Evidence for initial calcite–aragonite composition of Lower Algal Chert Member ooids and stromatolites, Paleoproterozoic Gunflint Formation, Ontario, Canada

M.G. Sommers, S.M. Awramik, and K.S. Woo

Abstract: The chert members of the Paleoproterozoic Gunflint Formation, Ontario, Canada, are commonly regarded as examples of primary silica chemical sediments. This interpretation is founded upon the ubiquitous nature of silica, high fidelity of preservation of microfossils found within, and lack of observed primary carbonate. Previous arguments for silica replacement of carbonate are based on indirect evidence and are largely dismissed. Thus, Gunflint microfossils are regarded as having lived in a silica-rich environment, which makes them unusual compared to most other pre-Phanerozoic microfossils that are known from silicified carbonates. We present evidence that carbonate was a primary mineral species of the Lower Algal Chert Member (where most of the microbiota are found). Most compelling are iron-stained, low-Mg calcite ooids containing (1) well-preserved growth laminae, (2) textures indicating a disrupted tangential fabric of growth laminae, and (3) quartz crosscutting the growth laminae. These indicate the initial mineral was a carbonate, possibly aragonite. Less-compelling evidence is found in stromatolite columns. Specularite crystals in low-Mg calcite display crosscutting relationships with calcite and quartz indicating that calcite was primary, specularite secondary, and quartz tertiary. The crosscutting relations show that silicification took place in at least two stages. One of the silicification events took place very early in diagenesis. Thus the Gunflint microbiota may not have existed in a radically different environment (silica precipitating) than those of most other known Proterozoic microbiota. High fidelity of preservation of microfossils does not always indicate that the mineral entombing them was the primary mineral precipitated from aqueous solution.

Résumé : Les membres de chert de la Formation de Gunflint, datant du Paléoprotérozoïque, en Ontario, au Canada, sont habituellement perçus comme des exemples de sédiments siliceux chimiques primaires. Cette interprétation est basée sur la nature très répandue de la silice, le taux élevé de fidélité dans la préservation des microfossiles qu'on y retrouve et le manque de carbonate primaire. Les arguments antérieurs pour le remplacement du carbonate par de la silice sont basés sur des évidences indirectes et sont largement rejetés. Ainsi, on croît que les microfossiles Gunflint ont vécu dans un environnement riche en silice, ce qui les rend exceptionnels par rapport à la plupart des autres microfossiles pré-Phanérozoïque qui sont connus à partir de carbonates silicifiés. Nous présentons des preuves que le carbonate était une espèce minérale primaire du Membre inférieur de Algal Chert (où ont été trouvés la plupart des microbiotes Gunflint). Les plus convaincantes sont les oolithes de calcite tachés de fer, à faible teneur en Mg, contenant (1) des lamines de croissance bien conservées (2) des textures indiquant une trame tangentielle perturbée de lamines de croissance et (3) du quartz qui recoupe les lamines de croissance. Cela indique que le minéral initial était un carbonate, peut-être de l'aragonite. Les colonnes de stromatolites présentent des évidences moins convaincantes. Des cristaux de spécularite dans une calcite à faible teneur en Mg recoupent la calcite et le quartz indiquant que la calcite était primaire, la spécularite, secondaire, et le quartz, tertiaire. Les relations intersécantes montrent que la silification a eu lieu en au moins deux étapes. Un des événements de silification a eu lieu très tôt dans la diagenèse. Ainsi, les microbiotes Gunflint peuvent ne pas avoir existé dans un environnement radicalement différent (précipitation de la silice) de la plupart des autres microbiotes connus au Protérozoïque. Une haute fidélité de préservation des microfossiles n'indique pas toujours que le minéral les enterrant était le premier minéral à précipiter de la solution aqueuse.

