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A REVIEW OF THE MICROBIAL GEOCHEMISTRY OF BANDED IRON-FORMATIONS

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ABSTRACT

The role of microorganisms in the deposition of banded iron-formations (BIF) has been discussed for many years, as it has been difficult to explain the accumulation of iron and silica in these deposits by chemical processes alone. In this paper, we survey the significance of the presence of microorganisms in microfossils and stromatolites associated with BIF. The requirements for the growth of bacteria are discussed. Microbially mediated geochemical processes involved in the deposition of iron and silica in these sediments are considered. The influence that microbial mats, hot springs, and deep-sea hydrothermal vents might have on current ideas in geochemistry also are examined. A recently discovered biofilm was able to sorb silica and precipitate iron both as hematite and siderite in close proximity; we suggest that the microbial reactions occurring in this biofilm could be similar to those that may have played a part in the deposition of BIF. Biofilms create microenvironments that allow the precipitation of minerals with distinctly different fields of stability. Since biomineralization can occur both by physico-chemical sorption and by metabolically induced reactions, such reactions could have played an important role in the deposition of iron and silica in BIF and in metalliferous sediments from the early Archean to the present day.

Keywords: banded iron-formations, biofilm, biomineralization, microbial reactions, microfossils, stromatolites.

SOMMAIRE

Le role des micro-organismes dans la déposition des formations de fer rubannées fait l'objet de discussions depuis plusieurs années, parce qu'il est difficile d'expliquer l'accumulation de fer et de silice dans ces gisements uniquement par processus chimiques. Dans ce travail, nous évaluons l'importance de la présence de micro-organismes dans les microfossiles et les stromatolites associés aux formations de fer. Nous passons en revue les exigeances des bactéries en croissance, ainsi que leur rôle dans les processus géochimiques menant à la déposition du fer et de la silice dans les structures géologiques. Nous examinons aussi l'influence qu'auraient pu avoir les colonies microbiennes, les sources thermales, et les évents hydrothermaux sous-marins. Une biopellicule découverte récemment, qui avait l'abilité d'absorber la silice et de précipiter le fer sous forme d'hématite et de sidérite dans le même milieu, nous fait penser que des réactions microbiennes semblables auraient pu jouer un rôle important dans la déposition des formations de fer. De tels biopellicules créent des micro-environnements qui permettent la précipitation de minéraux ayant des champs de stabilité nettement différents. Comme il est possible d'assurer une biominéralisation par sorption physicochimique et par réactions initiées par métabolisme d'organismes, de telles réactions pourraient avoir joué un rôle important dans la déposition du fer et de la silice dans les formations de fer et dans les sédiments métallifères depuis l'archéen précoce jusqu'à nos jours.

(Traduit par la Rédaction)

Mots-clés: formations de fer rubannées, biopellicule, biominéralisation, réactions microbiennes, microfossiles, stromatolites.

INTRODUCTION

Speculation on the various processes that produced the enormous concentrations of iron, silica and other metals in banded iron-formations (BIF) has stimulated research for many years, for it has been difficult to explain how such vast amounts of iron and silica could have been concentrated in sediments, notably during the Archean. Although there were various reports of the detection of stromatolites and microfossils by the turn of the century, it was not until Tyler's and Barghoorn's discovery in 1954 of coccoid and filamentous microfossils in the early Proterozoic Gunflint chert (~2.0 Ga old) that reports of microfossils in iron-formations have proliferated in the literature. The potential role of microorganisms in the genesis of metalliferous sediments, particularly in banded iron-formations, now provides an incentive for further research.

Bacterial activity has been demonstrated (Mann 1992) in the deposition of metals as well as in the weathering and leaching of rocks. Ferris *et al.* (1987) and Beveridge (1989) also have shown that bacteria are able to accumulate metals from solution by biosorption on a cell surface, as well as by active oxidative or reductive metabolism. A microbial biofilm (Brown *et al.* 1994, Sawicki *et al.* 1995) recently discovered in an Underground Research Laboratory (URL) in Manitoba (Brown *et al.* 1989) has shown that iron from biotite in the granitic host-rock can be mobilized by microbial action. The iron is used as a source of energy by a microbial consortium and then precipitated both in the oxidized and reduced forms as hematite and siderite, respectively. This biofilm provides new evidence for the role of biogenic processes in the deposition of metalliferous sediments, and since it preferentially accumulates silica as well as iron, we suggest that this type of microbial mediation could have been involved in the deposition of banded iron-formations.

In this review, we examine the history of research on BIF, the requirements of bacterial growth so the reader may be able to comprehend the various microbially mediated mineral deposits occurring today, and the implications of these microbial reactions and their relationship to the concepts and models proposed for the formation of both recent and ancient metalliferous sediments.

HISTORY OF MICROBIAL GEOCHEMISTRY ASSOCIATED WITH BIF

The suggestion that biological processes are important in the deposition of iron-rich sediments was initially put forward by Ehrenberg (1836), but it was not until 1888 that Winogradsky was able to show that a bacterium, *Leptothrix*, is able to live and grow only where ferrous iron is present in solution. These organisms grow a sheath surrounding the cells that is stained brown by accumulation of iron oxide. Since this coloration occurs only where living cells are present, Winogradsky (1888) proposed that they must actively produce the ferric iron that becomes enmeshed in the sheath. He concluded, therefore, that oxidation of ferrous compounds to ferric hydroxide is necessary for the growth of the organism. Since this process provides energy for cell growth, organic matter would not be required for energy production. However, Lieske (1911) proposed instead that carbon derived from ferrous bicarbonate would provide the necessary energy, and despite Winogradsky's findings, the consensus until recently has been that organic matter is indeed necessary for cell growth.

