

# Diversity of iron and silica precipitation by microbial mats in hydrothermal waters, Iceland: Implications for Precambrian iron formations

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## ABSTRACT

Direct examination of microbial mats from Icelandic hot springs with transmission electron microscopy and energy-dispersive X-ray spectroscopy revealed a consortium of bacterial cells in varying stages of mineralization. Differences in observed mineralogy largely reflect differences in the chemistry of the hydrothermal waters. Silica-rich spheroids formed epicellularly on cell walls and surrounding sheaths and capsules of microorganisms and, in some cases, intracellularly when presumably the cell(s) had lysed. Commonly, these precipitates were observed coalescing to form a matrix of amorphous silica that completely encapsulated the cells and/or replaced their cytoplasmic material. However, in other cells, the precipitates were composed of amorphous granules made exclusively of iron and silica in approximately equal proportions. At one locality, the bacteria formed several epicellular iron minerals, ranging from iron-mineralized capsules to fine-grained spheroids of amorphous ferric hydroxide and acicular aggregates of goethite. The complete encrustation of bacterial cells by silica, iron, or a combination of both may greatly enhance their preservation potential, such that these mineralized microorganisms may conceivably represent future microfossils. Thus, we may be witnessing contemporaneous biomineralization processes that are similar to those of the geologic past, particularly with regard to the origin of some Precambrian banded iron formations.

## INTRODUCTION

Much of what we understand about the evolution of early life forms comes from examination of ancient stromatolitic microfossils embedded in Precambrian cherts and iron formations. The preservation of these microfossils, typically composed of the sheaths and walls of degraded cells (Oehler, 1976), is attributed to the ability of microorganisms to bind metals (particularly iron) that denature their autolytic enzymes and prevent unrestricted cell degradation (Ferris et al., 1988). Penecontemporaneous mineralization, 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 (Oehler, 1976).

Although ancient microbial mat communities grew in most shallow, submerged environments, as is evident from the stromatolite record, the actual preservation of cells was rare and seems to be biased toward those mats that lived in hypersaline environments (Walter et al., 1992). The preferential preservation of marine microbial assemblages was further enhanced by silica supersaturation of Precambrian oceans (Beukes and Klein, 1992). Today, however, only a few extreme aqueous environments have sufficiently high silica concentrations to be conducive to microbial preservation; these

include the hydrothermal effluent from hot springs.

Previous studies of hot-spring geyser effluents of Yellowstone National Park (United States) indicated that algal and bacterial stromatolites (lining the outflow channels) are composed primarily of amorphous silica (Walter et al., 1972). Walter et al. suggested that the silica precipitated nonbiogenically, because of the cooling and evaporation of the supersaturated waters, and thereby completely encrusted the microbial communities (Oehler and Schopf, 1971). Further studies from the same area, using transmission electron microscopy, showed individual bacterial cells preserved in successive stages of iron-silica crystallization, some cells being thoroughly embedded in a mineralized matrix (Ferris et al., 1986). By providing detailed images of the mineralized cells, in conjunction with a geochemical description of mineral formation, Ferris et al. contradicted previous views by suggesting that the mineralization processes were biologically induced. Similarly, in a current study of hot-spring effluents in Iceland, Schultze-Lam et al. (1995) have provided a description of the organic and mineral interactions leading to silicification of bacterial mats.

We collected samples of microbial mats from three chemically unique hot springs in Iceland: Strokkur, near Geysir on the Haukadalur Plain; Krisuvik, on the south-

western Gullbringu Peninsula; and Lýsu-hóll, on the western Snafellsnes Peninsula. Analyses of these stromatolite-forming communities have provided valuable information on the biomineralization processes associated with hydrothermal waters. The results offer an insight into the mechanisms by which ancient microbial communities were preserved and how their mineralization may have contributed to the formation of some Precambrian sedimentary deposits.

