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Bacterial iron biomineralisation in nature

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Abstract

Transmission electron microscopy examination of bacterial cells, growing naturally in freshwater and marine environments, reveals that they can precipitate a variety of iron minerals. The development of these authigenic mineral phases may be either 'biologically controlled', whereby the cell regulates mineral formation, or 'biologically induced', with biominerals commonly generated as secondary by-products of microbe-environment interactions. With the vast majority of bacteria biomineralisation is a two-step process; initially metals are electrostatically bound to the anionic surfaces of the cell wall and surrounding organic polymers, where they subsequently serve as nucleation sites for crystal growth. Because of its relatively high activity in aqueous solutions, iron is preferentially bound to reactive organic sites. As the latter stages of mineralisation are inorganically driven, the type of iron mineral formed is inevitably dependent on the available counter-ions, and hence, the chemical composition of the waters in which the microorganisms are growing.

Keywords: Bacteria; Biomineralization; Iron mineral; Geochemistry

Contents

1. Introduction

Bacterial biomineralisation is a diverse and widespread phenomenon that results from cellularly mediated physiological processes. There appear to exist two different methods of mineral formation [1]. 'Biologically controlled mineralisation' is a completely regulated process whereby the organism precipitates essential mineral phases within a preformed framework. Because the site at which a mineral forms is isolated from the external environment by

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a barrier through which ions cannot freely diffuse, mineralisation may proceed under thermodynamically unfavourable conditions. In contrast, 'biologically induced mineralisation' is not specifically designed for mineralisation, but one in which minerals still form. Biologically induced mineralisation is the dominant process among bacteria, with biominerals commonly generated as secondary events from interactions between the activity of the microorganisms and their surrounding environment [2]. Minor perturbations such as the introduction of biologically produced metabolic end-products (e.g., OH^-, CO_2, H^+ and NH_3), the release of cations by the cell, or the development of a charged surface can all induce the nucleation of minerals with crystal habits similar to those produced by precipitation from inorganic solutions [3].

At the proper growth pH (between 5 and 8), structural polymers that reside in the cell wall and surrounding fabric of bacteria are ionised and naturally anionic (see Beveridge [4] for details about bacterial structures). Bacteria also have the largest surface area to volume ratio of cellular life forms [5], and, therefore, exhibit a remarkable potential to sequester and accumulate metals onto their surfaces (see Beveridge [6] for review and references therein). Some bacteria show extreme selectivity in binding one metal from a range of competing cations to fulfil essential physiological functions [7], whereas other bacteria react to dissolved ions as if they were an open ion exchange resin [8], presumably a function of living in a concentrated solution where salts abound [9]. In this regard, it is not surprising that biofilms are considered ideal cation scavengers, often accumulating quantities of metals comparable to those of cation exchange resins [10].

Based on this inherent metal-binding capacity Beveridge and Murray [11] proposed a two-step mechanism for the development of authigenic mineral phases in association with bacterial cells. The first step involves a stoichiometric interaction between metals in solution with the cell's reactive chemical groups. Transition metals show extremely high affinities for the polymeric material [12] due to their valence, hydrated radius, hydration energy and electronegativities. Iron in particular is commonly bound to organic sites, a finding that may in part be related to its greater concentration in natural waters compared to other trace metals [13]. Once bound, these metals reduce the activation energy barriers to nucleation by providing sites where strong surface chemical interactions can take place and more soluble components can be deposited [14]. Those sites within the interstices of the wall develop only small-grained precipitates, since the space between wall polymers constrains mineral growth. Surface sites (e.g., capsules and sheaths) have no such physical constraints, and with time and a sufficient supply of soluble components, very large epicellular minerals can develop [6]. The end-result is a mineralised cellular matrix that contains detectable concentrations of metal ions that are not easily re-solubilised [15].

In recent years, high resolution studies on bacterial communities, using transmission electron microscopy (TEM), coupled with energy dispersive X-ray spectroscopy (EDS) and selected area electron diffraction (SAED), have shown the almost ubiquitous presence of fine-grained iron minerals associated with bacterial cells. Because the second step in biomineralisation is inorganically driven, the biominerals formed will be largely dependent on the available counter-ions, and hence, the chemical composition of the waters in which they are growing. This paper reviews some of the environments where iron mineralisation has been observed, and outlines some common geochemical conditions associated with bacterial biomineralisation.