Since weathering of ordinary rocks should have continued on the same scale throughout the Precambrian and Phanerozoic, Van Hise & Leith (1911) questioned whether this could be the sole source of the iron and silica in BIF. Harder & Chamberlain (1915) suggested that, although the precipitation of ferric hydroxide from solution during the deposition of the Itabira (Brazil) iron-formation could have been purely chemical, it was more likely to have resulted from the operation of "well-known iron bacteria" (their term). Harder (1919) reviewed the early ideas on the relationship between iron-depositing bacteria and the geological environment. Gruner (1922) considered it probable that both algae and iron bacteria contributed to the precipitation of organic colloids during the deposition of the Biwabik (Minnesota) iron-formation.

LaBerge *et al.* (1987) proposed that the Precambrian iron minerals originated mainly as fine-grained, biologically precipitated ferric hydrates that later matured to ferrihydrite and hematite. This ferric iron was then reduced by concomitant microbial degradation of organic matter to siderite, which later altered to magnetite. They suggested further that in the sedimentary environment, ferric and ferrous iron minerals would have coexisted in metastable equilibrium.

Current reviews of energy metabolism by Nealson & Myers (1990) and Lovley (1991) show that metabolic oxidation and reduction of inorganic ions, notably of iron, by bacteria are not only important, but have a widespread influence also upon the natural environment.

If the source of ferrous iron had been the stagnant oceans beneath an anoxic atmosphere, as proposed by Cloud & Licari (1968), this iron could have been converted into insoluble ferric oxides only when there was a change in the Precambrian atmosphere due to the evolution of oxidative photosynthesis (Cloud 1973, 1983). Major BIF would therefore be found only within a short interval during the Early Proterozoic, before the atmosphere became fully oxygenated.

The highly metamorphosed Isua iron-formation in

Greenland is probably the oldest known BIF (3.8 Ga). It contains rounded carbonaceous, iron-coated microstructures (mainly oxides) that are more typical of organisms than of inorganic recrystallization (Robbins 1987). The oldest definite microbial fossils yet described are from the Warawoona Group (3.3 to 3.5 Ga) in Western Australia (Schopf & Packer 1987), where the cells of filamentous and colonial microfossils are preserved by the formation of stromatolites embedded in carbonaceous cherts. Microcrystalline siderite and hematite in the Transvaal BIF (2,5 to 2.1 Ga) are considered to reflect the chemical environment in the depositional basins, since the other minerals appear to be either diagenetic or metamorphic in origin (Beukes 1983). James (1954) pointed out that the composition and structure of the precursor sedimentary facies must have been controlled by environmental factors in the depositional basins, and that this would be reflected in the mineralogy and textural features of the lithofacies derived from them.

Although major deposition of BIF was suggested to have ceased when eukaryotic photosynthesis evolved sufficiently to produce a stable oxygenated atmosphere about 2.0 Ga ago (Cloud 1973), there are today many environments, smaller in extent, where iron and silica are being deposited under both oxidizing and reducing conditions (Gross & McLeod 1987, Rona & Scott 1993). Initially, the iron and silica in BIF were thought to be derived exclusively from sedimentary sources, but now hydrothermal plumes are acknowledged to have been the main source (Gross 1991, Isley 1995).

The discovery in the late 1960s of hydrothermal vents along spreading ridges on the seafloor (Jannasch & Wirsen 1981) and the investigation of surface hot springs at Yellowstone (Brock & Madigan 1991) provide partial analogues for the study of iron-rich metalliferous sediments. Modern hydrolithic sediments rich in iron, manganese, silica and sulfide minerals surrounding sites of hydrothermal discharge provide corroboration of the nature of the precursors and the lithofacies that could have developed from them.

In this review, we suggest that microbial processes could have mediated the precipitation of iron, either oxidized or reduced, in narrow bands interlayered with beds of silica. Microfossils and stromatolites associated with banded iron-formations indicate that prokaryotic organisms were present by the time these sediments were being formed, although their specific role in the deposition of BIF has yet to be determined.

REQUIREMENTS OF BACTERIAL GROWTH

Since microbial activity has such an impact on geological processes, it is important to understand what these reactions might be. Microorganisms have the ability to selectively gather nutrients into the cell and to modify them so that they may serve either as cell building blocks or as an energy source for growth, the consequence of which has a considerable effect on the pH and Eh of the natural environment.