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Introduction

The Gunflint Formation (Animikie Group, Paleoproterozoic) of Ontario, Canada, is famous for well-preserved, abundant microfossils within chert (cf. Barghoorn and Tyler 1965, Awramik and Barghoorn 1977 and others). The high fidelity of preservation of these microfossils, particularly in the vicinity of Schreiber Reserve, Ontario (Fig. 1), led Barghoorn and Tyler (1965) and Cloud (1965) to conclude that the silica was a primary gelatinous sediment that later recrystallized to quartz, and not a replacement product of preexisting carbonate. Later researchers, such as Simonson (1987) and Simonson and Lanier (1987), argued that the chert was a result of an initial silica gel.

Exceptional preservation of microfossils also led Hofmann (1975, 1976) to conclude that primary chert entombed the Paleoproterozoic Belcher Islands microbiota. Unlike the Gunflint, Belcher chert occurs in dolostone-dominated beds in the form of nodules, lenses, stromatolitic layers, and outlining individual stromatolites (stromatoids). In dolostone regions immediately adjacent to the chert, the carbonate preserves only the remnants of pigmented portions of laminae (Hofmann 1975, 1976). Neomorphism and diagenesis of primary carbonate almost always destroys organic-walled microbes. Hofmann and Grotzinger (1985) report an unusual example where diagenesis has altered but not destroyed microbial fossils in a carbonate matrix; many of these fossils are similar to Gunflint microfossils.

Horodyski and Donaldson (1983) presented evidence for both primary and diagenetic silica for the chert of the Mesoproterozoic Dismal Lakes Group (however, they indicated that the origin of the chert entombing the microbiota is not clear). They suggested three petrographic criteria for determining the origin of the chert: (1) osmotic filaments, reniform surfaces caused by coagulation of gels, and diffuse banding would support a primary origin (based on Lebedev 1967); (2) identical fabrics for ooids in chert and carbonate suggests chert is secondary; and (3) length-slow chalcedony (Folk and Pittman 1971) and zebraic chalcedony (McBride and Folk 1977) help to identify silicified sulfates.

The chert of the Neoproterozoic Bitter Springs microbiota also presents background to our discussions. Knoll and Golubic (1979) concluded the silica of the Bitter Springs precipitated from interstitial solutions early during diagenesis in a carbonate depositing regime that Southgate (1986) concluded were saline lakes.

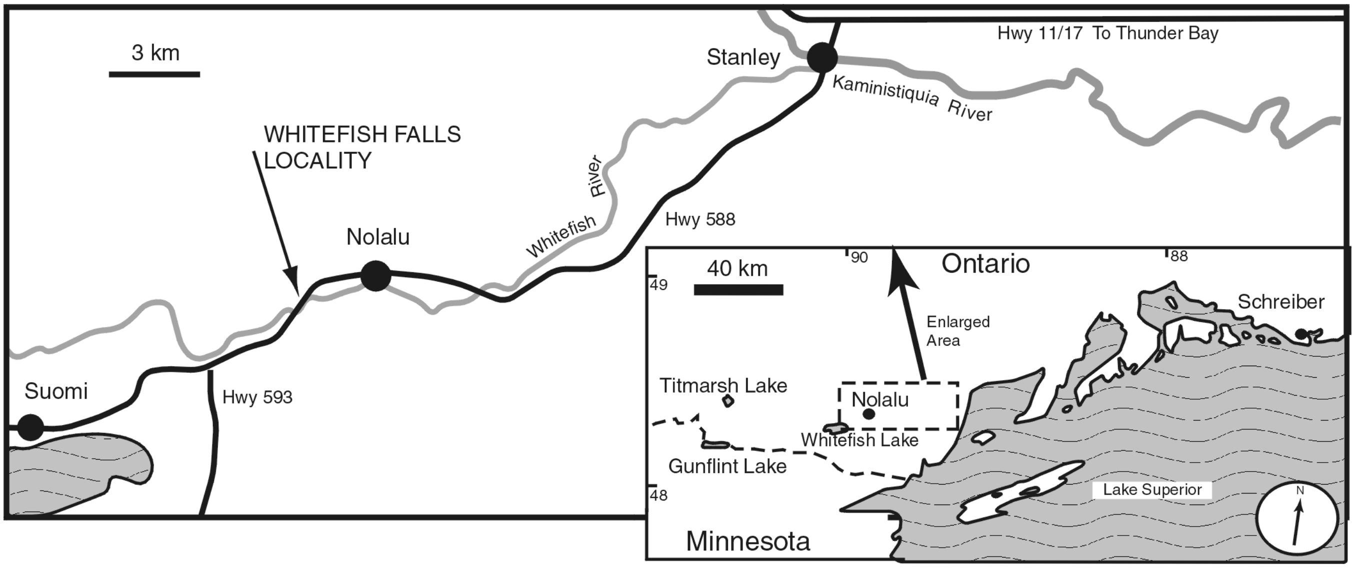
For the Lower Algal Member of the Gunflint, the lithology is almost entirely of chert. Carbonate is minor. The usual textural and geometric relationships, and sedimentary fabrics, found between carbonate and chert in the formations mentioned above are almost entirely lacking in this member of the Gunflint. Fortunately, we have recovered a suite of samples, one being unique in the extraordinary preservation of carbonate textures that have revealed the necessary information for a confident interpretation of primary carbonate in the Lower Algal Chert.

