

Hematite-coated microfossils: primary ecological fingerprint or taphonomic oddity of the Paleoproterozoic?

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ABSTRACT

Microfossils belonging to the 1.88-billion-year-old 'Gunflint-biota' are preserved as carbonaceous and hematitic filaments and spheres that are believed to represent ancient chemolithoautotrophic Fe(II) oxidizing bacteria that grew above a chemocline where ferruginous seawater upwelled into shallow, oxygenated waters. This 'biological' model posits that hematite formed during burial from dewatering of the precursor ferric oxyhydroxides that encrusted Fe(II)-oxidizing bacteria. Here, we present an alternate 'taphonomic' model in which iron-rich groundwaters discharged into buried stromatolites; thus, the mineralization reactions are more informative of diagenetic processes than they are for primary marine conditions. We sampled centimeter-scale columnar stromatolites from both the lower and upper stromatolite horizons of the Biwabik and Gunflint formations, across a range of metamorphic gradients including unaltered to prehnite-pumpellyite taconite, supergene altered ore, and amphibolite-pyroxene grade contact-metamorphic zones. Fossils are rare to very rare and comprise curved filaments that exist in clusters with similar orientations. The filaments from throughout the Biwabik are similar to well-preserved carbonaceous *Gunflintia* from Ontario. Spheres of *Huroniospora* are also found in both formations. Microfossils from the least altered sections are preserved as carbon. Prehnite-pumpellyite samples are composed of either carbon or hematite (Fe₂O₃). Within the contact aureole, filaments are densely coated by magnetite (Fe₃O₄); the highest grade samples are secondarily oxidized to martite. The consistency in stromatolite microstructure and lithofacies throughout the metamorphic grades suggests they formed under similar environmental conditions. Post-depositional alteration led to replacement of the carbon by iron oxide. The facies association, filament distribution, and lack of branching and attached spherical cells argue against *Gunflintia* being a direct analogue to common marine, chemolithoautotrophic Fe(II)-oxidizing bacteria. Instead, we propose that the presence of hematite-coated microfossils is a reflection of taphonomic processes and does not necessarily reflect the byproduct of an original microbial ecosystem.

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INTRODUCTION

Since the 1960s, it has been recognized that the microfossils of the Gunflint formation are preserved as both carbonaceous and iron oxide filaments and spheres within a microcrystalline quartz (chert) matrix (Barghoorn & Tyler, 1965; Awramik and Semikhatov, 1979; Tazaki, 1993; Kudryavtsev *et al.*, 2001; Igisu *et al.*, 2009). However, the taphonomic implications of multiple preservational states have not been fully explained, even as more locations con-

taining similar Gunflint microflora were discovered (e.g., Cloud & Licari, 1968; Knoll & Barghoorn, 1976; Walter *et al.*, 1976; Cloud and Morrison, 1980; Knoll & Simonson, 1981; Yun, 1984; Lager, 2001; Yongding *et al.*, 2004). The early focus has been on identification of the microfossils, and less on the processes of preservation (however, see recent papers by Wilson *et al.*, 2010; Edwards *et al.*, 2012).

Taxonomic placement of the microflora has followed exciting trends in microbiology. The original discoveries

by Moore (1918) and Gruner (1922) referred to the stromatolite fossils as ‘algae’. The seminal papers by Barghoorn & Tyler (1965) and Cloud (1965) placed the microflora in the phylum *Cyanobacteria*. The criteria used were the relatively large size of the filaments as well as the association with stromatolites. Further work in the 1970s continued to emphasize cyanobacterial affinity (e.g., Awaramik & Barghoorn, 1977). Interestingly, the possibility that the forms could be ‘iron-loving’ bacteria was voiced as early as 1965 by Barghoorn and Tyler. Indeed, nearly 100 years ago, Harder (1919) postulated the role of Fe(II)-oxidizing bacteria in forming major iron deposits. The taxonomic implications are critical as the preservation of Fe(II)-oxidizing bacteria would help solve major questions relating to iron-formation genesis and provides a provocative story in a critical chapter of Earth history—the oxygenation of the atmosphere (Knoll, 2003; Bekker *et al.*, 2010; Posth *et al.*, 2013).

The implication of these various studies is that the hematite coatings preserved in some Paleoproterozoic cherts formed directly from a primary ferric oxyhydroxide precipitate (e.g., ferrihydrite, $\text{Fe}(\text{OH})_3$) as a response of the metabolism of Fe(II)-oxidizing bacteria. An alternative hypothesis proposed here is that the hematite coatings formed post-depositional due to the input of reduced iron-rich fluids in the subsurface. In this regard, the presence of hematite cannot be used as a direct proxy for establishing a primary Fe(II)-oxidizing metabolism and, by extension, allows for an interpretation of seawater composition at the time of stromatolite formation.

Geologic setting

This study focuses on preserved microfossils from the 1.88 Ga stromatolite intervals of the Biwabik and Gunflint iron formations of the Lake Superior region (Fig. 1). The Biwabik and Gunflint are correlative but separated by the 1.1 Ga Duluth Complex gabbroic intrusions. The iron formations vary in thickness, ranging up to 240 m thick (Severson *et al.*, 2009). Microfossil-bearing stromatolites are confined within two separate meter-scale intervals of broadly similar facies but containing a diverse assemblage of stromatolite forms (Hofmann, 1969). The upper interval can be traced throughout the Gunflint. In the Biwabik, the upper interval extends from the contact with the gabbroic intrusion west to Hibbing, Minnesota (Severson *et al.*, 2009). The lower interval represents a basal flooding surface atop a detrital interval that ranges from sandstone to conglomerate. In places, stromatolites are observed growing directly upon the eroded Archean substrate. This interval is not continuous but can be found throughout the Biwabik and Gunflint. Stromatolitic boundstone ranges from 10 to 110 cm thick, and individual biostromes can be continuously traced for 10 s of meters along walls of open-

pit mines. In addition to boundstone, the stromatolite facies include flat-pebble conglomerate and cross-bedded oolite. There is no evidence of intertidal facies, such as herringbone cross-bedding, flaser-bedding, mud cracks, or birds-eye structures. However, rounded intraclasts with desiccation cracks are locally found dispersed with ooids between stromatolite columns (see Markun & Randazzo, 1980; Fralick, 1988; Pufahl & Fralick, 2004; and Planavsky *et al.*, 2009 for additional details on the stratigraphy).

The Biwabik–Gunflint iron formations were deposited in peritidal to deep shelf settings in a subsiding back-arc basin (Hemming *et al.*, 1995a,b; Schulz & Cannon, 2007). A volcanic arc lay to the south, separating the basin from the open ocean. Tholeiitic lava intruded the sequence in the southernmost exposures in Wisconsin and in the Gunflint formation. Following deposition of the iron formations, and postdating the Sudbury impact at 1.85 Ga, a major collision to the south led to the main phase of the Penokean orogeny with substantial faulting, metamorphism, and syn-orogenic plutonism toward the south and east. The collision led to the development of a foreland basin causing further subsidence of the Biwabik–Gunflint area. This region then became the depocenter for a thick sequence of shale and turbidites (Virginia and Rove Formations) (Hoffman, 1987; see review in Ojakangas *et al.*, 2011). The next major deformational event was significant rifting and intrusion of gabbro at 1.1 Ga (Miller & Severson, 2002). Subvolcanic sills of diabase and surface flows of basalt are associated with this large igneous province though there is no evidence of oceanic incursion (Hollings *et al.*, 2010).

Finally, there are regions of enriched ore—leached silica and enriched oxidized iron—associated with fault zones in the Mesabi Iron Range. These mines are known as ‘direct-shipment ore’ for their high iron content in contrast to the low iron taconite being mined today. The age of this supergene alteration is unknown but likely related to near surface weathering by heated vadose fluids in the Cretaceous (Simonson, 2011). For details on models of enriched iron ore formation, see Evans *et al.* (2013).