2. Iron mineral formation

2.1. Hydroxides and oxides

The microbial precipitation of ferrihydrite is widespread in nature. It has been shown associated with bacteria growing in acid mine drainage environments [16–18]; rivers [19–21]; deep groundwater [22]; geyser outflow channels [23]; marine sediments [24]; around deep sea vents [25]; and on exposed rock surfaces [26,27]. TEM analyses commonly indicate bacterial cells partially to completely enclosed within iron-rich epicellular matrices (Fig. 1) or with intracellular precipitates, where the cytoplasmic material has been completely replaced once the cell had lysed. Not only do the bacteria serve as templates for iron deposition, but in the acid mine drainage sites, for

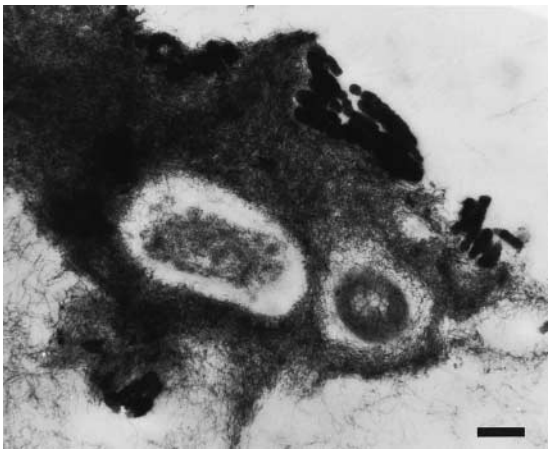

Fig. 1. TEM image of two bacterial cells surrounded by a dense, iron-rich capsule with ferrihydrite grains on outer surface. Scale bar, 220 nm. Reprinted with permission from the Geological Society of America ©21246 [23].

example, their organic remains were also incorporated into the mineral precipitates [16].

The formation of epicellular iron hydroxides by bacteria can occur either passively or actively. In the first instance, the oxidation and hydrolysis of cell-bound ferrous iron or the binding of cationic colloidal species (e.g., $Fe(H_2O)_5(OH)_5(OH)^{2+}$) can induce the transformation to insoluble hydroxide forms [17]. Alternatively, ferrous iron transported into an oxygenated environment spontaneously reacts with dissolved oxygen (at circumneutral pH) to precipitate rapidly as ferrihydrite (abiotically) on available nucleation sites. Bacteria merely represent such sites, and over a short period of time the microbial mats can become completely encrusted in amorphous iron. Indeed, ferrihydrite also develops on the organic remains of dead cells, implying that iron mineralisation can occur independent of cell morphology, trophic classification or physiological state [16].

The second means by which iron hydroxides form stems from the ability of Fe(II)-oxidising bacteria to oxidise ferrous iron as an energy source. Most enzymatic oxidation of Fe(II) occurs at extremely low pH (ranging from 1.5 to 3.5), and in acid mine drainage environments, the activity of *Thiobacillus ferroxidans* may promote iron hydroxide or iron hydroxysulfate precipitation [28,29]. Because very little energy is generated in the oxidation of ferrous to ferric iron, these bacteria must oxidise large quantities of iron in order to grow. Consequently, even a small number of bacteria can be responsible for precipitating vast amounts of iron [30]. At neutral pH, Fe(II) oxidation by *Leptothrix* and *Gallionella* genera occurs under partially reduced conditions ($< 0.1\%$ O_2). These bacteria produce an extracellular stalk and sheath that becomes heavily encrusted with amorphous iron hydroxide [31], as is commonly illustrated by the presence of iron precipitates in environments where they are growing (e.g., springs, wells and water pipes).

In most natural systems, ferrihydrite serves as a precursor to more stable iron oxides, such as goethite and hematite [32]. In two Canadian studies on surficial sediments from an acid mine drainage repository in northern Ontario [16] and subterranean biofilms in an underground research laboratory, Manitoba [22], ferrihydrite and poorly ordered hematite were found associated with individual bacterial cells. In both environments hematite was speculated to have formed through dehydration of the ferrihydrite precursor. More recently, extracellular grains of acicular goethite (Fig. 2) were identified on bacterial surfaces collected from microbial mats lining a geyser outflow channel in Lýsuhóll, Iceland [23]. Goethite reprecipitation is commonly favoured after ferrihydrite dissolution, particularly in the presence of organic compounds capable of complexing Fe^{3+} and keeping its activity low in solution [33].

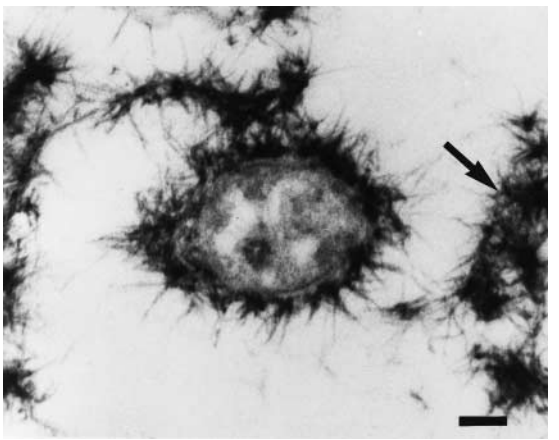

Fig. 2. Micrograph of a bacterial cell with crystalline, acicular goethite precipitated on cell wall. Grains around cell may have been shed (arrow). Scale bar = 50 nm. Reprinted with permission from the Geological Society of America ©21246 [23].