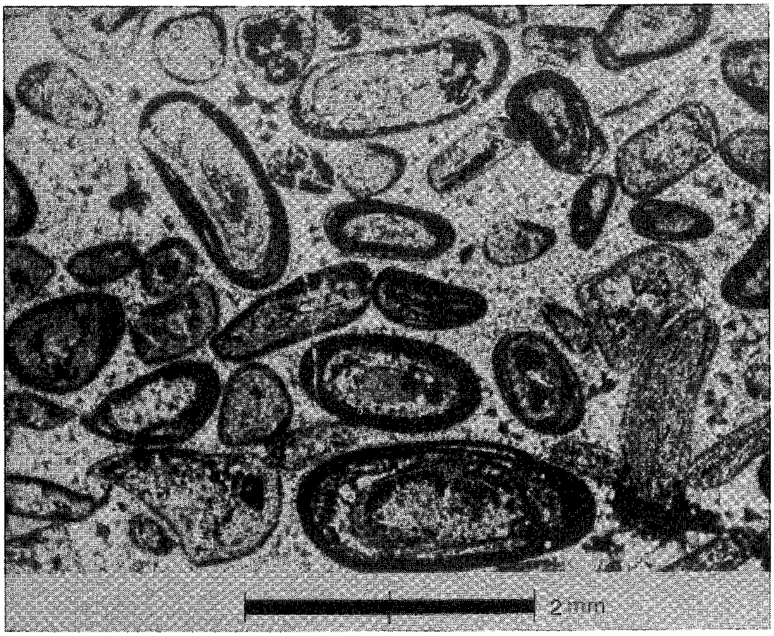

FIG. 1. Typical microfossil texture in magnetite – hematite – chert lithofacies in the Gunflint iron-formation, Thunder Bay, Ontario.

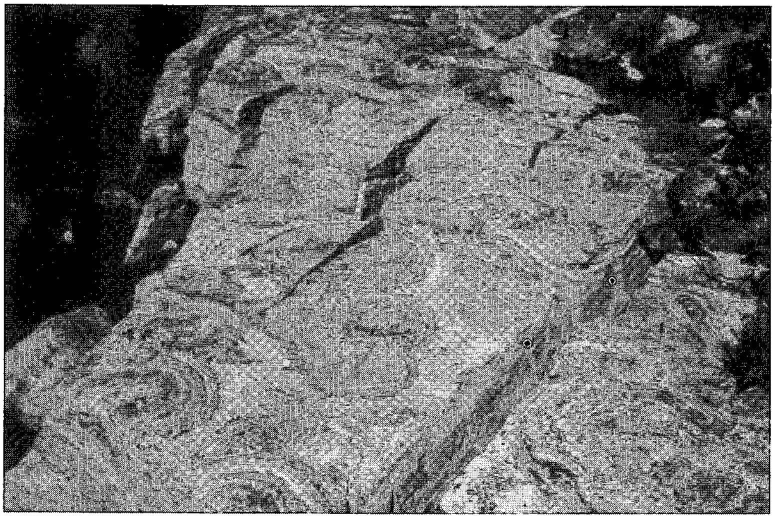

FIG. 2. Stromatolites, 20 to 30 cm in diameter, from the Gunflint iron-formation, Thunder Bay, Ontario.

It is difficult to demonstrate how microorganisms may have participated in the deposition of iron-rich sediments, since the only evidence we now have is their fossilized remains, and it is not possible to determine from the cell morphology alone what microbial reactions might have taken place. Evidence of microfossils and stromatolites in early Precambrian BIF is relatively rare, and even where they were originally present, in many cases they would have been destroyed by later metamorphism. Figure 1 shows microfossils from the Gunflint iron-formation in Ontario, and Figure 2, a stromatolite from the Biwabik iron-formation in Minnesota.

Microbes preferentially utilize the lightest isotope, so that an assessment of isotope depletion can provide further information on possible microbial activity. In some sediments, chemical remnants such as carbonates and kerogen contain anomalously light carbon, indicating that they were most likely formed through biological activity (Winter & Knauth 1992).

Microorganisms are usually visible only under the microscope. They are mainly unicellular and prokaryotic (without a separate nucleus), commonly consisting of a single cell enclosed by a membrane that separates the metabolically active unit from the external medium. Eukaryotes, on the other hand, enclose their genetic material within a membrane-bound nucleus; some are unicellular, but most are multicellular organisms. This group include the algae and plants, as well as all of the animal kingdom.

Bacteria, however, are the most important organisms that participate in chemical inorganic reactions in the natural environment; although the basic metabolic pathways for cellular growth and internal transfer of energy are similar in all organisms, only bacteria show such extraordinary diversity in their ability to obtain energy from external sources. Bacterial species are also versatile in their capacity to quickly produce enzymes (biological catalysts) to utilize any nutrient that may become available, thus enabling many extreme ecological niches to be rapidly filled (Ingraham *et al.* 1983). The availability of carbon substrates, energy sources and reducing power in the natural environment has influenced the evolution of the energy reactions that bacteria are able to accomplish. Many geochemical processes in natural systems take place within a wide range of pH, redox, and salinity, and these are often determined from the result of reactions of the indigenous bacteria at water–rock interfaces (Ferris *et al.* 1987).

Nutrients

All life on Earth is based on carbon, and this constitutes half of the bacterial cell mass. Other important elements are oxygen, nitrogen, hydrogen, phosphorus and sulfur, together with trace amounts of other elements, including iron. In the natural environment, these elements are generally leached from the bedrock either by weathering processes or microbial mediation. The requirements for cellular growth are, therefore, the availability of these necessary elements, a source of energy, and a suitable habitat (Brown 1994).

In marine and terrestrial groundwaters, where nutrients are limited, bacteria usually live in consortia within a biofilm or mat, where the members may also be symbiotic. The survival strategy of these associations is to adhere to a surface in a film of organic material. Nutrients tend to concentrate at rock – biofilm – groundwater interfaces, where fluid movement continually brings new supplies of nutrients to provide a richer food-source than that of the bulk fluid environment (Costerton *et al.* 1986). Sessile (sedentary) bacteria on these surfaces thus have an ecological advantage over those that are planktonic (free-swimming in the bulk fluid).