Both iron concentration and metamorphic grade increases toward the southwest so that the best preserved material is from the northernmost exposures of the Gunflint. In fact, the quality of preservation is so detailed that the region near Thunder Bay, Ontario, and particularly at Schreiber, has been deemed a Paleoproterozoic ‘lagerstätten’ (Nudds & Selden, 2008). Cloud & Licari (1968) purposefully investigated the Biwabik iron formation to expand the known areal distribution of the Gunflint microflora. They figured a mat of randomly oriented filaments (*Gunflintia*), a few spheres (*Huronisporia*), and the possible presence of *Eoastrion*, from a stromatolite collected from tailings of the direct-shipment ore Corsica Mine, near Gilbert, Minnesota. They also noted that the stromatolite beds of the Upper Cherty Member (= upper

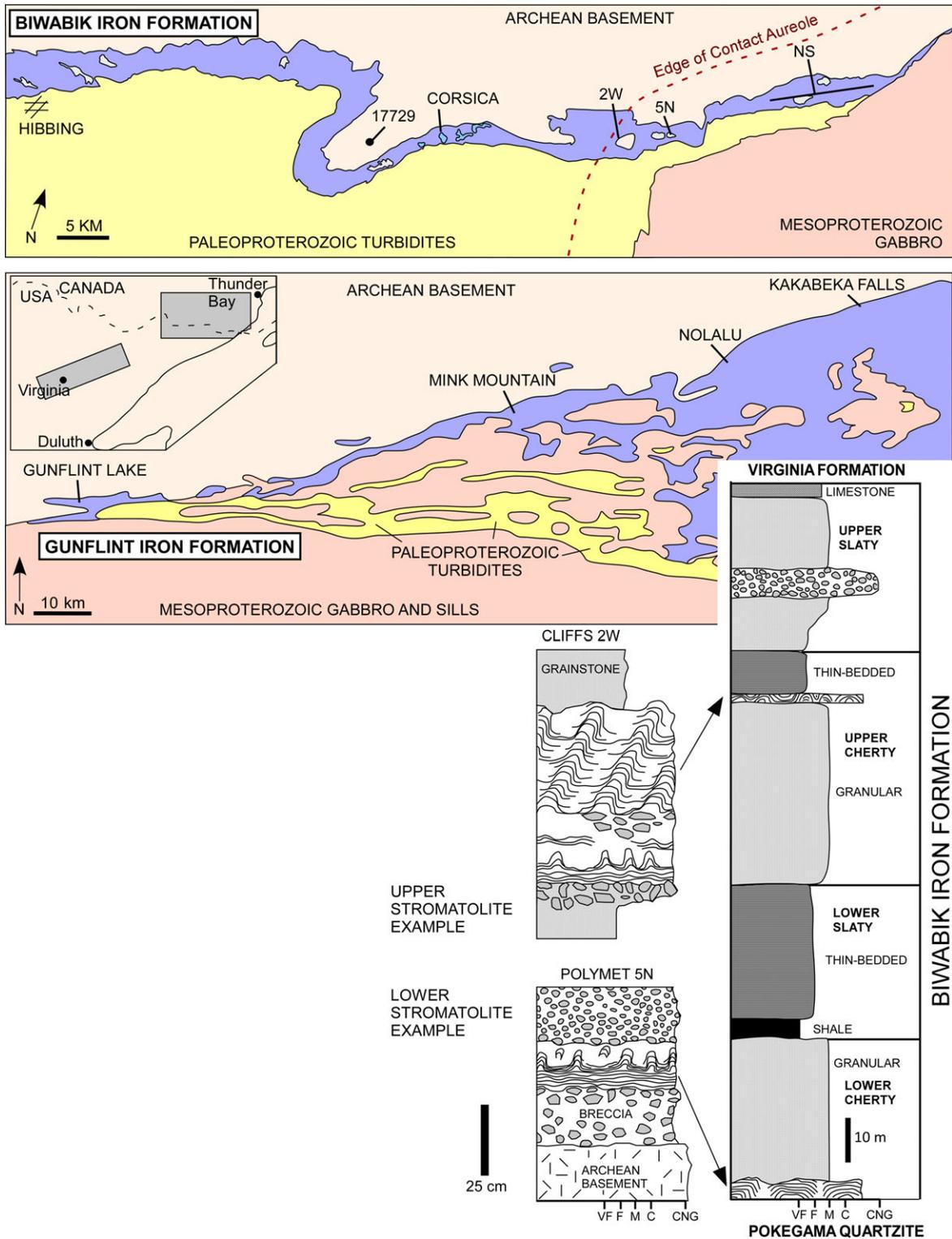


Fig. 1 Simplified geologic map and stratigraphic column. The upper two panels show the outcrop distribution of the Biwabik (upper) and Gunflint (Lower) iron formations relative to the underlying Archean basement and overlying Paleoproterozoic turbidites. Note the intrusive contact of the Mesoproterozoic gabbro and sills. Inset stratigraphic column shows the typical iron-formation lithofacies with details of the two stromatolite beds. Compiled from several columns at the Cliff-Erie mines near Hoyt Lakes, Minnesota. The Gunflint is broadly similar though facies variations substitute throughout. See Table 1 for locations.

Table 1 Sample locations from the Gunflint and Biwabik iron formations cited in this study

| Location | Latitude (N) | Longitude (W) | Collection | Metamorphic grade |
|-----------------|--------------|---------------|------------|--------------------------|
| Schreiber | 48.80 | 87.34 | Natural | Unmetamorphosed |
| Kakebeka Falls | 48.41 | 89.63 | Natural | Unmetamorphosed |
| Whitefish Falls | 48.29 | 89.84 | Natural | Unmetamorphosed |
| Mink Mountain | 48.24 | 90.16 | Mine | Contact (subgreenschist) |
| Gunflint Lake | 48.09 | 90.82 | Natural | Contact (subgreenschist) |
| Core 17729 | 47.53 | 92.72 | Core | Prehnite-pumpellyite |
| Corsica Pit | 47.51 | 92.12 | Mine Talus | High temperature leached |
| Cliffs-Erie 2W | 47.57 | 92.14 | Mine | Subgreenschist |
| Polymet 5N | 47.63 | 92.05 | Mine | Greenschist |
| Northshore | 47.66 | 91.93 | Mine | Amphibolite-Pyroxene |

interval in this paper) are ‘strikingly similar to and probably the equivalent of the stromatolitic zone that has yielded the Gunflint microbiota in Ontario’ (p. 781). Most critical to the present paper, they state that the former carbonaceous cell walls have been replaced by hematite. All of the fossils are confined to the stromatolites and are most abundant along ‘particular unequally spaced, upwardly convex laminae of the individual stromatolite fingers or ridges’.

MATERIAL AND METHODS

Stromatolite samples from both the lower and upper stromatolite intervals of the Biwabik and Gunflint iron formations were used in this study (Table 1). Because of the diversity in stromatolite forms, only centimeter-scale columnar to rarely branching columns assigned to *Gruneria biwabika* (Cloud & Semikhatov, 1969) was used in this study for consistency. Targets were chosen that represented relatively unaltered, slightly altered (prehnite-pumpellyite), low-grade altered (subgreenschist), and high-temperature leached iron-formations (direct-shiping ore). Samples were also collected from metamorphic gradients (up to amphibolite-pyroxene) within the contact aureole associated with the 1.1 Ga gabbroic large igneous province and associated diabase sills (contact metamorphism). Samples were carefully collected from drill core, natural exposures, and open-pit taconite mines. All samples were located aerially and stratigraphically. Field locations were recorded with an SX Blue II submeter global positioning system (Geneq, Montréal, QC, Canada). Core locations were provided by the state of Minnesota repository in Hibbing. Cores were also provided by U.S. Steel Corporation. In total, 75 thin sections were studied. For comparison between samples, only stromatolite laminae were investigated. Others have reported microfossils from interstitial cements and reworked intraclasts (e.g., Knoll & Simonson, 1981; Strother & Tobin, 1987; Edwards *et al.*, 2012).