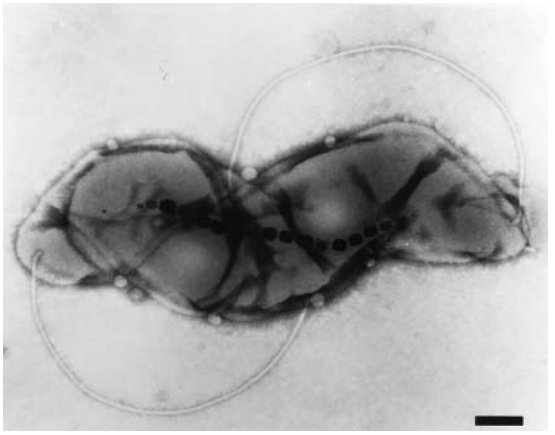

Fig. 3. Micrograph of a negatively stained cell of a magnetotactic marine spirillum, designated strain MV-4, that produces a single chain of parallelepipedal crystals of magnetite that longitudinally traverse the cell. Scale bar = 400 nm. Reprinted from cover of ASM News, Vol. 61(7) with permission of Dennis Bazylinski and the American Society for Microbiology.

Bacterial formation of magnetite is known to proceed under both 'biologically controlled' and 'biologically induced' conditions (see Blakemore and Blakemore [34] for review). In the first instance, magnetotactic bacteria produce intracellular chains of pure, single magnetite crystals (Fig. 3), under precise biochemical, chemical and probably genetic control [35]. The magnetite particles appear enveloped within an intracytoplasmic membrane comprised of a lipid bilayer [36] that presumably is the locus of control over the specificity of their morphology and size [37]. Three general morphologies of magnetite have been observed, including cuboidal, parallelepipedal and arrowhead- or tooth-shaped crystals, while the minerals generally occur within a narrow size range, from approximately 35 to 120 nm [38]. This establishes stable single magnetic domains, which arranged in a chain, provide the microorganisms with the ability to orient and swim along geomagnetic field lines [39]. This is a particularly useful navigational tool in guiding them to their preferred location in the water column or sediment, away from high oxygen or sulfide concentrations [35].

Magnetotactic bacteria are common in aquatic habitats, their greatest abundance being at the oxic-anoxic boundary [40]. Obligately microaerophilic bacteria, such as *Aquaspirillum magnetotacticum* strain MS-1, use oxygen, nitrate [41] and ferric iron [34] as terminal electron acceptors, whereas the marine bacterium strain MV-1 uses nitrous oxide [42] and the freshwater bacterium strain RS-1 uses sulfate [43] as terminal electron acceptors. The latter findings now extend the habitat of magnetotactic bacteria down into anoxic sediments, precluding the previously held belief that magnetogenesis occurs only in surface aerobic sediments.

Non-magnetotactic bacteria (biologically induced mineralisers) generate magnetite strictly under anaerobic conditions. Dissimilatory Fe(III) reducers (e.g., the bacterium designated GS-15) have been shown to produce magnetite as a by-product during the oxidation of organic compounds coupled to the reduction of poorly crystalline, synthetic Fe(III) oxide (see Lovley [44] for review). Because magnetite formation is an end-product of an energy-generating metabolism, on a per-cell basis, GS-15 typically generates 5000 times more magnetite than a magnetotactic bacterium [45], with the amount of magnetite produced primarily limited by the amount of available Fe(III) oxide [44].

The morphology and size of the biologically induced magnetite is quite different from those formed under controlled conditions (Fig. 4). The magnetite is extracellular, there is no evidence of cellular material associated with it, and the crystals typically consist of a mixture of round and oval particles that range in size from 10 to 50 nm [46]. Although the Fe(II) produced during iron reduction non-enzymatically reacts with some of the remaining solid Fe(III) to precipitate magnetite, the metabolism of

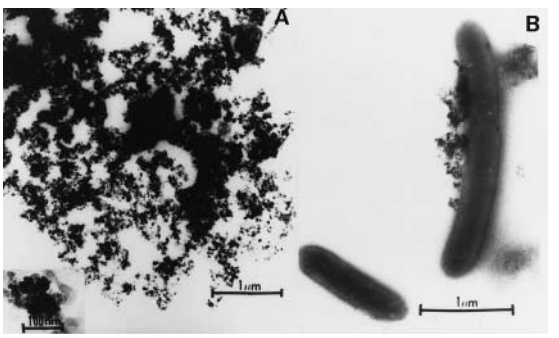

Fig. 4. A: Micrograph of extracellular magnetite precipitates. B: Cells of GS-15 with extracellular magnetite particles. Scale bars = 1 μm. Reprinted with permission of the author and Nature [46].