We have found direct evidence to indicate that carbonate was the primary mineral species in the Lower Algal Chert Member of the Gunflint at Whitefish Falls, Ontario, Canada. This evidence includes (1) calcite ooids with preserved primary textures and (2) calcite within stromatolites that partially define laminae. Both have chert crosscutting the calcite. These observations are significant, for the Lower Algal Chert contains the best preserved and most abundant microbial fossils of the Gunflint. Chert at Whitefish Falls does preserve microbial fossils (Edhorn 1973); however, they are not as uniformly well preserved and as abundant as those from Schreiber. Others have reported finding primary calcite in the Gunflint, suggesting that it predated the chert; however, these are from other facies or members and have no direct bearing on microfossils. Kimberly (1979, his figure 3E) illustrated a calcitic ooid from the Gunflint that was from the Upper Limestone Member (possibly another primary carbonate phase of the Gunflint; Shegelski 1982) and not associated with stromatolites or microfossils. Shegelski (1982, p. 23) described "rare" calcareous stromatolites from a unit that he favored as being similar to, but stratigraphically lower than, the Upper Limestone Member. To the best of our knowledge, there are no other published reports of preserved original calcareous ooids or stromatolites within the Gunflint. Moorehouse (1960, p. 29, his Fig., top photo) illustrated what he described as chert replacement of carbonate in some non-laminated granules from the Gunflint. Lougheed (1983, his figure 1A) illustrated carbonate stromatolites from the Biwabik Iron Formation at the Mary Ellen Mine, Biwabik, Minnesota. The Biwabik is from the same basin (Animikie) and is considered the stratigraphic equivalent of the Gunflint (Hofmann 1969; Morey 1972). It is unclear whether those stromatolites illustrated by Lougheed (1983) are from the upper or lower stromatolite-bearing member of the Biwabik. Fralick (1989) discussed stromatolites within the city limits of Thunder Bay, Ontario, that he described as "silicified," implying that they were not originally silica, but did not discuss the possible precursor mineral nor the evidence for silicification. Moorehouse (1960, p. 8) also preferred silicification of carbonate for the stromatolites of the Lower Algal Chert Member: "The presence of cherty oolites associated with them [the stromatolites] indicate that silicification has taken place, and it is considered probable that the growths were originally calcareous and have since been silicified."

The stromatolites of the Upper Algal Chert Member of the Gunflint (see Hofmann 1969) do not figure into our evidence nor interpretations of the primary mineral(s) of the Lower Algal member. The stromatolites of the Upper Algal Member may have formed by spring or hydrothermal activity, and are also in part abiogenic (Walter 1972; Sommers and Awramik 1996) and thus need to be treated separately.