Thick (40 µm) and thin (30 µm) sections of rock chips were investigated with standard petrographic and reflected light microscopy techniques. Microfossil and mineral

sizes were measured using PaxIT! and Olympus Stream software. Transmitted petrographic images were photographed through an Olympus BX-51 with a 100× oil immersion objective. Reflected light images were taken through a Nikon Optiphot-POL. Fossil-bearing zones are rare to very rare in the samples that produced fossils. Most thin sections contained no recognizable fossils.

Establishing biogenicity of the filaments

Recognizing biological filaments are a challenge in the more altered samples. For consistency, only stromatolitic margins were investigated. Areas of localized alteration, in particular fractures, were not studied. To be considered biogenic, filaments had to have curves, exist in clusters with similar forms of random orientations, and not align with crystallographic boundaries. This latter criterion is important as much of the chert is secondary and insoluble residue can be migrated along the growth front of the crystal leading to pseudofossils. An additional criterion, that the filaments occur in facies where they would likely be anticipated, is met by limiting collection to stromatolitic laminae. These criteria are not meant to be universally applied to any potential microfossil in the rock record (e.g., Buick, 1990; Cady *et al.*, 2003), but are thought to provide a sufficient screen for the Gunflint–Biwabik system. Filaments were measured for width and length. Where applicable, the sizes of hematite or magnetite crystals were also measured. It is believed that the filaments described herein can be assigned to *Gunflintia* Barghoorn (Barghoorn & Tyler, 1965), common in the Gunflint formation stromatolites.

In the Gunflint formation, spheres assigned to *Huroniospora* Barghoorn (Barghoorn & Tyler, 1965) may be quite common. This presumed planktonic form is exceedingly simple in its morphology but is often found in clusters. In this study, putative *Huroniospora* were noted whether there was a consistency of size, cluster of at least several individuals, and clearly circular outline. All examples were hollow in the center and permineralized by silica. The observations and data are presented here because the morphologies are

similar to those of better preserved *Gunflintia* and *Huroniospora* and may shed light on the taphonomic processes.

RESULTS

Microfossils were collected from centrimetric columns within domal stromatolites in the basal layer of the Gunflint, as well as centimetric columns and pseudocolumns (assigned to the Form *Gruneria biwabika*; Cloud & Semikhatov, 1969) from both the basal and upper layers of both formations (Fig. 2). Domal stromatolites are approximately 1 m across with irregular, pustulate laminae comprising columns. They are embedded within white to black chert with secondary euhedral ankerite ($\text{CaFe}(\text{CO}_3)_2$) crystals. *Gruneria biwabika* columns average 1.8 cm across and 5 cm tall. Laminae are generally smooth with a high degree of inheritance. Many columns display a wall margin

and linked laminae. Cross-laminae are rare but do occur. All stromatolites are preserved with very fine-grained superficial ooids between columns. Microstructure of the stromatolites becomes increasingly altered toward the gabbroic intrusion (Shapiro, 2009). Microfossils occur in discontinuous intervals along darker laminae.

The best preserved microfossils are found in black chert in the Gunflint; lesser quality fossils are found within iron-rich laminae in the Biwabik. Even in the best preserved stromatolites of the Gunflint formation near Kakebeka Falls and Schreiber, Ontario, microfossils are rare, while in the Biwabik, they are very rare though they have been recovered from all metamorphic and diagenetic facies (Fig. 3). There was no definable pattern in location of preservation relative to stromatolite margin, axis or diagenetic front, and even within a defined region of preservation, the quality (sharpness, continuity of outline) is variable.

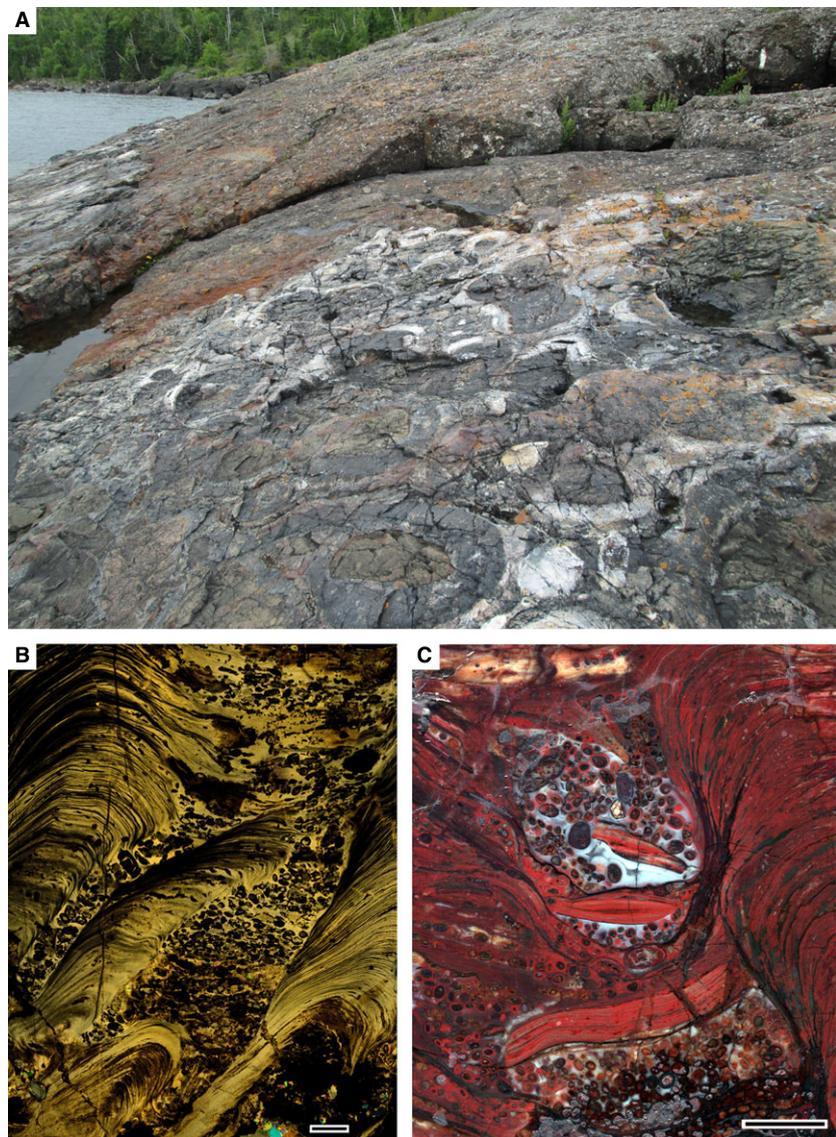


Fig. 2 Representative stromatolites. (A) Field photo of domal stromatolites composed of 0.5–1 cm wide columns growing upon conglomerate at base of the Gunflint formation at Schreiber, Ontario. (B) Polished section of tilted columns from prehnite-pumpellyite facies of the Biwabik iron formation at Corsica Mine, Minnesota. Upper stromatolite layer. (C) Polished section of hematite-rich hornfels with columns and ooids in the Gunflint formation at Mink Mountain, Ontario. Upper stromatolite layer. Scale bars: B = 2 mm; C = 0.5 mm.

