbial organic matter mineralization; or (iii) as siderite/ferrous silicate when substantial Fe-reduction occurred (Morris, 1993). Magnetite and siderite are both major components in iron-oxide facies and S-macrobands, respectively (Ewers and Morris, 1981), and their presence suggests that a significant fraction of BIFs were diagenetically modified under suboxic to anoxic conditions (Walker et al., 1983). That the latter diagenetic reactions were microbially catalyzed is suggested by isotopically light  $\delta^{13}\text{C}$  values in BIF carbonate minerals (Perry et al., 1973; Baur et al., 1985), which implies that isotopically light organic carbon in the bottom sediments was oxidized to bicarbonate with the concomitant reduction of some electron acceptor, presumably ferric iron (Walker, 1984). This oxidation may also explain the absence of organic matter in BIFs. The by-product of Fe-reduction could be either magnetite, commonly evident as overgrowths on hematite (Morris, 1980), or siderite, which is present in the Gunflint Iron Formation, Canada, for example, as uniform, spherical grains (approximately 30–40  $\mu\text{m}$  in diameter) with organic-rich cores (Goodwin, 1956). This correlates well with the suggestion that during the hundreds of millions of years when ferric iron was being deposited and organic matter accumulated in the sediment, that a simple respiratory chain to ferric iron developed and eventually served as a precursor to more complex respiratory chains associated with extant organisms (Nealson and Myers, 1990).

The fundamental differences between mineralization in present-day hydrothermal environments and the Precambrian oceans are (i) the size of the deposits and (ii) the relationship between the microorganisms and the chemocline (where anoxic, ferrous-rich waters meet oxygenated surface waters). In the first instance, the oxygenated conditions on the ocean floor today preclude the formation of large-scale deposits in modern hydrothermal environments. Mineral precipitation occurs peripheral to the vent, where anoxic hydrothermal fluids are

mixed with oxygenated deep-sea waters (Juniper and Tebo, 1995). In the presence of oxygen and at pH~8 (the half-life of ferrous iron being only a few minutes, Millero et al., 1987), ferrous iron is rapidly oxidized to ferric iron and precipitated as ferric hydroxide (Schwertmann and Fitzpatrick, 1992). Even if the hydrothermal effluent is hot (giving low oxygen solubility) and acidic, and the surrounding ambient ocean bottom waters are low in dissolved O<sub>2</sub>, ferric hydroxides still accumulate in relative proximity to the vents, with a gradual depletion outwards (Juniper and Tebo, 1995). Thus, high concentrations of ferrous iron are not found in modern marine waters. Similarly, in hot spring effluents there is an almost immediate precipitation of ferric hydroxide near the geyser. In contrast, the anoxic bottom waters of the Precambrian oceans allowed for iron to dissipate greater distances away from the vent, and subsequently precipitate out of solution in the deep oceans during the Archean or in huge basinal areas (e.g., 100,000 km<sup>2</sup> for the Hamersley Group, Trendall and Blockley, 1970) during the Proterozoic (Beukes and Klein, 1992; Simonson and Hassler, 1996). Precipitation occurred over hundreds of millions of years as the oceans became increasingly oxygenated, and it was only when the rate of photosynthetic oxygen production exceeded the rate of supply of ferrous iron that it became substantially depleted in marine waters and free oxygen accumulated (Walker et al., 1983). Based on the oxidation state of paleosols, the nature of uranium ores, the presence of red-beds, trace metal content in black shales, and the evolution of eukaryotes, this may not have occurred until after 2.2 Ga (Holland, 1994).

The second key difference between present-day hydrothermal environments and those under which BIFs were deposited is that today, extant microorganisms, growing as mats in hot spring effluent or on vent chimneys and in surrounding marine sediments, are found at the chemocline. In the Precambrian, however, biomineralization was removed from the site of hydrothermal emissions, allowing the “biogenic” deposits to form thick accumulations of great lateral extent. The disparity is due to radically different conditions on the early Earth. The Archean (at the time 3.5–3.2 Ga) was characterized by high rates of mantle outgassing, limited chemical weathering, elevated atmospheric CO<sub>2</sub> levels and surface temperatures of perhaps 30–50°C that prevented the accumulation of polar ice, cold-water sinking, and deep ocean stirring (Lowe, 1994). The Archean oceans were thus strongly stratified with a shallow, wind-mixed surface layer containing dissolved CO<sub>2</sub> and small amounts of O<sub>2</sub>, which were derived from oxygenic photosynthesis in areas of high planktonic productivity (Cloud, 1965, 1973; Schidlowski, 1976), and from photochemical processes that dissociate water vapor (Walker et al., 1983). The deeper, reducing waters were enriched in ferrous iron (Klein and Beukes, 1989; Beukes et al., 1990; Beukes and Klein, 1992).