In the natural environment today, biofilms are initiated by planktonic organisms that colonize rock surfaces. Bacterial succession then leads to a mature community, similar to that found in other ecosystems. Exopolymeric substances, generally polysaccharides, are excreted by the bacteria, which accumulate and form a charged layer of slime surrounding the consortia (Characklis & Marshall 1990). Ultimately, owing to transfer limitations, the inner layer of a biofilm may become anoxic, stimulating the development of an anaerobic population (Costerton *et al.* 1994). Finally, ciliate protozoa within the biofilm may graze on the bacterial population and thus help to maintain a climax community (Lock *et al.* 1984).

Energy

The major source of energy for organisms living on earth today is the sun. Solar energy is utilized by plant photosynthesis to produce oxygen whilst fixing carbon into organic compounds (that have reducing potential). This carbon incorporated as plant biomass is then utilized by animals for their growth.

However, in the Archean, before oxidative photosynthesis had evolved, and even today, in environments where neither sunlight nor biomass produced from solar energy can penetrate, primitive organisms (bacteria) must find other sources of energy. Since the maintenance of complex biological structures of the living cell is thermodynamically unfavorable, to sustain themselves and grow, organisms must couple energy-producing oxidation–reduction reactions to their endergonic biosynthetic ones. These redox reactions are able to transfer electrons from a donor (reducing potential), which becomes oxidized, to an acceptor, which is then reduced.

Oxygen is the most common electron donor to be utilized by living organisms, but in environments where this is not available, such as the early anoxic Earth, other donors are required. The sequence of electron donors involved in nature are, in descending order of thermodynamically available energy: oxygen, nitrate and nitrite, Mn^{6+}, Fe^{3+}, sulfate and carbon dioxide. The reduction of these compounds (electron acceptors) is generally coupled to the oxidation of organic matter (electron donor). This sequence of bacterially mediated redox reactions is the same as that found in the water columns of lakes and sediments (Stumm & Morgan 1981).

Environment

Bacteria play a major role in the control of the natural aqueous milieu by their influence on the biological reactions of photosynthesis, respiration, and oxido-reductive changes in the iron, sulfur and carbon systems, largely determining the pH and Eh limits of the natural environment (Baas Becking *et al.* 1960). Terrestrial life requires water in the liquid phase, thus the temperature limits for growth may range from below –5°C in Arctic seas to above 100°C (and possibly much higher) in deep-sea thermal vents.

When living organisms first arose approximately 4.0 Ga ago on this planet, the atmosphere was reducing, so the early organisms evolved in the absence of oxygen. Early anaerobes would also have had to develop mechanisms to prevent being poisoned by oxygen radicals, the successful ones becaming aerobes, and those that could not cope with oxygen poisoning remaining anaerobic; as well, some bacteria (facultative) are able to live in either environment.

Although filamentous bacteria ~3.5 Ga old have been found that have fossil morphology similar to cyanobacteria (blue-green prokaryotic algae) (Schopf & Packer 1987), it is almost certain that stromatolites older than ~2.5 Ga were composed of anoxygenic phototrophs (purple and green bacteria) rather than oxygen-evolving cyanobacteria (Brock & Madigan 1991). Recently, it has been reported (Ehrenreich & Widdel 1994) that purple bacteria are able to oxidize Fe^{2+} to Fe^{3+} when this is coupled to the reduction of organic matter. Biological oxidation of iron would therefore have been possible before the evolution of oxidative photosynthesis, so that the formation of Precambrian stromatolites would have been possible without the participation of oxygen-producing cyanobacteria (Castenholz 1994).

Eventually, as life evolved and became more complex, efficient oxidative photosynthesis developed in eukaryotic algae and green plants, but before oxygen could have begun to accumulate in the atmosphere, the surface waters would first have had to become saturated. However, once the atmosphere did become oxic, eukaryotic and multicellular animals would have been able to proliferate (Woese 1994). These eukaryotes may have grazed on the prokaryote communities, possibly ending the age of stromatolites, since microbial mats cannot persist where there are efficient grazers (Castenholz 1994).

MICROBIAL MINERAL DEPOSITION TODAY

There are various geological features being fashioned today by microbial mediation that can be related to ancient fossilized forms. Descriptions of the biological involvement in several of these structures are described below.

Microbial mats

Microbial mats contain layers of different microbial communities; today, they generally consist of cyanobacteria in the uppermost layer, various phototrophic bacteria in deeper layers until light becomes limiting, and then degrading bacteria such as sulfate-reducers occupying the lowest and darkest layer (Brock & Madigan 1991). These are dynamic systems, where photosynthesis that occurs in the surface layer of the mat is balanced by decomposition at its base. Microbial mats are found in a variety of environments, notably those of volcanic hot springs and shallow marine basins.

Algal mats up to 30 cm thick have been described from Baja California (Horodyski 1977, Horodyski *et al.* 1977). A variety of microorganisms contribute to their formation, but their morphology is controlled by filament abundance, flooding history, water depth and, most importantly, by the degree of desiccation. Several types of filamentous organisms contribute to the primary organic deposit, which is subsequently degraded and modified by further bacterial activity. If heavy rains flood these mat communities, the deposition of laminated sediment ceases, and instead, up to 10 cm of siliceous sediment may be deposited over the surface of the mat (Stolz & Margulis 1984). This new layer of sediment is then recolonized by a different suite of organisms. Meanwhile, the siliceous sediments are reworked into an anaerobic mud that contains metals, sulfur, and well-preserved sheaths of filamentous and coccoid bacteria. An active microbial community can thus produce a large amount of organic material which, although preserved as a thin layer in the underlying mud, provides little other evidence of the organisms that produced it. Stolz & Margulis (1984) suggested that these recent laminated sediments of Baja California bear a striking similarity to the laminated sediments and associated cherts of the Archean Swaziland System.