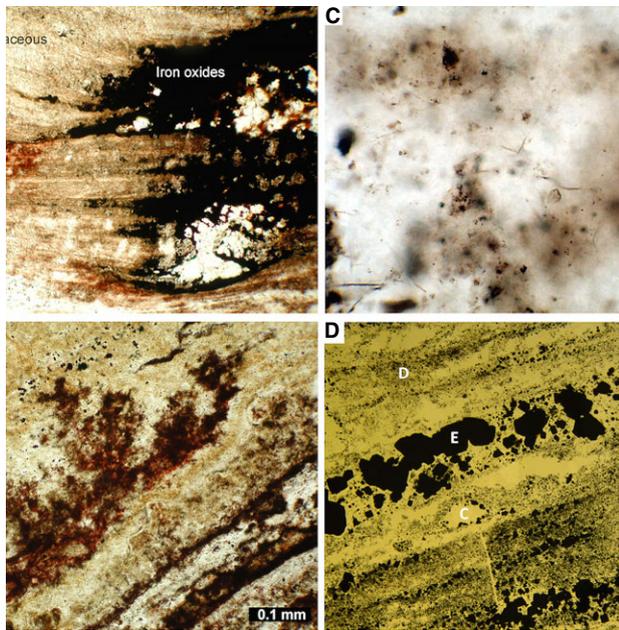


Fig. 3 Examples of stromatolite laminae showing different stages of preservation in relationship to iron oxides. (A) Carbonaceous laminae on left being replaced and destroyed by iron oxides, low-grade contact metamorphic. Mink Mountain, Ontario. (B) Detail of hematite-rich laminae, low-grade contact metamorphic. Mink Mountain, Ontario. (C) Detail of fossiliferous laminae. Microfossils preserved as hematite, subgreenchist metamorphism. Corsica Mine. (D) Detail of stromatolite laminae showing multiple forms of iron oxide replacement. The laminae are composed of chert with disseminated sub-micron crystals [D] of iron oxides. Larger euhedral crystals [E] are found along the laminae at the center and bottom, as well as lining voids associated with fabric-destructive calcite [C]. Crystals grossly preserve the original lamination. High-grade contact metamorphism (amphibolite). Northshore Mine.

Carbonaceous zones can be common and are often fossiliferous in the Gunflint. In the Biwabik, carbonaceous zones are very rare though anthraxolite is noted in non-stromatolitic facies associated primarily with calcite veins. In most cases, dark laminae that appear promising at lower magnification are dominated by non-fossiliferous iron oxide (hematite or magnetite) aggregates. In general, more carbonaceous zones are found toward the margins of the stromatolite columns.

Submillimeter-scale iron oxides are common components of the background chert throughout the Biwabik and more rarely in the Gunflint. Near Thunder Bay and Schreiber, Ontario, iron oxides are concentrated in small pockets several millimeters across that do not have a preferred orientation or stratigraphic position relative to the stromatolite fabric. Additional iron oxides are present as sub-micron euhedral to subhedral crystals that preferentially concentrate along stromatolite laminae. Opaque iron oxides are also observed along margins of superficial ooids and disseminated between grains in the intercolumnar fill.

In all locations, the dominant microfossil is assigned to *Gunflintia* though poor preservation precludes a species diagnosis (Fig. 4A–C). *Huroniospora* is rare but can locally dominate some laminae and they always occur in association with *Gunflintia* (Fig. 4D–E). Other genera, such as *Eoastrion*, are noted in the Gunflint but have not been clearly identified in the Biwabik. What is noteworthy is that there is size variation amongst microfossil type depending on locality yet the span is within the range of error (Fig. 4F; see references in Table 2). For instance, *Gunflintia* can vary twofold at the same location (i.e., Kakabeka Falls, Northshore Mine), whereas *Huroniospora* ranges in size depending on actual location. In the case of *Huroniospora*, unaltered fossils at Kakabeka are larger than the iron-encrusted cells at Northshore Mine or Corsica Mine. This is surprising because with primary iron-staining one would predict the opposite trend that being that the cell-mineral aggregate should exceed the size of the unmineralized cell. One plausible explanation is that the Northshore and Corsica cells had already degraded, and thus were smaller in size, prior to iron mineralization (see Oehler, 1976 for experimental studies on bacterial silicification). Another explanation is that the simple morphology represents two or more species of spherical structures.

Preservation of the microfossils occurs as both carbonaceous and iron oxide-coated structures (e.g., Bower *et al.*, 2010). In all cases, the filaments (*Gunflintia*) or spheres (*Huroniospora*) are embedded within chert. The preservational state is, in part, related to metamorphic conditions. Carbonaceous filaments are only found in the lowest grade (sub-prehnite-pumpellyite) outcrops in the northern exposures of the Gunflint near Thunder Bay (e.g., Kakabeka Falls; Schreiber) (Fig. 4A,D). In those locations, cellular outline is well preserved, with for example, some of the *Gunflintia* filaments appearing to have their septae visible (Fig. 4A), while in *Huroniospora*, the cell wall clearly stands out in contrast to the chert background (Fig. 4B). Where the Gunflint is close to contacts with the diabase sills, the microfossils are carbon-poor and replaced by hematite (Fig. 4E), as evident with reflected light microscopy. In these locations, such as Mink Mountain, Ontario, there is abundant dispersed fine hematite throughout the stromatolite lithofacies, including the ooids and intercolumnar spaces. In the Biwabik, deep cores outside of the contact aureole contain microfossils preserved in hematite (e.g., core 17729). Indeed, stromatolites from the enriched, ‘direct-shipment ore’ mines contain exclusively microfossils preserved in fine-grained hematite. Closer to the contact with the main gabbro body, there is an increase in the hematite crystal size (Fig. 5). In addition to coating microfossils, there is also an increase in dispersed submicron-scale hematite throughout the microquartz. At the highest grades (amphibolite), the hematite coating is remineralized (and partly reduced) to magnetite, with the

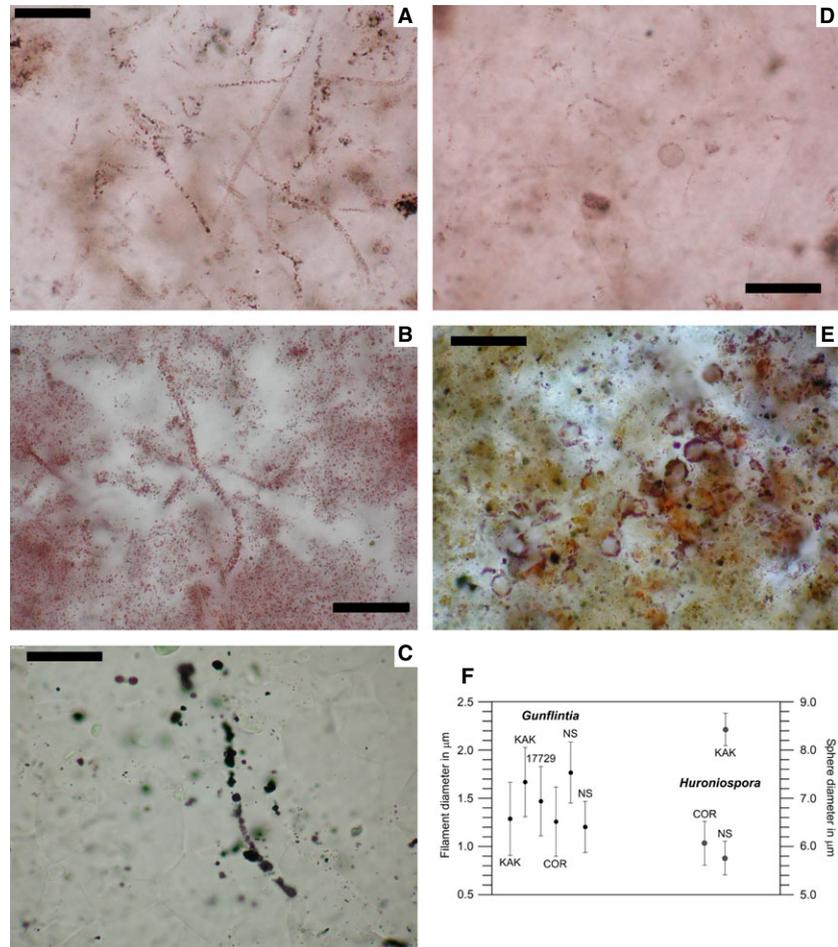


Fig. 4 Comparison of microfossils from different locations. All images are at the same scale (bar is 25 μm) and images are in plane polarized light. A–C are of *Gunflintia* and D–E are *Huroniospora*. (A) The least altered carbonaceous filaments from Kakabeka Falls, Ontario. (B) Well-preserved hematite coated sheath from core 17729. (C) Martite-magnetite preserved filament from the amphibolite-grade Northshore Mine directly adjacent to the gabbro intrusion. (D) Unaltered carbonaceous *Huroniospora* from Kakabeka Falls. (E) Low-grade alteration of the filaments to coarse hematite, Corsica Natural Ore mine. (F) Graph comparing sizes of microfossils. $N = 141$. All values given in micrometers. See Fig. 1 and Table 1 for locations.