The distribution of Archean iron-formations suggests that these relatively small deposits (compared to Proterozoic BIFs) were ubiquitous in deep water, not overwhelmed by coarse clastic debris (Lowe, 1994), and presumably represented local accumulations close to marine vents (Simonson and Hassler, 1996). The relative absence of shallow-water BIFs indicates that the upper, wind-mixed layer of the ocean contained little dissolved

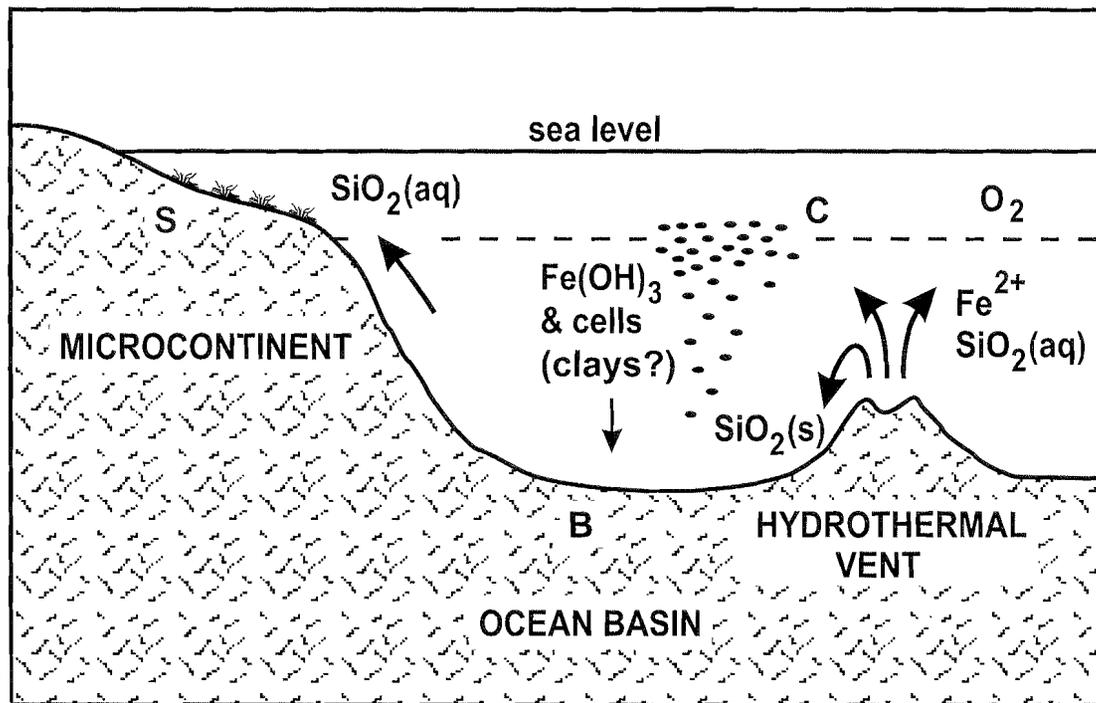


FIG. 7.—Schematic diagram of the Archean environment, modified from Lowe (1994). The Archean oceans were strongly stratified with a shallow surface layer containing small amounts of oxygen, while the deeper reducing waters were enriched in ferrous iron. Benthic mats grew on the shallow sediments of the microcontinental shelf (S), while bacterial plankton grew in the open ocean above areas of dynamic upwelling or hydrothermal plumes. At the chemocline (C), ferric hydroxide precipitation was catalyzed by plankton through binding of cationic iron onto their cells; the source of the ferric iron was a combination of photochemical processes, anoxygenic or oxygenic photosynthesis. Thus, all iron was removed from the deep waters before it spread onto the shelf. Upon death, these iron-rich cells accumulated in the bottom sediments (B), where diagenetic reactions associated with burial led to the transformation of ferric hydroxide into hematite, magnetite, or siderite. Iron deposition may have been episodic due to fluctuating nutrient supplies for the overlying plankton. Precipitation of silica occurred on the ocean floor due to pressure/temperature changes after venting. At the chemocline, some silica may also have reacted with cell-bound iron to form clay-like phases. The remaining dissolved silica was transported onto the shelf, where silica supersaturation (via evaporation) allowed microorganisms to induce silicification, leading to the formation of silicified stromatolites.