Hot springs

Stromatolites and algal mats are laminated organosedimentary structures that form through repeated cycles of sediment accretion, in general reflecting periodic interruptions in their deposition. They are generally built at present by eukaryotic algae, but before eukaryotes evolved, prokaryotic organisms had formed similar organic complexes. Today, stromatolites are being formed at Yellowstone both by eukaryotic algae and by prokaryotic bacteria. Prokaryotes preferentially grow where eukaryotes are unable to survive, usually when the conditions are too hot. Phylogenetic characterization of the hot-spring sediments by molecular genetics has recently revealed a remarkable diversity of prokaryotic species (Barnes *et al.* 1994). Although Yellowstone waters generally have only a low concentration of iron, in some geysers both iron and silica are being deposited. Moreover, modern stromatolites are usually found only in carbonate environments, but the siliceous stromatolites being formed here are comparable to those found in the Gunflint cherts. This similarity supports the concept that hot springs were a primary source of silica in Precambrian iron-formations, and also that many early fossil stromatolites must have been bacterial, not algal in origin, since algae only evolved later (Walter *et al.* 1954).

Shallow seas

Contemporary hydrothermal sediments are being formed at several places within the Santorini caldera, in the eastern Mediterranean (Boström & Widenfalk 1984). The sediments are largely authigenic iron hydroxide, carbonate, and sulfide minerals mixed with rock fragments and some clay. The topmost surface of the sediments, however, consists almost entirely of biogenic iron oxide–hydroxide formed on the stalks of the bacterium *Galionella ferruginea* (Holm 1987). Owing to the proximity of the surface, there is extensive downward advection of oxygen, which reacts with the vent hydrogen sulfide to form sulfuric acid. This acid produces a local environment quite different to that of the deep sea, and hence the sediments also are dissimilar.

Deep-seafloor vents

Metalliferous sediments around hydrothermal vents in deep basins in the Red Sea contain facies of soft red to grey-brown banded sediments that are composed of iron and base-metal oxides, hydroxides, sulfides, silicates and clay minerals (El Shazly 1990). These partially consolidated sediments are generally muddy, with micrometer-size particles. The organisms found associated with these sediments are mainly planktonic foraminifera, with only a few sulfate-reducing bacteria at the seawater interface, although isotopic data indicate that pyrite was biologically formed.

Sediments deposited around deep seafloor thermal vents appear to provide a good analogy for the study of BIF (Jannasch & Wirsen 1981, Jannasch & Taylor 1984). The submarine food-chain here is based on hydrogen sulfide, which chemosynthetic bacteria utilize to provide the primary source of food for the invertebrate population. The major sites of microbial activity are suspensions of bacterial cells (Haymon *et al.* 1993), biofilms growing on various surfaces (Tunnicliffe & Fontaine 1987) and filamentous microorganisms (Juniper & Fouquet 1988), as well as symbiotic associations between chemoautotrophic prokaryotes and vent invertebrates. Most surfaces are covered with bacterial biofilms that contain iron-rich encrustations. The biological productivity around the vents is extremely high compared to that of the surrounding water, and dense swarms of shrimp feeding near the points of emission indicate these are optimal sites for the chemosynthetic growth of their filamentous microbial epiflora (Wirsen *et al.* 1993). Tunnicliffe & Fontaine (1987) considered that although initial precipitation of the iron is bacterially mediated, further deposition of metals is determined by the geochemical conditions of the ambient environment.

Extensive deposits of polymetallic sulfide and oxide sediments around vent sites are formed by the transfer of geothermal energy to microbial biomass by bacterial lithoautotrophy (growth on inorganic compounds). This transfer of energy contributes significantly to the large-scale geochemical processes of the ocean floor, so that present-day hydrothermal environments could be comparable to the processes that occurred in the Precambrian seas. Baross & Hoffman (1985) further suggested that complex microbial ocean-floor communities in the Archean could have evolved relatively rapidly around such active hydrothermal vents.

BIOFILM FROM AN UNDERGROUND RESEARCH LABORATORY (URL)

The stimulus for this paper was our discovery of a biofilm that was able to precipitate both hematite and siderite as well as to adsorb silica. This biofilm formed in the URL excavated in the Lac du Bonnet granitic pluton of the Canadian Shield (Brown *et al.* 1994, Sawicki *et al.* 1995). The excavation is naturally dry, with only two water-bearing fractures, but the biofilm (Fig. 3) was able to form on the surface of a large borehole in the floor of a drift (420 m deep), where it was irrigated by surface water used for mining activities (Brown *et al.* 1994). The water contained a range of microorganisms, and it had also been contaminated with blasting materials containing carbon and nitrogen, both essential for microbial growth. The biofilm grew over a period of several months to a thickness in places of 10 mm. Initially, it appeared grayish with light-brown streaks, but orange markings developed later. Runnels, formed within the biofilm by flowing water, were stained black internally. Later, a white precipitate formed over these runnels.