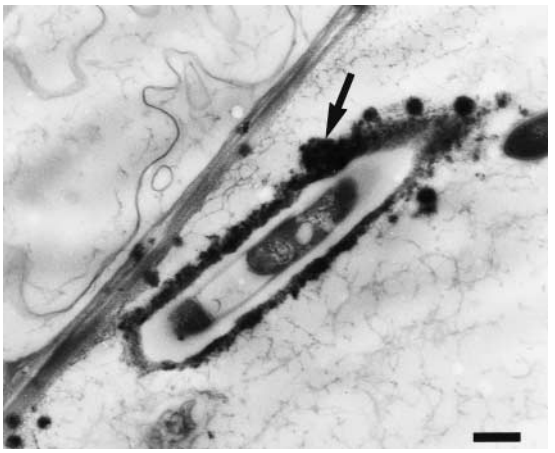

Fig. 5. TEM image of bacterial cell from Krisuvik, Iceland with (1) siliceous spheres embedded within dense, iron-rich capsule and (2) amorphous iron-silicate grain (arrow). Scale bar = 400 nm. Reprinted with permission from the Geological Society of America ©21246 [23].

the Fe(III)-reducing bacteria contributes more than just Fe(II) to magnetogenesis [44]. Magnetite formation is also favoured by high pH; a condition met during Fe(III) reduction:

$$CH_3COO^- + 8Fe(OH)_3 \rightarrow 8Fe^{2+}$$

$$+2HCO_3^- + 15OH^- + 5H_2O$$

Therefore, the appropriate combination of a high Fe(II) concentration and high pH at the contact of the Fe(III) solid provides a unique interface for magnetite formation [44].

The characteristic properties of both intracellular and extracellular magnetite are often clearly recognisable in both recent and ancient sedimentary environments. Extant magnetotactic bacteria have been recovered from freshwater swamps [47], anoxic freshwater sediment [43]; soils [48], marine salt marshes [42], marine sediments [49] and hypersaline stromatolites [50], while fossil magnetotactic bacteria have been found in deep sea sediment [51,52] and Precambrian stromatolites [53]. Magnetofossils extracted from the 2000 Ma old Gunflint Iron Formation represent the oldest evidence of biomineralisation [53]. In modern anoxic marine and freshwater sediments, much of the magnetite has morphologies similar to that produced during Fe(III) reduction [54], while ^{13}C analyses by Perry [55] and Baur [56] suggested that the extensive deposits of magnetite in some Precambrian Banded Iron Formations may be the result of organic carbon oxidation and concomitant Fe(III) reduction.

2.2. Silicates

Examination of acidic hot spring sediments from Yellowstone National Park, USA [57] and from mats growing in hot spring outflow channels, Krisuvik, Iceland [23] have revealed bacterial cells completely encrusted with granular and spheroidal crystallites (Fig. 5). These crystallites (< 500 nm) were composed exclusively of iron and silica, and their formation is presumed to result from initial binding of iron to anionic cellular sites, after which dissolved silica was added to the growing mineral via hydrogen bonding of hydroxyl groups.

The reaction of dissolved silica to bound iron has important implications for the mineral's stability over time. In freshwater sediments, amorphous iron hydroxides are the most important source of Fe(III) for Fe(III)-reducing bacteria; most other iron minerals are usually unavailable for microbial reduction [58]. The complete encrustation of bacterial cells by iron and silica may, therefore, present iron reducers with an inefficient energy source, greatly enhancing the mineral's preservation potential. The ability of bacteria to bind metals (particularly iron) that denature their autolytic enzymes and prevent unrestricted cell degradation also enhances their preservation [59]. Penecontemporaneous mineralisation, usually through silicification, is essential to prevent heterotrophic microorganisms from completely degrading the cells prior to their incorporation into the sedimentary record and for maintaining intact organic residues within a relatively impermeable matrix [60]. Thus, it is conceivable that some of the hydrothermal mats from both Yellowstone and Iceland today may become future microfossils.