Table 2 Locations of Paleoproterozoic *Gunflintia*-biota and preservation

| Formation | Age (Ga) | Location | Preservation | Reference |
|-------------|----------|-------------------|-------------------|--|
| Xuanlong | ~1.8 | Hebei, China | Carbon + Hematite | Juying (1996) |
| Frere | 1.85 | Western Australia | Carbon + Hematite | Walter <i>et al.</i> (1976) and Tobin (1990) |
| Duck Creek | 1.85 | Western Australia | Carbonaceous | Knoll & Barghoorn (1976) |
| Ferriman | 1.88 | Quebec, Canada | Silica | Edwards <i>et al.</i> (2012) |
| Sokoman | 1.88 | NE Canada | Carbonaceous | Knoll & Simonson (1981) |
| Gunfint | 1.88 | Ontario, Canada | Carbon + Hematite | Barghoorn & Tyler (1965) |
| Biwabik | 1.88 | Minnesota, USA | Hematite | Cloud & Licari (1968) |
| Tyler | 1.87 | Michigan, USA | Hematite | Cloud & Morrison (1980) |
| Dannemora | ~1.9 | Sweden | Hematite | Lager (2001) |
| Franceville | 2.0 | Gabon | Carbonaceous | Amard & Bertrand-Sarfati (1997) |

latter showing an increase in size closer to the contact (Fig. 4C). In rare cases, the magnetite is secondarily oxidized back to a variety of hematite known as martite. In these cases, it retains the octahedral crystal shape of magnetite.

While there is a consistency of facies within the shallow-water deposits, the concentration and distribution of iron varies widely on all scales from hand samples to cores and within a mine to locations between mines.

The most obvious example is the essentially iron-poor microfossil-bearing stromatolite beds of the northern Gunflint formation. Yet, even in the classic locality at Schreiber and outcrops at Whitefish Falls near Nolalu, there are centimeter-scale zones of iron oxides within the iron-poor stromatolites (Fig. 6). Other authors noted the patchiness in hematite with regard to microfossils (Barghoorn & Tyler, 1965). The Cliffs-Erie Mine near Hoyt Lakes also shows dramatic iron variation at the 10s



Fig. 5 Field shot showing zone of red, oxidized iron-rich stromatolite surrounded by iron-poor stromatolite preserved as white and black chert. Nolalu, Ontario.

to 100s of lateral meter scale (mapping by Shapiro, 2002–2010). Severson *et al.* (2009) present stratigraphic correlations of the Biwabik iron formation that show iron variation as economic zones.

DISCUSSION

The biologic model

There are a number of micro-organisms, the so-called iron-depositing bacteria, that facilitate ferric oxyhydroxide

mineralization by having surface ligands that promote Fe (II) oxidation, although it is not believed that they gain energy from the process (see Emerson, 2000 for review). The most common visible inhabitant of many modern, freshwater, low-oxygenated iron seeps is *Leptothrix ochracea*. This chemoheterotroph frequently forms thick filamentous layers comprising tangled matrices of tubular sheaths (extracellular organic structures) encrusted in the mineral ferrihydrite. In an iron seep in Denmark, cell counts are approximately 10^8 – 10^9 cells cm^{-3} (Emerson & Revsbech, 1994a). Those high bacterial densities promote ferrihydrite accumulation rates of 3 mm day^{-1} (Emerson & Revsbech, 1994b). One interesting observation made was that it was rare to find intact filaments of *L. ochracea* cells inside the sheaths. This correlates well with experiments that have shown *Leptothrix* continuously abandons its sheath at a rate of 1 – $2 \mu\text{m min}^{-1}$, leaving behind sheaths of 1–10 cells in length that continue to deposit ferrihydrite. This would seem to indicate that the micro-organisms actively prevent themselves from becoming permanently fixed into the mineral matrix (van Veen *et al.*, 1978) by producing a sheath that acts both as an alternative mineral nucleation site to cell wall and/or cytoplasmic mineralization and by providing a physical filter that restricts mineral formation to its outer surface (e.g., Phoenix *et al.*, 2000). Moreover, Nealson (1982) suggested that *L. ochracea*, induces ferrihydrite precipitation on its sheath as a means to remove any free oxygen and thus detoxify its environment. Other heterotrophic bacteria, such as filamentous species from the *Sphaerotilus*, *Crenothrix*, *Clonothrix*, and *Metallogenium* genera, as well as unicellular cocci of the *Siderocapsaceae* family, can induce ferrihydrite precipitation through oxidation of organic iron

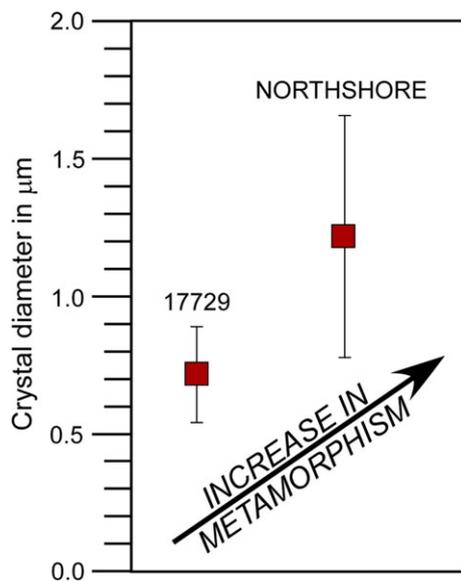


Fig. 6 Graph comparing sizes of iron oxides from low-grade alteration (core 17729) and from within the contact aureole (Northshore). See images in 4B and 4C for examples of preservation.

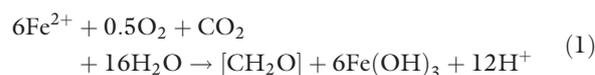
chelates (i.e., they use the organic carbon of such ligands as an energy source), and in doing so, the iron is freed and easily hydrolyzed (Ghiorse & Ehrlich, 1992).

The formation of ferrihydrite may also stem from the ability of some chemolithoautotrophic bacteria to oxidize ferrous iron as an energy source. Although most enzymatic oxidation of Fe(II) occurs at extremely low pH, such as in acid mine drainage environments, the activity of *Acidithiobacillus ferrooxidans* or *Leptospirillum ferrooxidans* generally does not promote *in situ* ferrihydrite precipitation because the Fe³⁺ formed remains soluble until more alkaline pH conditions ensue. However, at neutral pH, and under partially reduced conditions, chemolithoautotrophic Fe(II) oxidation by the genus *Gallionella* does undeniably lead to high rates of ferric iron mineralization (e.g., Søgaard *et al.*, 2000). *Gallionella ferruginea* has a bean-shaped cell that grows at the terminus of a helical structure called a stalk, which is made up of polysaccharides. Interestingly, *G. ferruginea* does not form a stalk at pH <6, or under very microaerobic conditions where O₂ is present but the redox potential is −40 mV. This suggests that the stalk represents an organic surface upon which ferrihydrite can precipitate and, in doing so, protects the cell itself from becoming mineralized (Hallbeck & Pederson, 1990; Fleming *et al.*, 2013; Saini & Chan, 2013). Similar to *L. ochracea*, *Gallionella* species are common inhabitants of iron springs, and where they are abundant, the stalk material appears to form the substratum upon which subsequent Fe(II) oxidation occurs. The recent discovery of an iron-encrusted and stalk-forming bacterium from a freshwater seep in Delaware (FeOB strain R-1) that is physiologically similar to *G. ferruginea* but phylogenetically distinct, extends the known diversity of Fe(II) oxidizing bacteria in freshwater environments (Krepeski *et al.*, 2012). Several strains of marine Fe(II)-oxidizing bacteria (e.g., *Mariprofundus ferrooxydans*) have also been isolated from the Loihi Seamount at Hawaii (Emerson & Moyer, 2002; Emerson *et al.*, 2007), submarine volcanoes on the South Tonga Arc (Forget *et al.*, 2010), and a salt marsh in Maine (McBeth *et al.*, 2011). Similar to their freshwater counterparts, *M. ferrooxydans* grows under microaerophilic conditions and produces filamentous stalks composed of ferrihydrite.