Deposits of iron and silica (detected by electron microscopy, X-ray diffraction and energy-dispersion spectroscopy) were rapidly formed on the bacterial cell walls and extrapolymeric slime (Fig. 4), although the concentrations of iron and silica in the water were low. Mössbauer spectroscopy (Sawicki *et al.* 1995) showed that small particles of protoferrihydrite were formed on the outer aerobic face of the biofilm, which later showed alteration to hematite. By contrast, at the inner anaerobic face of the biofilm next to the rock wall, ferrous iron was formed, which was then either sorbed directly onto the biofilm itself, or reacted with carbonate from microbial fermentation to be precipitated as siderite. The white precipitate was found to be gypsum. Both siderite and gypsum are rarely found in this pluton.

MICROBIAL GEOCHEMISTRY

The microbial reactions that can cause the formation of different minerals in these environments will now be considered. Mobility of mineral ions in the geological

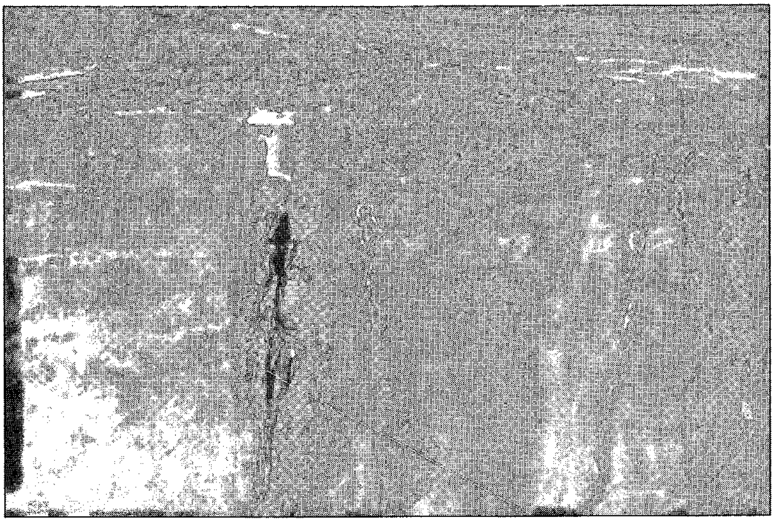

FIG. 3. Biofilm formed in a borehole in the Underground Research Laboratory, resulting from the precipitation of ferrihydrite, siderite, and gypsum in the slime layer.

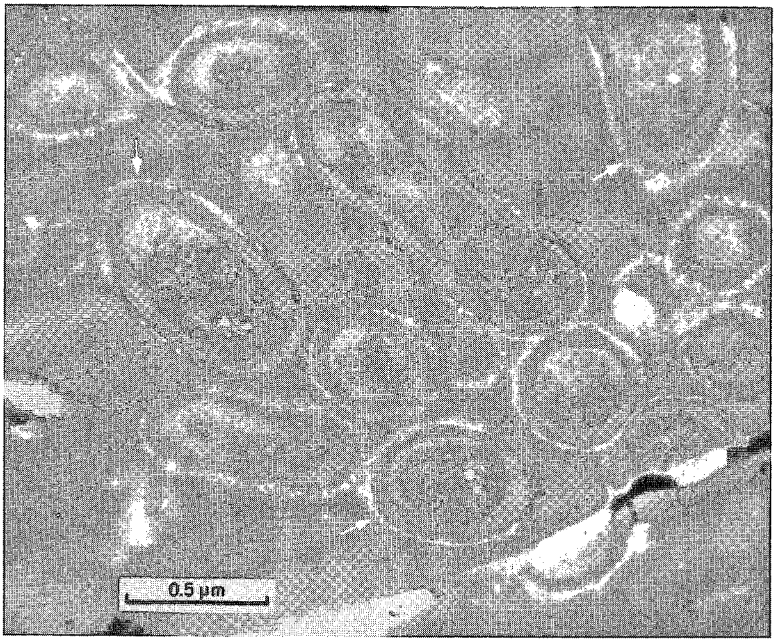

FIG. 4. Thin section of the biofilm showing *in situ* biomineralization (arrows) around bacterial cells.

environment is influenced by the bacterial processes of sorption, accumulation, and precipitation. These reactions include dissimulatory metabolism of various compounds as energy sources, active assimilation of metal ions into the cell, notably as metalloenzymes, and passive physicochemical accumulation.

The greatest effect of microbial activity upon the environment is through dissimilatory metabolism (not incorporated into the cell biomass), notably of iron and manganese as a source of bacterial energy. Since these metals do not have to enter the cell and can be relatively inefficient, vast amounts may have to be altered to provide sufficient energy for cell growth. Iron is the fourth most abundant element on Earth, such that it is readily available to provide an almost unlimited inorganic source of energy, albeit not a particularly efficient one. Bacterial reactions utilizing iron can have a considerable effect on the environment by altering the pH and Eh, producing microniches of different fields of stability that allow the deposition of various iron compounds dependent upon the redox state.