## METHODS

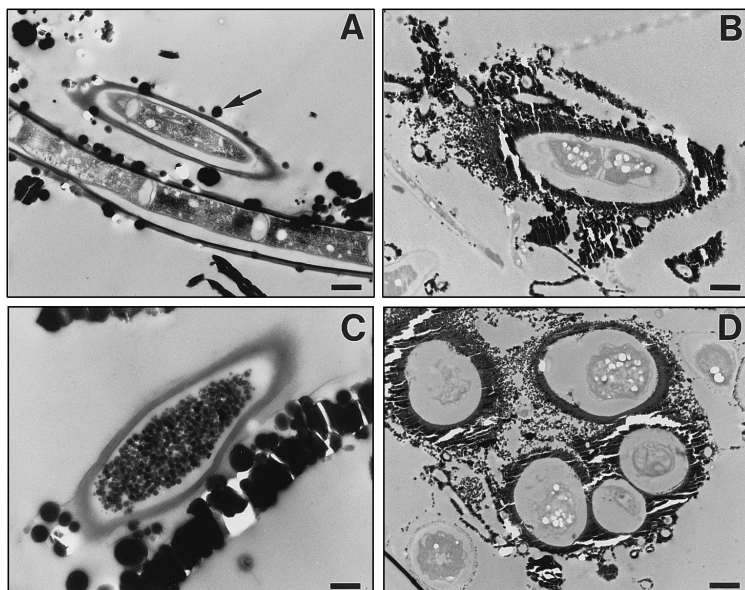
Samples of microbial mats were collected from the outflow channels, several metres away from the geysers, where they were growing as hard, finely laminated crusts. Sections of biofilms (~4.0 cm<sup>2</sup>) were scraped off the top few millimetres of the hard substratum with a sterile scalpel and immediately placed in 5 ml metal-free plastic tubes containing aqueous 2.0% (vol/vol) glutaraldehyde. The microorganisms were prepared for thin sectioning by methods described by Konhauser et al. (1994). Grids were viewed with a Philips EM400T transmission electron microscope-scanning transmission electron microscope (TEM-STEM) equipped with a model LZ-5 light-element detector and an exL multichannel analyzer (both from Link Analytical) operating at 100 keV. Energy-dispersive X-ray spectroscopy (EDS) was conducted by using an electron-beam current of 0.1 mA and a spot size of 400 nm and by collecting counts for 100 s (live time). Mineral phases were determined by means of selected-area electron diffraction (SAED).

Approximately 250 mL of water was collected from the outflow channels, filtered through 0.45 µm filters, and acidified with HNO<sub>3</sub> on site. In the laboratory, chemical analyses of the waters were conducted with atomic adsorption spectroscopy (AAS).

## RESULTS

### Strokkur

In the Strokkur geyser outflow channel, the hydrothermal waters were alkaline (pH 8.5), with a chemical composition dominated by dissolved silica (476 ppm), sodium (224 ppm), and potassium (14 ppm), and iron levels below the detection limit for



**Figure 1.** Transmission electron micrographs of bacteria (stained) from Strokkur. **A:** Filamentous bacteria with epicellular, Si-rich spheroidal grains on outer sheath surface (arrow). Grains around cell may be remains of previously shed sheath material. Scale bar = 900 nm. **B:** Completely encrusted cell where individual siliceous spheres have begun to coalesce. Scale bar = 1  $\mu$ m. **C:** Lysed bacterial cell undergoing intracellular mineralization. Note that siliceous spheres are still recognizable. Scale bar = 600 nm. **D:** Colony of bacteria completely encrusted by silica-rich matrix. Remnants of cytoplasm are still evident inside cells. Scale bar = 1.6  $\mu$ m.

AAS. TEM analyses revealed that the dominant microorganisms growing in the encrusted microbial mat were the filamentous bacteria *Chloroflexus* (Schultze-Lam et al., 1995), the same microorganisms encountered in laminated mats in Yellowstone (Doemel and Brock, 1977). EDS and SAED indicated that the microbial cell walls, sheaths, and capsules (the latter two being different forms of encompassing extracellular polysaccharide) served as nucleation sites for the epicellular precipitation of amorphous, silica-rich spheroidal grains (Fig. 1A).

The siliceous spheres formed in the capsules were smaller than those on the cell walls (200 nm vs. 500 nm), presumably because of physical constraints imposed by the density and structure of the extracellular material. In many cells, the spheres appeared to merge, such that individual precipitates were no longer distinguishable (Fig. 1B). Commonly so much silica was deposited around the cell that it was completely surrounded by a thick, amorphous layer (several micrometres thick). Eventually, of the original organic framework on which the silica was precipitated, only the mineralized matrix remained. Within the same samples, several bacterial cells also exhibited intracellular mineralization. It is likely that mineral formation occurred after the cell(s) had lysed, since the presence of mineral precipitates within the cell(s) would be a serious detriment. In some cells, the individual silica spheres are still recognizable (Fig. 1C), whereas in other cells, the

spheres have coalesced to form an amorphous matrix resembling the epicellular precipitates.

During silicification of the microbial mat, some bacterial cell structures were preserved. Such microfossilization is clearly seen in Figure 1D in which some of the organic material is still identifiable. Apparently, silicification was extremely rapid, and the preserved cells may have been completely embedded within months (Ferris et al., 1986).