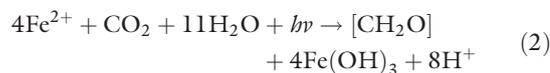
Planavsky *et al.* (2009) recognized that the simple morphology of *Gunflintia* Barghoorn (Barghoorn & Tyler, 1965) is as comparable to *Leptothrix* sp. as it is to the cyanobacteria. A similar conclusion was drawn earlier by Knoll & Simonson (1981) in their study of the coeval fossils from the Sokoman Iron Formation in the Labrador Trough, Canada. Other fossil forms are morphologically similar to modern *Gallionella*, *Mariprofundus*, *Crenothrix*, and other aerobic Fe(II)-oxidizers. Planavsky *et al.* (2009) acknowledged that morphology alone cannot prove the existence of Fe(II)-oxidizers at 1.9 Ga so they employed

Ce anomalies, Eu concentrations, and Fe isotopes to show that the stromatolites formed at or just below a strong redoxcline in suboxic conditions. Therefore, it was their opinion that chemolithoautotrophic Fe(II)-oxidizers produced the stromatolites and not cyanobacteria. Schelble *et al.* (2004) similarly discussed the Gunflint formation samples from Mink Mountain as an example of how bacterial filaments became fossilized in ferric oxyhydroxides by drawing attention to processes such as iron adsorption to bacterial cell walls. Wilson *et al.* (2010) also placed similar microfossils within an Fe(II)-oxidizing ecosystem based on facies analysis in the coeval Duck Creek Formation of Western Australia. Recently, Edwards *et al.* (2012) revisited the Sokoman and again suggested the presence of Fe(II)-oxidizers based on inferred primary hematite cements and microbial morphology revealed by secondary electron imaging (SEI) scanning electron microscopy. However, the microfossils themselves are not preserved in hematite but are permineralized by silica. The authors attributed this preservation to the microfossil's position above the Fe-redox interface where rapid rates of silicification dominate.

In all of the models above, there is a general assumption that the iron coatings are a primary feature in that the initial Fe(II) oxidation took place in the water column by benthic bacteria to form ferrihydrite, the ferric iron precursor to more stable iron oxides (e.g., hematite) found in iron formations (Fig. 7A). For instance, it was Holm (1989) who postulated that aerobic chemolithoautotrophs (e.g., *Gallionella*) could have produced the enormous iron formation deposits of the Archean–Paleoproterozoic under microaerobic conditions [reaction 1]:



Following this possibility, Widdel *et al.* (1993) built a model where Fe²⁺ was oxidized by anoxygenic phototrophic purple and green bacteria when coupled with CO₂ reduction, thus removing the need for free oxygen during Fe(II)-oxidation [reaction 2]:



Konhauser *et al.* (2002) and Kappler *et al.* (2005) extended these hypotheses to quantify the Fe(II) oxidation capabilities of the bacterial populations and showed that these bacteria could be responsible for precipitating the vast volume of iron now incorporated into banded iron formations (BIF) even without cyanobacterial influence. The original ferrihydrite precipitate then became buried and through diagenesis transformed into hematite. Indeed, this view correlates well with models pertaining to the origins of BIF in

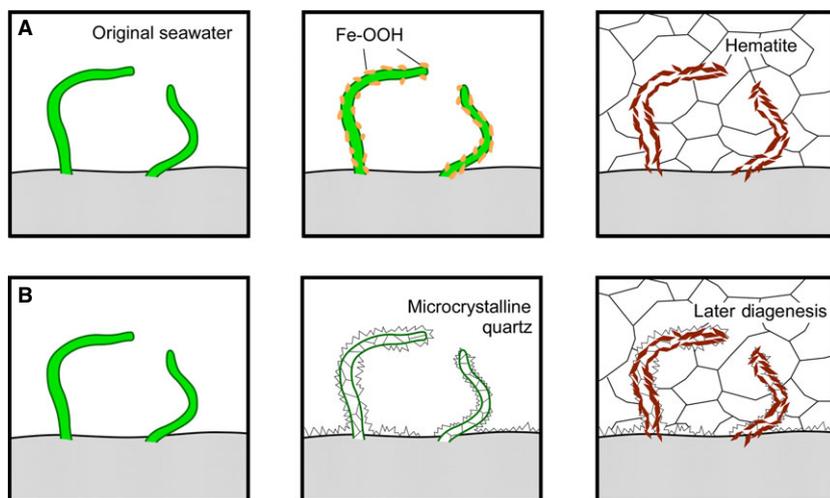


Fig. 7 Models to explain hematite-encrusted microfossils. (A) In the 'Biological Model', iron-oxidizing bacteria promoted the precipitation of iron oxyhydroxides, such as ferrihydrite, onto their sheaths. The ferrihydrite was transformed to hematite on the seabed and preserved in microquartz. (B) In the 'Taphonomic Model', filaments were initially preserved as carbonaceous sheaths. During burial, Fe(II)-rich groundwater infiltrated porous zones of the stromatolite. The cellular remains then either adsorbed Fe²⁺ or became encrusted via siderite precipitation. At a later stage, the percolation of oxygenated groundwaters oxidized both the Fe(II) and organic carbon, while porosity was eventually occluded by a second stage of silica cementation.

which there were hydrothermal pulses of dissolved Fe²⁺ into the photic zone of Archean and Paleoproterozoic oceans where it was oxidized to ferrihydrite via biologic activity, and ultimately, incorporated into the sedimentary record (Konhauser *et al.*, 2002; Kappler *et al.*, 2005; Bekker *et al.*, 2010; Li *et al.*, 2011; Posth *et al.*, 2013). Konhauser *et al.* (2005) further developed a model that used phytoplankton biomass to fuel microbial Fe(III) reduction, whereby the reduced iron (as Fe²⁺) would subsequently be incorporated in the sediments as magnetite or siderite (FeCO₃). This model has since been supported by experimental studies which have demonstrated that the iron-containing BIF minerals can be formed by subjecting mixtures of organic carbon (i.e., biomass) and ferrihydrite to pressure and temperature conditions encountered during burial (e.g., Köhler *et al.*, 2013; Li *et al.*, 2013).

One important aspect that the above models do not readily explain is the variable distribution of iron content in the shallower-water granular iron formations (GIF) that may host stromatolites. Nor do they adequately explain why some microfossils are preserved as carbonaceous filaments (*Gunflintia*) or spheres (*Huroniospora*), while in other locations those same microfossils are preserved in hematite if one assumes that the iron was sourced from the open oceans via upwelling (Holland, 1973) or hydrothermal plumes (Isley, 1995). Finally, the critical steps of (i) conversion to hematite via dehydration near the sediment surface and (ii) burial preservation of the hematite-enclosed biota in deep time has not been demonstrated for a significant area outside of hydrothermal vents (e.g., Slack *et al.*, 2007; Krepski *et al.*, 2013). In this regard, we provide an alternative explanation which proposes that those fossils were iron mineralized during burial, and that neither *Gunflintia* or *Huroniospora* are actually fossilized remains of Fe(II)-oxidizing bacteria.