Oxidation of ferrous iron

Pyrite is formed in sedimentary rocks by the bacterial reduction of sulfate (generally from marine waters) to hydrogen sulfide; this reacts chemically with ferrous ions to form an initial precipitation of amorphous ferrous sulfide, altering later to pyrite. When these iron sulfide minerals are exposed at the surface, either by erosion or by mining, they can form the substrate for chemolithic sulfur-oxidizing microorganisms, notably *Thiobacillus ferrooxidans* (Jorgensen 1983). These bacteria are able to derive sufficient energy for growth from the oxidation of pyrite. The optimal pH for this reaction is 2.0, whereas the internal pH of the cell is close to neutrality. This difference in pH provides a sufficient proton-motive force across the cell membrane that iron and sulfur can be oxidized by the removal of electrons. To maintain electroneutrality, there is a concomitant inward flow of protons that are transformed into cell energy with the consumption of oxygen (Cox & Brand 1984). In a similar manner, manganese may be oxidized by bacterial mediation and form manganese nodules and concretions (Ehrlich 1963).

Reduction of ferric iron

The dissimulatory reduction of ferric to ferrous iron, coupled to the oxidation of organic matter, is widespread in the natural environment (Lovley 1991). Although an early study concluded that microbial reduction of ferric iron was non-enzymatic (Starkey & Halvorson 1927), it has since proved impossible to demonstrate that ferric iron can indeed be reduced non-enzymatically. In fact, it has been consistently shown that ferric iron in microbial cultures is only reduced as a result of direct enzymatic action (Lovley 1991).

The organisms responsible for the enzymatic reduction of ferric iron have only recently been isolated, although they have been known for more than a century (Winogradsky 1888). Geochemical evidence indicates that dissimilatory respiratory reduction of ferric iron may have evolved prior to other respiratory processes, such as the reduction of sulfate or nitrate (Walker 1984). Since ferric iron reducers are able to outcompete both sulfate-reducers and methanogens (reducers of carbon dioxide) as electron acceptors (Stumm & Morgan 1981), this reaction is the one that will preferentially occur in nature. These bacteria have been identified in sediments, suggesting that they could have also been responsible for late post-depositional reduction of ferric iron (Lovley *et al.* 1990). The iron reactions are among the most important geochemical processes in anaerobic sedimentary environments, since they can release the highly insoluble ferric iron from the rock mass into the groundwater by reducing it to the more soluble ferrous state.

Until recently, all black iron precipitates in natural environments were considered to be iron sulfides, mainly pyrite as described above. However, it has now been found that since bacterial reduction of ferric iron is energetically preferred to the reduction of sulfate, ferrous iron is produced rather than sulfide. The ferrous iron then reacts with dissolved carbonate to form siderite (Coleman *et al.* 1993, Roden & Lovley 1993). The formation of siderite has also been demonstrated in the biofilm from the URL (Brown *et al.* 1994, Sawicki *et al.* 1995).

Magnetite formation

Many bacterial enzymes require a metal to conduct catalysis; these are usually transition metals that have several oxidation states in the natural environment (Wackett *et al.* 1989). The metals are assimilated into the cell by specifiic transport-systems, allowing the bacteria to collect the metals from an environment where they may be present in only minute amounts. Some bacteria contain chains of magnetosomes (magnetite crystals), which make them magnetotactic and cause the cells to become oriented in the geomagnetic field (Brock & Madigan 1991). However, the amount of magnetite incorporated into these bacteria is minuscule in comparison to that formed by the dissimilatory energy-producing reactions. Studies of anaerobic sediments suggest that bacteria are able to produce large quantities of ultrafine-grained magnetite when reduction of ferric iron is coupled to oxidation of organic matter (Lovley *et al.* 1987). This process is likely to have caused the accumulation of large amounts of magnetite in iron-formations, presumably under conditions that are more oxidizing than where siderite is formed.

Examination of modern deposits and experimental syntheses suggest that ironstones are formed by the crystallization of Si–Fe–O–OH gels (Duhig *et al.* 1992), which occur as a result of hydrothermal fluids mixing with seawater. Since it is unlikely that there would have been a sufficient period of time for significant quantities of iron to be precipitated, other factors, such as iron-oxidizing bacteria able to facilitate low-temperature precipitation of ferric iron, may well have been involved.

Sorption: the cell as a polyionic trap

Passive physiochemical biosorption is the type of microbial mediation that occurs between inorganic ions and microbial cellular components, whether dead or alive. Many bacteria produce an outermost envelope of slime that serves as a buffer between the cell and the external environment, which has unsatisfied charges that promote a polyionic trap for ionic and electrostatic binding of metals and silicates (Geesey & Jang 1990). Bacterial cells are efficient in forming metallic silicates and fine-grained minerals, since these reactions reduce the level of toxic metals in solution.

Silicate binding to *Bacillus subtilis* has been demonstrated (Urrutia & Beveridge 1993), in a case in which the deposition of silicate is dependent on the electropositive charge of the cell. The formation of fine-grained minerals also occurs in the S-layer (slime) of *Synechococcus*, a cyanobacterium found in freshwater lakes (Schultze-Lam & Beveridge 1994). In this case, mineral formation begins as the deposition of minute crystals of gypsum, but as the pH of the microenvironment is increased by metabolic activity, the precipitate changes to calcite. Active cells can shed the mineralized S-layer, but as they age they become entombed, and form calcite bioherms.

Epilithic microbial communities found ubiquitously on submerged rocks are highly mineralized (Konhauser *et al.* 1994), and the biofilms, regardless of their substratum lithology, consistently form iron and aluminum silicates, indicating that biomineralization is a surface process associated with the anionic nature of the cell wall. These biofilms seem to dominate the rock–water interface and to determine which minerals will ultimately become part of the riverbed sediment.