#### Krisuvik

In Krisuvik, the microbial cells were associated with diverse mineral assemblages. Figure 2 shows a bacterial cell with several spheroidal grains (~200 nm) embedded in the dense capsular material. EDS of the capsule alone determined that the organic polymers were iron rich, whereas analyses of the individual spheres indicated that they were siliceous; identical to those in Strokkur. At the top of the cell, a different mineral is apparent. This amorphous precipitate (~500 nm), composed almost exclusively of iron and silica in approximately equal amounts, is somewhat reminiscent in composition and morphology to the amorphous granules associated with bacterial biofilms collected from temperate (Konhauser et al., 1994) and tropical rivers (Konhauser et al., 1993), a metal-contaminated lake (Ferris et al., 1987), and the hydrothermal waters of Yellowstone (Ferris et al., 1986).



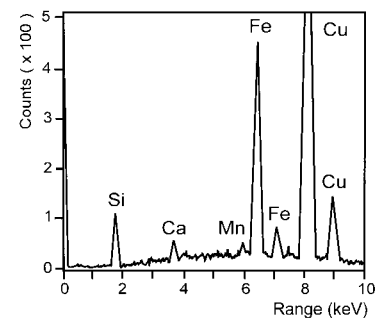
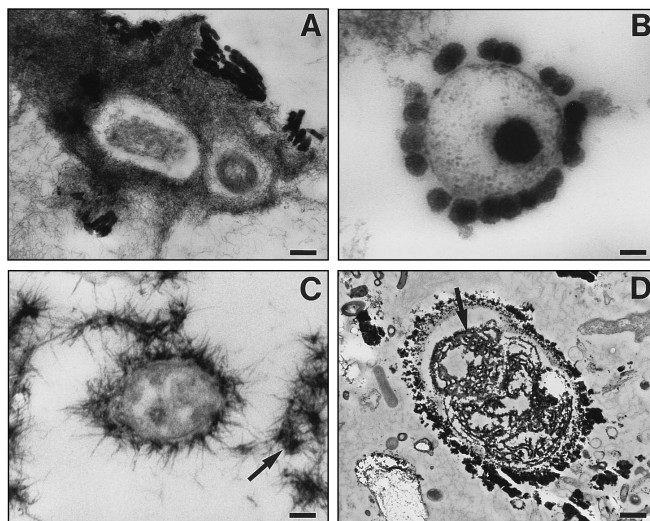
**Figure 2.** TEM image of bacterial cell from Krisuvik with (1) siliceous spheres embedded within dense, iron-rich capsule (arrow) and (2) amorphous, gel-like grains. Scale bar = 450 nm.

#### Lýsuhóll

TEM analyses of the microbial mats growing in the Lýsuhóll hot-spring outflow channels indicated that a community of unidentified bacteria was highly mineralized, ranging from naturally stained capsules to fine-grained (<100 nm) authigenic mineral precipitates. Capsules varied considerably in nature; some only encapsulated an individual cell, whereas other microorganisms produced so much extracellular material that several cells became encapsulated (Fig. 3A). EDS indicated that the bacterial surfaces bound significant amounts of iron (found in relatively low dissolved concentrations, 0.83 ppm), with minor amounts of silicon (178 ppm in solution), calcium (80 ppm), and manganese (Fig. 4). Conversely, other major dissolved cations such as sodium (486 ppm), potassium (36.5 ppm), and magnesium (20.8 ppm) were not complexed in detectable quantities.

The precipitation of iron phases was not restricted to cells with encapsulating material; the partial and complete encrustation of other bacterial cells by fine-grained spheroids, composed of amorphous ferric hydroxide, presumably ferrihydrite (Fig. 3B) and acicular aggregates of goethite (Fig. 3C), was also detected. The spheroidal grains (<100 nm in diameter) were consistently found on the outer cell wall, and they were similar in size and morphology to extracellular magnetite crystals formed by dissimilatory Fe(III)-reducing bacteria (Lovley, 1992). However, the presence of magnetite could not be verified with electron diffraction. The acicular grains (~50 nm in length) were also formed extracellularly on the surface of the cell wall. Frequently, the precipitates were observed several micrometres away from the cell surfaces, suggesting that the microorganisms may have shed the grains at an earlier stage. Goethite reprecipitation is commonly favored after ferrihydrite dissolves, particularly in the presence of organic compounds that are capable of complexing Fe<sup>3+</sup> and keeping its

**Figure 3. TEM images of bacteria from Lýsuhóll.** **A:** Two bacterial cells surrounded by dense, iron-rich capsule. Scale bar = 230 nm. **B:** Bacterial cell with amorphous iron hydroxide, spheroidal grains precipitated on cell wall. Scale bar = 100 nm. **C:** Bacterial cell with crystalline, acicular grains (goethite) precipitated on cell wall. Grains around cell may have been shed (arrow). Scale bar = 70 nm. **D:** Microbial cell with iron-rich epicellular and intracellular mineralization (arrow). Scale bar = 1.6  $\mu\text{m}$ .