In addition to the hydrothermal deposits, in the past decade, a number of studies on bacterial communities have shown the common presence of authigenic clays associated with freshwater biofilms. In the neutral pH waters of the Rio Solimões, Brazil [19], the alkaline, carbonate-saturated waters of the Speed River, Ontario, Canada [20], the Mahanadi

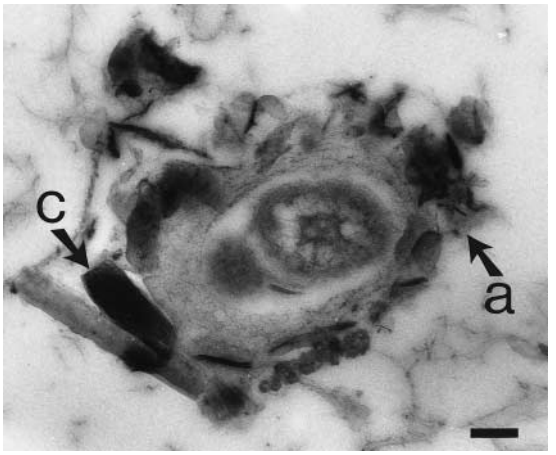

Fig. 6. Micrograph of a completely encrusted epilithic bacterial cell from the Speed River, Canada with amorphous (a) and crystalline (c) clay minerals. Scale bar = 300 nm.

River, Orissa, India [21], and metal-contaminated lake sediment in northern Ontario [61], all bacterial populations, regardless of physiology, substrate type (i.e., sediment, plants, different rock types), and aqueous composition, consistently formed complex (Fe,Al)-silicates with variable composition (Fig. 6). SAED patterns generated on the samples with good crystallinity did not correspond to any identifiable clay mineral. A ternary plot of Fe, Si, and Al (on an atomic percent basis), with the position of various major clay minerals labelled (Fig. 7), shows that poorly ordered structures were similar in composition to chamosite ($(Fe_5Al)(Si_3Al)_{10}(OH)_8$), whereas crystalline phases were increasingly siliceous, and more similar in composition to kaolinite ($Al_4(Si_4O_{10})(OH)_4$).

It is likely that the initial (Fe,Al)-silicate phases were precipitated directly when dissolved iron, silicon and aluminum, reacted with cellularly bound iron. Ferris et al. [61] found that an increasing incorporation of Fe (in a metal-contaminated lake sediment) accompanied the conversion of the low-order (Fe,Al)-silicates into a crystalline form of chamosite. In the biofilms from the Rio Solimões and the Speed River, the initial clay appeared especially reactive to silicic acid (H_4SiO_4). Continued adsorption of these dissolved metallic ions, and dewatering through hydrogen bonding of the hydroxyl groups in the bound cations with the hydroxyl groups in the soluble iron and silica, accompanied the solid-state transformation from the amorphous to crystalline phase. Eventually this process led to the complete encrustation of the bacterial cells within a mineralised matrix.

The ability of freshwater bacterial populations to bind, immobilise and retain Fe, Al, Si and other trace metals from solution has important implications for their transfer from the hydrosphere to the sediment [19]. In the microenvironment overlying a biofilm, the aqueous chemistry will invariably be determined by the activity of the microorganisms present. Although this water layer is very thin, when one takes into consideration the large surface area of solid substratum on a river's bed that is colonised by biofilms, the volume of water that falls directly under microbial contact is substantial. In this regard, biofilms dominate the reactivity of the water-substrate interface and through the adsorption of dissolved constituents, influence river chemistry. Furthermore, planktonic bacterial populations are similarly capable of binding metals from solution, and it is not difficult to imagine that these microorganisms could effectively cleanse the water of dilute metals and further partition them into the sedi-

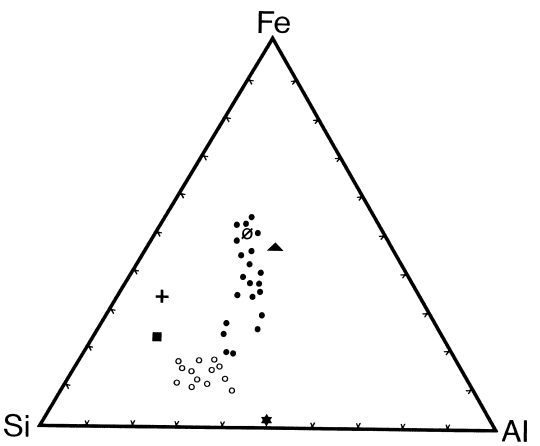

Fig. 7. Distribution of Fe, Al and Si (on an atomic percent basis) in amorphous grains (solid circles) and crystalline grains (open circles) collected from bacterial cells in the Speed River, Canada. Fe, Al and Si contents are indicated for several 'ideal' clay minerals, including chamosite (slashed circle), kaolinite (star), nontronite (plus sign), glauconite (square) and berthierine (triangle).