The taphonomic model

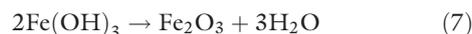
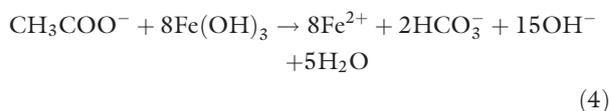
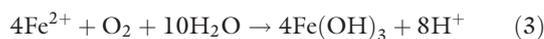
The general rarity of microfossils points to pervasive, but incomplete, decomposition before fossilization. In the 'taphonomic model' presented here, the critical point is that the microfossils were initially preserved as carbonaceous remains that morphologically outlined the original microbe, and it is during burial conditions that the carbon was oxidized and hematite preserved the morphology. The taxonomic affinity of the organism is not relevant, but what is important is that some of the carbonaceous organic material was preserved through burial and early diagenesis (Fig. 7B). We do not know how this occurred, but several possibilities exist. First, primary silicification of intact microbial biomass could have preserved certain cellular features that are more recalcitrant to decomposition, such as the sheaths or cell walls of filamentous species (e.g., Knoll, 1985). The processes of microbial silicification are well described at modern hot springs today (see Konhauser *et al.*, 2004 for review), and for this to have been a viable mechanism for the Gunflint, it would have necessitated that the seawater in which the stromatolites grew became supersaturated with respect to amorphous silica; Proterozoic seawater itself would not have facilitated silicification unless the waters were evaporated (Orange *et al.*, 2013) or significantly cooled (Yee *et al.*, 2003). Second, in many modern marine stromatolites, cyanobacteria are preserved by calcification (see Dupraz *et al.*, 2009 for review). Although there is no evidence in favor of calcium carbonate preserving the initial micro-organisms, it cannot be ruled out because diagenetic fluids moving through the stromatolite may have been slightly acidic, leading to replacement of the primary carbonates by silica (e.g., Knauth, 1979; Knoll, 1985; Hesse, 1989). This replacement can often be highly selective in that silicification

occurs preferentially in facies with relatively high concentrations of organic matter (e.g., Fairchild *et al.*, 1991; Altermann & Schopf, 1995). Third, and irrespective of a primary mineralization mechanism, the organic polymers comprising cell sheaths and walls are more resilient to degradation than other cell components, and as long as the constituent autolysins are deactivated (i.e., by the presence of adsorbed iron to the cell wall), they can persist in the environment long after the cell dies (Ferris *et al.*, 1988). The preservation of some organic remains may also have been enhanced due to the lower levels of dissolved sulfate in the oceans around 1.88 Ga (Poulton *et al.*, 2004); in modern marginal marine settings sulfate serves as the terminal electron acceptor for the oxidation of up to 50% of buried organic carbon (Jørgensen, 1982). Similar to the modern, the organic matter that was degraded by anaerobic respiration would have led to increased pore-water alkalinity via the production of bicarbonate, and possibly carbonate mineral precipitation. Indeed, both fine-grained siderite, followed by early diagenetic ankerite rhombs, are commonly associated with stromatolites in the Gunflint and Biwabik iron formations (Shapiro, 2009). During later contact metamorphism, coarse calcite formed as a fabric-destructive petrofabric along with hematite.

In the case of the hematite-coated microfossils described herein, we suggest that iron mineralization itself was not associated with the mat-forming species (e.g., Fischer & Knoll, 2009; Planavsky *et al.*, 2009), but instead when some of those preserved cellular remains reacted with dissolved ferrous iron after stromatolite burial. The source of the Fe²⁺ was not from the water column (e.g., marine hydrothermal plumes or upwelling events), but iron-rich groundwater moving through the still porous sedimentary rocks. With numerous avenues for fluids to flow, some stromatolites were more susceptible to iron mineralization than others, hence the patchiness in iron concentrations. Interestingly, the same porosity that allowed iron-rich fluids to flow through the stromatolite also eventually caused it to become occluded. Based on textural evidence, it is clear that multiple stages of silicification took place during the stromatolite's history. As mentioned above, some silicification may have played a primary role in preserving some of the initial cellular remains. Some of the silica was likely early diagenetic based on crystal orientation mimicking fringing cement and occluding primary porosity. The majority of silica is clearly late, filling secondary porosity and encasing hematite coatings in chert that replaces primary fabrics.

The actual timing of Fe(II) oxidation is unclear. On the one hand, as the reduced ferruginous fluids moved upwards into the buried, but still porous, stromatolite, the ferrous iron might have reacted with shallow O₂-bearing fluids [reaction 3], and ferrihydrite precipitated upon the

cellular remains (scenario 1). Alternatively, Fe²⁺-rich groundwaters permeated the stromatolite earlier, with cellular remains electrostatically adsorbing Fe²⁺ (e.g., see Clarke *et al.*, 1997; Konhauser *et al.*, 1998 for examples of natural iron biomineralization of cellular remains) or with Fe²⁺ precipitating as a ferrous iron mineral phase, such as siderite, greenalite or stilpnomelane (e.g., see Rasmussen *et al.*, 2014 for 2.5 Ga Dales Gorge Formation). Thereafter, shallow oxygenated waters oxidized the cell-bound Fe(II) to Fe(OH)₃ (scenario 2). In either case, the ferrihydrite later transformed into secondary minerals, including (i) magnetite or iron carbonates when organic mineralization was coupled with Fe(III) reduction [reaction 4–6], or (ii) hematite when the organic material was depleted [reaction 7]. The key point with regard to hematite formation is that the Fe(III):C ratio exceed 4:1—the Fe(III) reduction ratio [reaction 4]—so that ferric iron is retained without an available reductant. The excess Fe(III) may have resulted from either all initial organic carbon being oxidized or a secondary input of dissolved iron.



Given the known geological history of the region, it is most likely that the ferruginous groundwater was driven firstly by the tectonic front of the Penokean Orogeny to the south ~40 million years after deposition of the iron formation (Schulz & Cannon, 2007), but the exact timing of the oxygenated fluids cannot be clearly delineated. This would account for the much broader distribution of iron in the Biwabik (and southern Superior formations such as the Ironwood in Wisconsin and the Negaunee in Michigan; Ojakangas *et al.*, 2011) relative to the Gunflint. Additional Fe(II)-rich groundwaters would be locally sourced from the intrusive dikes and sills associated with the large igneous complex at 1.1 Ga. Indeed, the Mink Mountain locality contains much higher iron content than other sections of the Gunflint and is more closely associated with a large diabase sill than other locations in the Thunder Bay area. In the Mesabi iron range, there is a well-established increase in metamorphic grade and increase in hematite and magnetite in the stromatolite layers with proximity to the main Duluth Gabbro body (French, 1973; Frost *et al.*, 2007; Hyslop *et al.*, 2008;

Shapiro, 2009). Late stage oxidation of reduced iron silicates and carbonates was also described by Rasmussen *et al.* (2014) to account for hematite deposits that post-dated deposition and pre-dated modern weathering processes in a Neoproterozoic iron formation.

Taphonomic support

The Gunflint microbiota may be constrained to the late Paleoproterozoic but representatives are found in many non-contiguous locations and in different facies (Sergeev, 2009 and Table 2). Therefore, any discussion on the taxonomic affinity needs to take into account the varied ecologic settings. For instance, a similar microflora was reported from the coeval Sokoman iron formation (Knoll & Simonson, 1981). A dense population of *Gunflintia* filaments comprises the thin laminae of a stromatolite that is similar to a type described from the Gunflint formation. Like the Biwabik, these microfossils are preserved as fine hematite outlines. Twenty percent of the stromatolite microflora is composed of *Huroniospora* spheres. The authors noted that they were unable to determine whether the fossils were of cyanobacteria or *Sphaerotilus/Leptothrix*-like iron-depositing bacteria. A rich biota of carbonaceous fossils, including *Gunflintia*, *Huroniospora*, as well as *Eoastrion* and the rare *Archaeoestis*, were also reported from cherty stromatolites in the coeval Franceville Group of Gabon (Amard & Bertrand-Sarfati, 1997). A survey of other locations shows that Gunflint-type microbiota were similarly recovered from rip-ups and finely laminated chert (Awramik & Barghoorn, 1977; Wilson *et al.*, 2010). These observations confirm earlier reports that the Gunflint microbiota—including the morphologically simple *Gunflintia* and *Huroniospora*, as well as the more complex *Eoastrion*—is widespread and occurs in multiple diverse ecologic settings (e.g., Tobin, 1990).