**Figure 4. EDS spectrum of mineralized capsule from cells at Lýsuhóll. Copper peaks are from supporting grid.**

activity in solution low (Schwertmann and Fitzpatrick, 1992).

As in the bacterial cells in Strokkur and Krisuvik, many bacteria appear to be preserved in Lýsuhóll through mineralization. Some cells were observed within an amorphous iron-rich epicellular matrix, comparable to the mineralized remnants of bacteria shown in Figure 1D. Other cells underwent intracellular mineralization, so that the cytoplasmic material was replaced with amorphous iron hydroxide once the cell(s) had lysed (Fig. 3D).

## DISCUSSION

The role of bacteria in forming authigenic minerals involves the reaction between metals in solution with the organic polymers of the cell. The cell wall, encompassing layers, and cytoplasm (when exposed after cell autolysis), provides special microenvironments for the electrostatic binding of soluble metallic ions. Because of their exceptional ability to accumulate metals, some bacteria have been advocated as living cation-exchange resins (Geesey et al., 1988), the concentration of metals adsorbed being indicative of the soluble metal concentrations (Konhauser et al., 1993). In other instances, metals found in extremely low soluble concentrations may still be sequestered when biologically required. In either case, once bound, these metals may then serve as nucleation sites for the precipitation of authigenic mineral phases (Lowenstam, 1981).

In Strokkur, the hydrothermal waters are sufficiently supersaturated with dissolved  $\text{SiO}_2$  for the spontaneous precipitation of amorphous silica. However, even under these conditions, silica flocculation will not occur unless some electrolyte is present or an appropriate nucleation site is available. In the biofilms, it is apparent that the latter condition is satisfied, the microorganisms supplying stable sites for both epicellular

and intracellular mineralization. The abundance of hydroxy groups, associated with polysaccharides in the capsule, sheath, and cytoplasm, allows for hydrogen bonding with hydroxyl ions in the silicic acid, resulting in silica being bound from solution. The presence on the cell wall of spheres that have a limited number of available hydroxy groups may be attributed to cation bridging with bound iron (Urrutia and Beveridge, 1993). Both examples of silicification most likely represent a passive process of Si fixation.

In Lýsuhóll, the anionically charged cell wall and extracellular material, composed of ionized carboxyl and phosphoryl groups, were able to bind conspicuous quantities of iron from solution. This is particularly interesting because the concentration of iron is exceeded by that of several major cations (Ca, Na, K, etc.). The selective accumulation of iron by bacterial surfaces can occur either passively or actively. In the first instance, as water emanates from the geyser and passes over the biofilm, ferrous iron spontaneously reacts with dissolved oxygen (at circumneutral pH) to precipitate rapidly as an amorphous ferric hydroxide (ferrihydrite) 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. Even under low dissolved concentrations, iron is effectively chelated. As a multivalent cation, iron is favorably bound to reactive organic sites in the outer cell wall because of its valence, ionic radius, hydrated radius, and hydration energy, and subsequently, it will outcompete alkaline earth metals, such as calcium, for any available binding sites. The second means by which iron is preferentially bound stems from the ability of Fe(II)-oxidizing bacteria, such as *Leptothrix* and *Gallionella*, to oxidize ferrous iron as an energy source. Through their met-

abolic activity, these bacteria commonly become encrusted in ferric hydroxide (Ghiorso and Ehrlich, 1992). Although we have not identified the bacteria with iron precipitates, the almost ubiquitous association of iron with bacteria (in Lýsuhóll) implies that the bacteria must be controlling its concentration proximal to the cell. Furthermore, the presence of anaerobic conditions within a few millimetres of the biofilm surface (Doemel and Brock, 1977) may certainly provide a suitable habitat for Fe(III)-reducing bacteria to supply ferrous iron (Lovley, 1992).