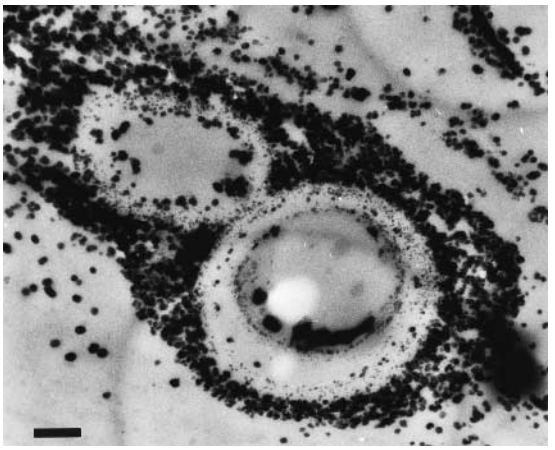

Fig. 8. TEM image of two stained bacteria completely encrusted by iron phosphate grains of chemical composition similar to that of the mineral strengite. Scale bar = 300 nm. Reprinted with permission from the Canadian Journal of Earth Sciences [27].

ments [15]. Through diagenesis, the cellularly bound metals may either be recycled to the overlying water column or become immobilised as stable mineral phases [62]. If the latter occurs, it is reasonable to expect that microdeposits of (Fe,Al)-silicates would develop. From a geological standpoint then, it is clear that freshwater bacterial populations can be viewed as important agents in metal deposition, low temperature clay formation, and, invariably, mudstone diagenesis.

2.3. Phosphates

The formation of phosphate minerals has frequently been observed in both ancient and modern sedimentary environments under high biological productivity. The organic matter not only serves as a source of phosphate to sediment pore waters through bacterial degradation [63], but it also provides a substrate upon which phosphate preferentially nucleates [64]. In a study of Cambrian phoscrete profiles from Australia, Southgate [64] observed phosphate cements (with goethite rims) occurring as irregular coatings on chasmolithic and epilithic cyanobacterial filaments. Similarly, Riggs [65] noted the association of bacteria in phosphate grains of Miocene deposits in Florida, while O'Brien et al. [66] proposed that Eastern Australian continental margin phosphorites (some phosphatic nodules have up to 43.12% Fe_2O_3) originated through the slow bacterial assimilation of phosphorus from seawater. This is not surprising since phosphorus is an essential nutrient for bacteria [67], and organic phosphorus has been shown to be a major source of phosphorus for the production of phosphate minerals [62]. In other studies, Jensen et al. [68] and Jensen and Thamdrup [69] described how the availability of iron hydroxide surfaces significantly decrease the concentration of dissolved phosphate in oxidised lake and marine sediments, respectively.

Direct evidence of bacterial iron phosphate formation comes from analysis of dark-coloured biofilms that grow on exposed rock outcrops on Ellesmere Island, in the Canadian Arctic [27]. TEM analysis of these epilithic biofilms, consisting of cyanobacteria and fungi symbiotically associated in a lichen, together with a consortium of free-living bacteria and algae indicated that the microbial community was highly mineralised, with precipitates ranging from relatively large polyphosphate granules (approximately 250 nm in diameter) within their cytoplasmic membranes to smaller iron phosphate grains (generally less than 50 nm in diameter) associated with the periplasmic space and encompassing capsule (Fig. 8). Some cells were completely encrusted by the mineral grains. In EDS spectra, these aggregates exhibited Fe:P ratios compositionally similar to the mineral strengite ($FePO_4 \cdot 2H_2O$), the expected stable solid phase predicted under the low pH conditions created by the production of organic acids in the biofilms [70]. The formation of the iron phosphate involved a series of independent steps beginning with the solubilisation of the underlying rock, including apatite for phosphorus [67], transport of the ions along the rock surface in a continuous liquid-phase water film [71], the concentration and immobilisation of metals (e.g., iron) within the biofilm, and subsequent reactions between dissolved phosphate with the bound iron [72], as might be expected given the large surface area and high adsorptive affinity of ferrihydrite for phosphate [73]. As a result, nutritional requirements by the microorganisms were actively maintained through a relatively closed recycling mechanisms which restricted the immediate loss of phosphorus from the biofilm, and thereby allowed a thriving microbial population to survive in an environment of low nutrient availability.