iron, quite possibly due to iron being removed from upwelling deep waters before it spread onto adjacent continental shelves (Lowe, 1994). This is reflected in Archean shallow water deposits that are depleted in iron (Beukes and Klein, 1992). Thus, it seems likely that in the Archean major BIFs would have formed above oceanic hydrothermal vents or in areas of upwelling, where ferrous iron and dissolved silica were brought into contact with oxygenated water at the chemocline (Beukes and Klein, 1992), yet below the level of the shallow continental shelf (Lowe, 1994). Plankton growing in the surface waters of the open ocean could have provided reactive sites to catalyze iron mineralization (Fig. 7). Quite possibly some of the cell-bound iron may also have reacted with dissolved silica, forming iron-silicate phases reminiscent of those formed today (Siever and Woodford, 1973; Siever, 1992). Such reactions would have kept dissolved silica concentrations in the open ocean below saturation with respect to amorphous silica (Knoll, 1985), although amorphous silica could have precipitated on the ocean floor due to the supersaturated conditions created by the sudden physical and chemical changes induced through venting. As iron was removed from the upwelled waters, the remaining Si-rich waters may have been transported onto the flat margins of the microcontinents where supersaturated conditions (via evaporation) would have allowed benthic microorganisms to induce silicification. That microorganisms may have facilitated this form of mineralization is evident from the associations of silicified

microfossils with ancient microbial mats and organic-rich mud, as represented by silicified stromatolites and carbonaceous cherts (Knoll, 1985). The lack of extant bacteria that actively control silica precipitation (i.e., in the manner of diatoms), and the natural and experimental studies that show silicate minerals commonly associated with microbial cells (when subject to high dissolved silica) suggest that it is possible to invoke a passive biological interpretation for Precambrian cherts, and hence BIFs.

The end of the Archean witnessed significant environmental changes, beginning with the formation of several large blocks of continental crust about 3.3–3.1 Ga, increased physical and chemical weathering, removal of  $\text{CO}_2$  from the atmosphere, and the subsequent deposition of large carbonate platforms by 2.6 Ga (Lowe, 1994). The shallow sea hosted enormous bacterial mats, which both consumed more  $\text{CO}_2$  through photosynthesis and released  $\text{O}_2$  to the atmosphere. The depletion of atmospheric  $\text{CO}_2$  by weathering, biological activity, and sedimentation on these new continental blocks was accompanied by the Huronian glaciation 2.4–2.1 Ga ago, which led to the formation of polar shelf ice, cold water sinking, and inevitably the mixing of ocean waters (Lowe, 1994). As the stratified ocean began to break down, ferrous iron and silica were actively transported onto the continental slopes and shallow shelves, leading to thick, laterally extensive BIF deposits (Simonson and Hassler, 1996), in waters ranging from 10–700 m (Isley, 1995). The lateral grading of BIFs into stromatolites or oolites, along with sedimentary