The presence of iron silicates in the Krisuvik biofilms corresponds to those authigenic mineral phases formed in similar aqueous environments, where the concentrations of iron and silica are high (Ferris et al., 1986, 1987). The mechanism involved in iron-silica precipitation has been described as a two-step process (Beveridge and Fyfe, 1985): iron is electrostatically bound to the anionic polymers of the cell wall, where it subsequently serves as nucleation sites for further metal deposition. In waters where the concentration of iron is relatively high, dissolved iron will chemically react with those metallic ions already adsorbed onto the cell wall (Ferris et al., 1987). Similarly, if the concentration of silica exceeds that of iron, then dissolved silica will be bound; this has been confirmed in experimental studies of fine-grained mineral formation by bacterial surfaces, whereby Urrutia and Beveridge (1994) observed that iron pretreatment of bacterial cells enhanced the binding of silicate at alkaline pH values. Therefore, the formation of iron silicates simply becomes an unavoidable consequence of the bacterial mats living in a concentrated solution.

The binding of silica to ferrihydrite has important implications for the mineral's stability over time. In fresh-water 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 (Lovley, 1992). The complete encrustation

of bacterial cells by a silica-iron combination may, therefore, present iron reducers with an inefficient energy source, greatly enhancing the mineral's preservation potential. Thus, it is conceivable that some of the Icelandic microbial mats may become future microfossils.

The significance of the observations made on the extant microbial mats is that we may be witnessing biomineralization processes that are similar to those of the geologic past, particularly with regard to the origin of some Precambrian banded iron formations (BIFs), the most abundant type of chemical sediment in the early and middle Precambrian. BIFs consist of intimate mixtures of chert and iron minerals, and the chemistry of Precambrian oceans, from which they precipitated, appears analogous in terms of silica and iron concentrations to the hydrothermal waters in Iceland today. Furthermore, because of the common presence of spheroidal structures in BIFs (which have been interpreted as relict microfossils), it has been suggested that microorganisms were partially involved in their deposition (LaBerge, 1973).

During the Archean and early Proterozoic, the ancestors of the first green-plant photosynthesizers (marine planktonic bacteria) produced free oxygen that they may have either obligatorily or permissively attached to a convenient oxygen acceptor, which at the time could have been the abundantly available ferrous iron (Cloud, 1965, 1973; McNamara and Awramik, 1992). The result of both forms of biomineralization was the precipitation of ferric hydroxides, the deposition of mineralized bacterial cells, and the systematic accumulation of iron-rich sediments on the ocean floor (Walker et al., 1983). Simultaneously, oversaturation of the oceans with respect to silica could have caused the almost continuous precipitation of chert (Beukes and Klein, 1992), with cell walls and capsules (of marine bacterial mats) acting as templates for the nucleation and mineralization of silica (Urrutia and Beveridge, 1993). The silicification of microorganisms has, in fact, been used to support the interpretation of the origin of silica in some Precambrian iron formations (LaBerge, 1973), whereas the banding may be attributed to episodicity of iron deposition, the result of either a temporary depletion in ferrous iron or diminished plankton productivity (Cloud, 1973).

Many of the events described above are currently observed in the stromatolite-forming mats of Icelandic hot springs, the fundamental difference being the relation between the microorganisms and the chemocline (where anoxic, ferrous iron-rich waters meet oxygenated surface waters). To-

day, microbial mats (growing in hydrothermal effluent adjacent to the geysers) are found at that interface, in contrast to planktonic bacteria living in the stratified Precambrian oceans (Lowe, 1994). Subsequently, the lack of banding in Icelandic mats may simply be due to the constant presence of attached microorganisms that are capable of forming biominerals reflective of the aqueous chemistry of the site in which they are growing (e.g., iron in Lýsuhóll and Krisuvik and silica in Strokkur). However, when all Icelandic sites are considered together, it is clear that microorganisms are able to effectively mediate the precipitation of the major mineralized components of Precambrian iron formations. Comparisons can also be made regarding Precambrian microfossils and extant hot-spring microorganisms (Walter et al., 1992). For example, some silicified microfossils analyzed from the Gunflint Iron Formation in Ontario, Canada, bear a striking resemblance to the photosynthetic bacteria of modern hot springs (Walter et al., 1972), and other "thread-shaped" microfossils in the Gunflint appear analogous to present-day iron-oxidizing bacteria such as *Leptothrix* and *Gallionella* (Cloud, 1965). Because of the distinct similarities in aqueous composition, the forms of biomineralization (both silicification and iron mineralization), and the types of microorganisms present, we suggest that the processes described in the extant microbial mats in Iceland may be analogous to the processes that led to the accumulation of some Precambrian iron formations.

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