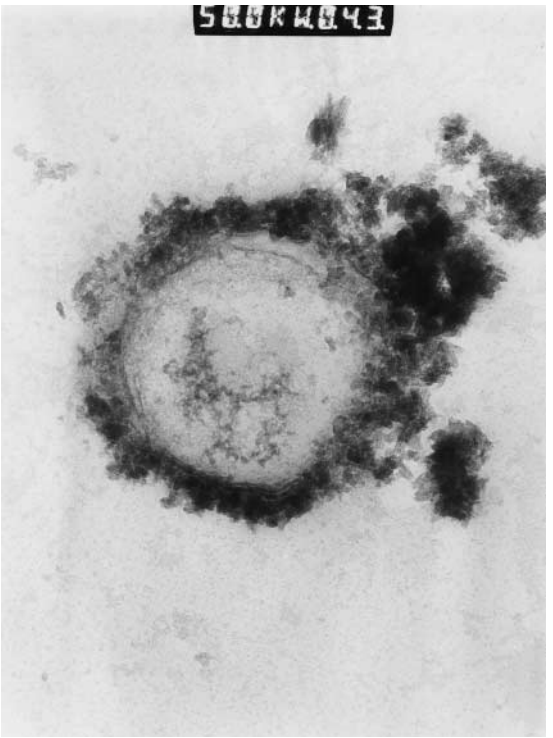

Fig. 9. Micrograph of bacterial cell (collected from 15 cm depth in a mine drainage lagoon, Wales) with ferric hydroxysulfate precipitates on outer cell. Magnification 50 000×.

2.4. Sulfates

In areas receiving acid mine drainage (AMD) effluent, ferrihydrite and ferric hydroxysulfates frequently occur as surface precipitates, resulting from the exposure and subsequent oxidation of iron sulfides. The general processes have been described as follows [74]:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-} \quad (1)$$

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \quad (2)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (3)$$

$$Fe^{2+} + 2.5H_2O + 0.25O_2 \rightarrow Fe(OH)_3 + 2H^+ \quad (4)$$

Most emphasis to date has been placed on describing the initial abiotic oxidation mechanisms (reaction 1), the subsequent microbial oxidation of Fe^{2+} under acidic conditions, which appears to be the rate-limiting step (reaction 2), and the accelerated oxidation of metal sulfides by dissolved Fe^{3+} (reaction 3). The final off-site oxidation and hydrolysis of Fe^{2+} (reaction 4) has only recently been addressed [28,29,75]. A voluminous yellow precipitate forms almost immediately when AMD comes into contact with fresh water. However, the characterisation of this precipitate is still uncertain, particularly since it has a variable composition [29].

In West Glamorgan, Wales, analyses of sediment samples from a mine drainage lagoon indicated an abundance of mineralised bacterial cells (Fig. 9), with surface bacterial samples predominantly encrusted in a ferrihydrite-like mineral, whereas subsurface bacteria exhibited a greater proportion of fine-grained Fe-S precipitates, presumably a form of ferric hydroxysulfate [18]. The presence of an iron sulfide phase is unlikely due to a lack of sulfate reduction within the sediment profile. Using atomic weight ratios, the Fe:S ratio decreases from 3.5:1 at 15 cm to 1.9:1 at 30 cm, further suggesting the continued reactivity (with depth) of dissolved sulfate for the growing mineral.

The ability of these bacteria to precipitate iron hydroxysulfates has important implications for acid mine drainage remediation. Artificially reducing wetlands have been constructed with a view to increasing the pH and removal of dissolved metals from the effluent as stable sulfide phases. Unfortunately, wetland efficiency is limited to a few years before sulfate reduction rates drastically decrease [76]. However, the ability of Fe(III)-reducing bacteria to reduce ferric hydroxysulfates has not yet been addressed, and it may be possible that creating artificially reducing conditions are unnecessary if the indigenous microorganisms cannot effectively degrade these authigenic biominerals.

2.5. Sulfides

In natural, anoxic environments, dissimilatory sulfate reduction is the major process by which dissolved sulfide is formed. This process is carried out by several anaerobic bacteria that generate the energy required for growth by coupling the oxidation of simple organic molecules to the reduction of sul-

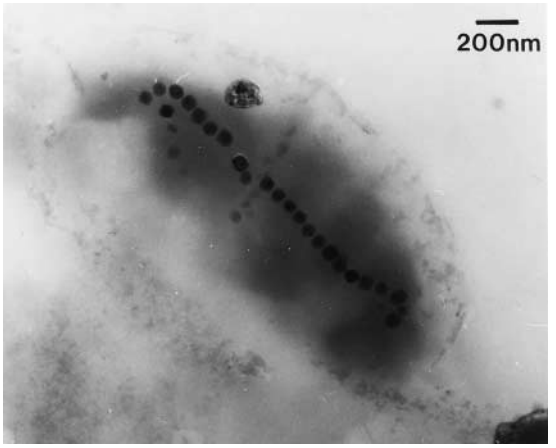

Fig. 10. TEM image of a chain of cubo-octahedral greigite crystals within an unidentified, uncultured, rod-shaped bacterium collected from a sulfidic salt marsh pool. Scale bar = 200 nm. Reprinted with permission of the author and the American Society for Microbiology [35].