Silica is one of the major components of BIF, but any microbially mediated system for silica deposition poses a problem, since silica-metabolizing prokaryotes are unknown, and eukaryotes only evolved later. Therefore, mediation by bacteria of the precipitation of silica in Archean iron-rich banded sediments would have had to be by passive physiochemical sorption such as described above, rather than by active metabolism.

BIOMINERALIZATION MODEL FOR THE GENESIS OF BIF

Microorganisms have been present on Earth for 90% of its history, and so it is to be expected that they should have played a fundamental role in the evolution of our natural environment. Significant alteration of the biosphere by microorganisms is caused by their need to obtain nutrients and energy for growth. One of the major effects of this requirement is the change in valency in the case of inorganic ions that are utilized by bacteria as a source of energy; this is reflected in the modification of pH and Eh, thus altering the solubilities of the dissolved ions.

Organic life may leave its signature in the sediments, and evidence of organic remains have been found in BIF and the associated black shales. In many cases, the carbon is isotopically light, indicating microbial activity; this also can be correlated with an increase in the concentration of iron (Walker 1984).

Stromatolites are fossilized microbial mats that contain entrapped sediment between layers of filamentous organisms. Although silica is not directly metabolized by prokaryotes, it can be precipitated by physicochemical reactions with the microbial slime layer or cell wall. Modern stromatolites are usually carbonaceous, not siliceous, and contain oxygen-producing organisms, but in appropriate environments, such as Yellowstone and Baja California, stromatolites are today being formed that contain prokaryotic organisms in a siliceous matrix. These stromatolites have a similar morphology to those of the Archean, suggesting that they could have been formed by similar means.

Microorganisms require a source of energy for growth, but this does not necessarily have to be light from the sun. Metalliferous sediments presently forming at the deep-sea vents utilize chemolithotrophic, not photosynthetic, energy. Furthermore, bacterial photosynthesis did not initially produce oxygen; it was only later when cyanobacteria evolved that oxygen was directly generated, but it would still have been limited in amount and rapidly utilized. Oxygen could only have accumulated in the atmosphere when the water became saturated, after eukaryotic algae and green plants evolved in the late Proterozoic.

However, oxidation of ferrous iron probably was the earliest photosynthetic ability evolved by primitive organisms (Ehrenreich & Widdel 1994), which suggests that free oxygen would have been unnecessary for the deposition of oxidized iron beds. Microbial organisms in shallow seas during the Archean would have received unrestricted light from the sun, which they could have utilized to lay down thin layers of iron-rich mats over large lateral areas. Episodic or seasonal flooding of these mats may have covered them with siliceous sediments, which would then have been recolonized by photosynthetic bacteria once the water retreated. The question is not, therefore, whether the atmosphere contained sufficient oxygen for the deposition of oxidized iron, but rather, whether precipitation of large quantities of ferric iron could have occurred by microbial mediation in the aqueous depositional environment of that time. To judge from the BIF that we know today, this whole process would have had to be repeated many times over the millennia to allow such numerous beds to accumulate.

Many BIF contain thin bands of silica alternating with millimeter-thick bands of minerals containing ferrous or ferric iron (or both). It has been difficult to explain how chemical processes alone could have produced these results. Our recent study of the URL microbial biofilm does offer an explanation, since it shows that microbial consortia are capable of forming different microenvironments (stability fields) within a biofilm, thus allowing precipitation of both oxidized iron as ferrihydrite and reduced iron as siderite. This microbial mediation permits two very dissimilar iron minerals to be precipitated in close proximity. Both oxidized and reduced states of iron are found in BIF, but the state in which they were originally precipitated would have been determined by the oxygen potential (possibility of metabolic microbial oxidation) in the environment at the time of deposition. Since iron can be precipitated in both oxidized and reduced forms by bacterial mediation, it is no longer necessary to postulate later metamorphic alteration in order to explain the state of the iron in BIF.

Stromatolites at Yellowstone and the biofilm in the URL show that iron, even in very low concentrations, may be precipitated by microbial action from solution. Although the present ocean environments do not provide large areas of iron-rich shallow waters under an anaerobic atmosphere, such as were required for the massive Archean and Proterozoic BIF, there are metalliferous sediments being deposited today under comparable environments, but in smaller areas around hot springs and hydrothermal vents (Gross & McLeod 1987).

CONCLUSIONS

The microbial precipitation of iron and silica in BIF would have depended upon the natural environment at the time of deposition. Silica could have been accumulated by physicochemical sorption on the microbial biomass, whereas iron would more likely have been metabolically utilized by the bacteria as a source of energy that could have been deposited either in an oxidized or reduced state, dependent upon the prevailing pH and Eh. In the absence of oxygen, iron would have been precipitated in the reduced form as siderite or iron silicate, or possibly as pyrite in a marine environment. Where oxidizing potential was available, the iron would more likely have been precipitated as ferrihydrite or magnetite, possibly altering later to hematite. Microbial mediation appears to be essential for the deposition of narrow interbedded layers of minerals rich in iron and silica found in the typical oxide, silicate, and carbonate BIF lithofacies. The mineral bands appear to be discrete and to have maintained their chemical composition and integrity throughout subsequent diagenesis and metamorphism. Although it is extremely difficult to unravel the genesis of Precambrian BIF, our present understanding of the relevant microbial reactions, taken in conjunction with investigations of modern analogues of BIF, show that most, if not all, of these metalliferous sediments could only have been accumulated through microbial mediation.

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