It is also interesting to note that in a recent study, Salama *et al.* (2013) presented observational evidence for diagenetic ferruginous stromatolites and oncoids in the Eocene of Egypt. These meter-scale deposits accumulated in lagoonal-peritidal settings associated with syndepositional tectonism. The stromatolites are both stratiform and microcolumnar; oncoids range from 2 to 60 mm diameter. Laminae consist of alternating goethite and ferrihydrite with goethite-encapsulated sheaths. Some organic components are preserved (carotenoids, carbohydrates, lipids, etc.). The authors postulated that the ferrous iron was sourced from below via a porous aquifer under reducing and acidic conditions (Dabous, 2002). The actual growth medium is believed to have been at approximately neutral pH, low $f(\text{O}_2)$ conditions. It is interesting to note that calcareous skeletal material (algae and benthic foraminifera) were also replaced by iron oxyhydroxides, demonstrating the post-deposition, diagenetic source of iron mineralization.

The most convincing support of the ‘Taphonomic Model’ is the fact that *Gunflintia* (and *Huroniospora*) are found in different modes of preservation (carbonaceous filaments, encapsulated by hematite, and as siliceous molds). Either the simple *Gunflintia* is a morphotype for both cyanobacteria in some locations and Fe(II)-oxidizing bacteria in other locations (Planavsky *et al.*, 2009) or there has been replacement. The first hypothesis is reasonable because the simple morphology (slightly to moderately curved, unbranched, unsegmented) can describe many different bacteria from a wide variety of settings. However, it is rejected because this study focused on a very narrow microfacies: the laminated portion of columnar and pseudocolumnar stromatolites from two correlative beds that share similar sediment and sedimentary structures. Therefore, the likelihood of two vastly different localized microbial ecosystems producing the same structures is not high.

Furthermore, several papers have shown strong evidence of fossilized Fe(II)-oxidizing bacteria from hydrothermal vent settings and these are very different from the *Gunflintia* examples described in this manuscript. Little *et al.* (2004) compared modern microbes to fossilized examples from ancient hydrothermal iron oxide deposits. They found distinctive morphologies, such as hollow sheaths, twisted ribbons, and branching and dendritic filaments—the latter three forms are not characteristic of *Gunflintia*. They also noted that in fossil deposits, the filaments form up to 40% of the laminae, which is much higher than recognized in the Gunflint and Biwabik iron formations. Slack *et al.* (2007) described preserved Fe(II)-oxidizing bacteria from a Paleoproterozoic (1.7 Ga) volcanosedimentary deposit that similarly showed a dense accumulation of highly curved filaments that are not morphologically analogous to *Gunflintia*. Most recently, Krepiski *et al.* (2013) showed a variety of fossilized Fe(II)-oxidizing bacteria throughout the Phanerozoic and suggested that there are some key morphological indicators. Specifically, the authors compared fossilized Fe(II)-oxidizing bacteria to hematite-encrusted cyanobacteria for distinguishing the two populations in the rock record. They noted that cyanobacteria contain a wider variety of sheath widths, while Fe(II) oxidizers are recognized by helical growth, branching, and very random directionality within a dense accumulation of filaments. While this first point allows for *Gunflintia* to be analogous to *Leptothrix*, the latter features are not shared with the Gunflint microbiota. Fru *et al.* (2013) presented a similar study on an early Quaternary marine hydrothermal vent field and demonstrated that in the silica- and iron-rich deposits preserved bacterial molds displayed features distinctly different from *Gunflintia* in the common occurrence of spherical cells adhered to stalks, branching, and exospores-like features. Moreover, studies of modern Fe(II)-oxidizing bacteria

show that the iron oxyhydroxides are concentrated as waste product on the outside of the stalks and sheaths, not as cells, so the stalks are carbon poor (Chan *et al.*, 2011).

The Taphonomy hypothesis is better supported by the consistency of facies (shallow-water, centrimetric to decimetric stromatolites of similar microstructure used in this study, associated with ooids and syneresis-cracked, rounded mud rip-ups) and the relationship of preservation to metamorphic gradient. The observations presented in this paper, coupled with Raman studies (Kudryavtsev *et al.*, 2001; Schopf *et al.*, 2002; Bower *et al.*, 2010), show that the least altered units preserve the microfossils as carbon. Areas less protected from the regional prehnite-pumpellyite metamorphism preserve hematite casings. Hematite also dominates in regions associated with contact diabase sills and dikes. Near the main gabbro body, hematite first increases in size and then becomes reduced to magnetite. In localized areas, the magnetite even shows secondary oxidation back to martite. This pattern is also seen in other iron formations globally that have been subjected to different levels of alteration. Furthermore, even the non-stromatolitic occurrences that are not the focus of this paper show cellular remains preserved as carbonaceous (Knoll & Barghoorn, 1976; Awramik & Barghoorn, 1977), hematitic (Cloud & Morrison, 1980), and siliceous outlines (Edwards *et al.*, 2012). Multiple states of microfossil preservation (carbonaceous, hematitic, magnetitic) are also related to iron content and ore genesis in the Neoproterozoic Wadi Kareim banded iron formation of Egypt (El-Habaak & Mahmoud, 1994).

Finally, it should be noted that the Gunflint microflora, like other fossils, may occur in other preservational states though rare. In a recent paper, Wacey *et al.* (2013) describe pyritized *Gunflintia* and *Huroniospora*, along with epibionts, from the Schreiber locality. Their observations have an important bearing on the present manuscript as it shows that even the most excellent, 'primary' preservation of Paleoproterozoic microfossils show evidence of secondary replacement.

CONCLUSIONS

The various filaments described in this study are all assigned to *Gunflintia* Barghoorn (Barghoorn & Tyler, 1965). The similarity in stromatolite microstructure and lithofacies between collection sites permits the interpretation that all stromatolites studied formed under broadly similar conditions. Therefore, taphonomic variability is a function of post-depositional alteration and not *in situ* localized microbial ecosystems. Unaltered microfossils were preserved as carbonaceous remains that outlined the original micro-organism, either by early silicification, calci-

fication or simply due to the recalcitrant nature of the organic materials. Hematite-bearing microfossils formed when Fe(II) was brought to the still porous stromatolites via groundwater. The timing and mechanisms for this are unclear, but it could have involved the cellular surfaces of the primary stromatolite builders either adsorbing Fe(II) or nucleating authigenic, ferrous mineral phases, such as siderite. Low-grade alteration by tectonically driven and younger O₂-bearing fluids—perhaps tens to hundreds of millions of years later—then led to the subsequent oxidation of the ferrous iron to ferrihydrite, which ultimately transformed into hematite. Alternatively, ferric oxyhydroxides formed directly at the interface where Fe(II)-bearing groundwater came into contact with shallow oxic fluids. In either case, the regional to localized variations in iron content within the stromatolites argues against iron being sourced from bulk seawater. At higher metamorphic pressures and temperatures within the gabbro contact aureole, the crystal size of the hematite coatings increased and, in some cases, reduced to magnetite (and locally re-oxidized to martite). Therefore, the presence of hematite-coated microfossils is a reflection of taphonomic processes in which the remains of the primary stromatolite builders interacted with Fe(II)-rich groundwater; they do not reflect an original Fe(II)-oxidizing microbial ecosystem. However, it is important to point out that these findings do not negate nor support the hypothesis that Paleoproterozoic oceans were teeming with Fe(II)-oxidizing bacteria, particularly below a chemocline that separated oxygenic cyanobacteria from underlying anoxic and ferruginous waters. The shallow-water ecosystems described in this paper are not associated with banded or 'primary' iron formation, leaving open the possibility that anoxygenic Fe(II)-oxidizing bacteria are yet primarily responsible for sourcing the ferric iron in the bulk of iron formations.

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