fate [77]. The sulfide generated subsequently reacts with solid-phase iron oxides or hydroxides within the sediment, locally precipitating iron monosulfide phases (mackinawite and amorphous FeS) and elemental sulfur at the iron source [78]. The elemental sulfur then becomes the oxidant required to eventually convert FeS to pyrite [79]. Although most ferric iron is reduced by the preceding reaction with dissolved sulfide, in some microenvironments, soluble ferrous iron is produced by Fe(III)-reducing bacteria, where it freely migrates into the zone of sulfate reduction to further react with porewater sulfide at the site of organic decay [80].

In a metal-contaminated lake sediment in Sudbury, Ontario, Ferris et al. [61] observed the formation of iron sulfides (mackinawite) directly on the outer surfaces of bacterial cells and their membranous debris. Most of the metal sulfides appeared as dense aggregates which ranged from 10 to 50 nm in diameter. Experimental evidence suggests that metals chemically complexed to bacteria are more reactive towards dissolved sulfide [81], and it is likely that the mackinawite in the Sudbury study formed due to dissolved sulfide reacting with cellularly bound iron. Because there was less than 0.75 wt.% organic carbon associated with the lake sediment, the intensity of sulfate reduction was limited, and thereby allowed for the persistence of the poorly crystalline, sulfide phase [61]. In other studies, the preservation of very degradable soft, organic parts occurred as a pyritised layer of bacteria which pseudomorphed the original structure [78]. More recently, sediment collected from the Humber Estuary, England [24] showed extracellular iron monosulfide and pyrite associated with bacterial cell surfaces at depths greater than 5 cm. The interesting feature in this ongoing study is that bacterial cells themselves may provide much of the reactive iron essential for sulfide formation, since the surface marine bacteria commonly had ferrihydrite deposits associated with them.

The formation of greigite (Fe_3S_4) is also known to proceed through controlled intracellular mineralisation by magnetotactic bacteria [82]. Individual greigite particles appear to be membrane-bound, organised into chains (Fig. 10), and ferromagnetically ordered [38], providing the bacteria with properties similar to magnetite-producing bacteria, with the exception that greigite is one-third as magnetic [83]. Morphologies of greigite include cuboidal and rectangular prismatic crystals in the size range of 35–120 nm [35]. In one magnetotactic bacterium pyrite crystals were observed along with greigite [83]. Although pyrite may simply represent the slow transformation of greigite into a more stable phase under strongly reducing conditions at neutral pH, the lengthy conversion time seems to preclude this process during the cell's lifetime [35]. Instead, greigite and pyrite may be biomineralised separately, indicating that the stoichiometry of the metal (Fe) and nonmetal (S) can change in some magnetotactic bacteria resulting in different mineral assemblages [35].

While magnetite-producing bacteria prefer growing above the oxic-anoxic boundary, the greigite producers seem to prefer to be below the point where oxygen concentrations are zero and hydrogen sulfide is present, thus behaving as anaerobes [35]. Interestingly, one bacterium as described by Bazylinski et al. [84] produced magnetite in the oxic zone and greigite in the anoxic zone, implying that local oxygen and/or hydrogen sulfide concentrations regulated biomineralisation in this microorganism.

3. Conclusions

Bacteria are found throughout nature, inhabiting

every conceivable environment where liquid water is freely available. They are found in enormous numbers and form a major proportion of the Earth's global biomass. Because of their ubiquity and their inherent ability to concentrate trace metals, it becomes apparent that these microorganisms must significantly affect biogeochemical cycling in both modern and ancient sedimentary environments. Certainly in terms of iron biomineralisation, the variety and quantity (if Precambrian BIFs are, in part, of microbial origin) of minerals suggests that they must be playing a major role in shaping their immediate surroundings.

One of the most important issues that remain unanswered is what benefit, if any, microorganisms derive from the predominantly passive biomineralisation processes. It has been established that bacteria have the ability to partially control their surface charge, and therefore should be able to inhibit biominerals from forming on their cellular surfaces, particularly in dilute environmental solutions. The mere presence, therefore, of biominerals implies that biomineralisation must be advantageous. While some Fe-hydroxides and iron phosphates may concentrate needed trace metals and anions, respectively, what is the possible explanation, for example, of the (Fe, Al)-silicates? Is it the increased surface area for metal adsorption or possibly a mechanism to protect themselves from predation by other bacteria or small deposit feeders? Finding the answer to these questions will undoubtedly provide an invaluable insight into the way bacteria influence low-temperature geochemistry.

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