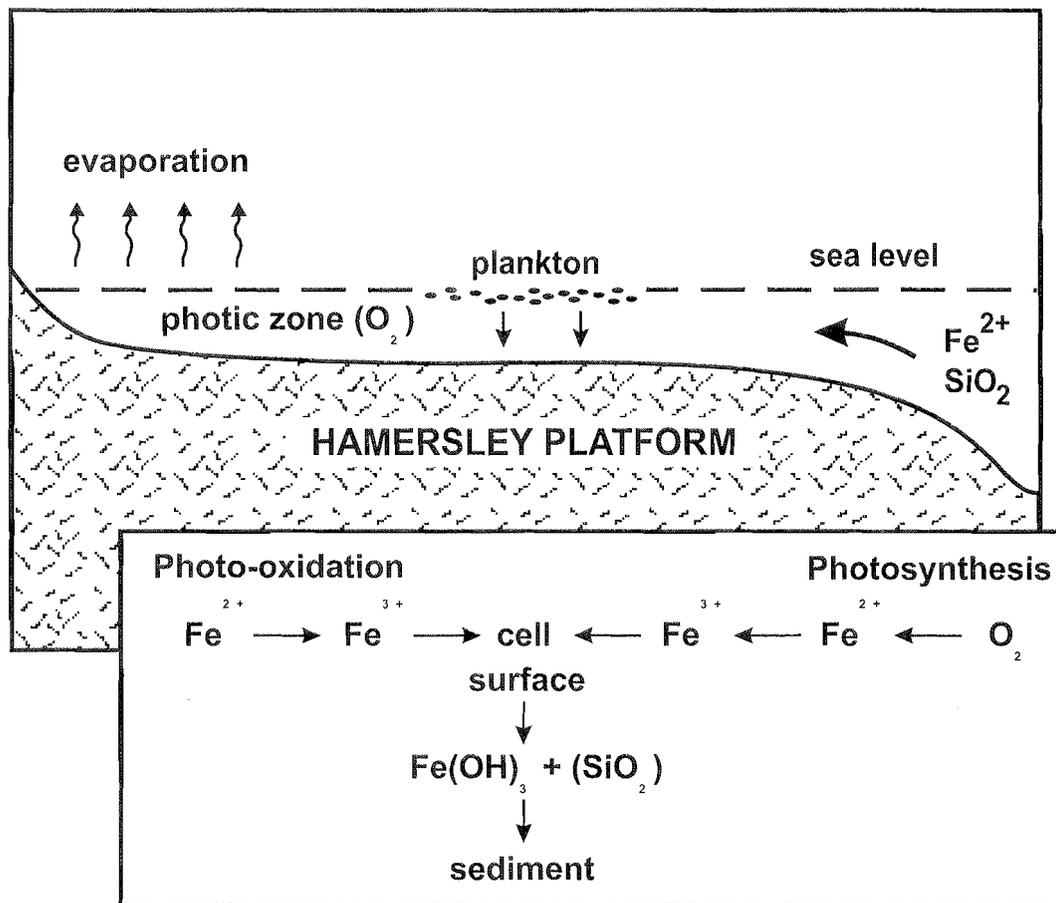


FIG. 8.—Schematic diagram of BIF deposition in the Proterozoic, modified from a genetic model of the Hamersley Group (~2.5 Ga) from Morris (1993). When the stratified ocean began to break down, ferrous iron and silica were transported onto the continental shelf. Upwelling also supplied nutrients to the depository, triggering a parallel growth of microorganisms. These bacterial communities subsequently served as passive nucleation sites for ferric iron deposition (as iron-rich mesobands) by catalyzing reactions rendered possible by supersaturated conditions developed at the chemocline (see inset). Within these iron oxide mesobands, the alternating Fe-rich and Si-rich microbands signified seasonal and climatic changes, with iron precipitated when upwelling currents recharged the depository with Fe(II) and nutrients, and amorphous silica precipitated due to evaporation on the shelf when iron was depleted.

structures consistent with wave agitation and shallow water deposition (Gole and Klein, 1981; Simonson, 1985), also confirms that paleodepositional depths had decreased. This transition may have been imposed by a transgressive sequence that inhibited siliciclastic input and shifted primary organic matter and carbonate production shoreward (Klein and Beukes, 1989; Beukes and Klein, 1992). The chemocline thus moved from the open oceans onto the continental shelves, thereby facilitating BIF deposition in these relatively shallow waters (Schissel and Aro, 1992; Simonson and Hassler, 1996).

According to a genetic model for the banded-iron formation of the Hamersley Group (~2.5 Ga), Morris and Horwitz (1983) and Morris (1993) proposed that during periods of vigorous and sustained mid-ocean ridge activity, which allowed high levels of Fe(II) to reach the continental shelf, the combined effects of photo-oxidation (which possibly included anoxygenic photosynthesis, Widdel et al., 1993; Ehrenreich and Widdel, 1994) and oxygenic photosynthesis in the Precambrian oceans caused ferric iron deposition and the formation of iron-rich mesobands (Fig. 8). Upwelling also supplied nutrients to the depository, triggering a parallel growth of microorganisms. If, as modern

hydrothermal systems suggest, bacteria have an important role as nucleation sites for the precipitation of minerals (Juniper and Tebo, 1995; Konhauser and Ferris, 1996), then it is possible that in the Precambrian, these bacterial communities also catalyzed the mineralization process. Within iron oxide mesobands, the alternating Fe-rich and Si-rich microbands further signified seasonal and climatic changes. Iron precipitated when upwelling currents recharged the depository with Fe(II) and nutrients, while amorphous silica precipitated due to evaporation on the shelf when iron was depleted. Si-levels likely reflected background surface ocean concentrations from a composite of sources including continental weathering and hydrothermal input. Superimposed on this background deposition were sustained periods of volcanicity which resulted in the Si-rich macrobands gradually returning to the normal Fe-oxide macrobands as volcanic input waned. Once the chemical stratification in the oceans broke down completely, they became completely mixed and depleted in iron, as is indicated by the general absence of major iron-formations after 1.8 Ga (Beukes and Klein, 1992).

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