The importance of determining the primary mineral(s) of the formation is realized when attempting to discern the depositional environment of the Gunflint, especially the composition of the water precipitating the mineral(s). This is particularly important for the conditions under which the microbes lived. The fact that most researchers have concluded the formation is primary silica would also make the Gunflint microbiota unusual in comparison to most other known pre-Phanerozoic microfossil-bearing units where the microbiota is found in chert replacement of carbonates (e.g., Beck Spring Dolomite, U.S.A. (Licari 1978); Bitter Springs Formation, Australia (Knoll and Golubic 1979); (Allison and Awramik 1989); Doushantuo Formation, China (Zhang et al. 1998)).

Fig. 1. General map of the study areas; locality map of the Whitefish Falls study area (inset).



General geology and locations of study

The Gunflint Formation was originally named by Van Hise and Clements (1901) for iron-rich sedimentary rocks in the Thunder Bay region of Ontario, Canada. The name was changed to the Gunflint Iron Formation by Leith and others (1935). The formation, which averages 122 m in thickness, crops out nearly continuously from Gunflint Lake on the Minnesota–Ontario border to east of Thunder Bay, a distance of approximately 177 km (Franklin 1991; Fig. 1). Isolated outcrops continue further east along the northern shore of Lake Superior as far as 750 m to the east of the mouth of Blind Creek, Collingwood Bay, another 108 km along strike.

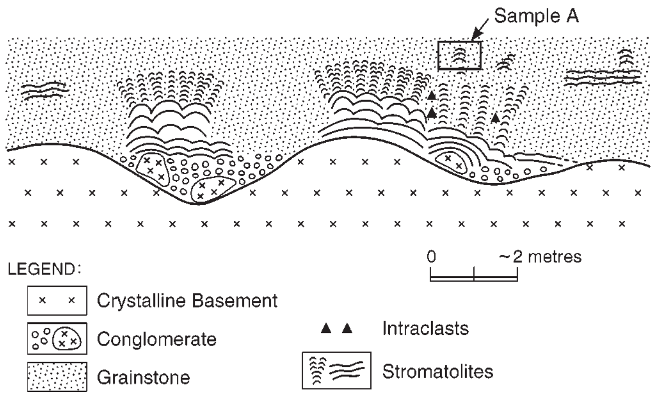
Goodwin (1956) originally divided the Gunflint into four members: the Basal Conglomerate, the Lower and Upper Gunflint, and the Upper Limestone. He further subdivided the Lower and Upper Gunflint into four submembers, each based on lithofacies: algal chert, tuffaceous shale, taconite, and a banded chert-carbonate that is laterally gradational with the taconite. In his later work on the Gunflint, he changed his stratigraphic scheme, eliminating the submember (lithofacies) divisions, 'promoting' them to full member status (Goodwin 1960; see his Table I, p. 46, Tables II and III, p. 48, and descriptive text, pp. 49–58). Shegelski (1982, 1991) considered the lithofacies of Goodwin (1956), and hence the members of Goodwin (1960), too simple as they belied the true complexity of the stratigraphic relationships among the lithofacies (or members; see also Franklin 1991). Pufahl (1996) concurred with this assessment, and divided the Gunflint into five numerical members (in ascending order) comprised of eleven types of lithofacies. Despite these complexities, and the fact that a complete, up-to-date facies analysis of the Gunflint has not yet been done, the Lower Algal Chert Member as originally described by Goodwin (1960) is straightforward in terms of its stratigraphic position and lithology. Since both Shegelski (1991) and Pufahl (1996) recognize the general lithofacies, the name is adequate for the rocks discussed here.

The age of the Gunflint has not been established with precision. Floran and Papike (1975) considered a 2000 Ma age for the sedimentation based on a synthesis of early isotopic studies (Faure and Kovach 1969; Hurley et al. 1962; Misra and Faure 1970) and indirect evidence (Hanson and Malhotra 1971). Stille and Clauer (1986) provided an age of 2.08 ± 0.25 Ga based on whole-rock Sm–Nd isotope analyses of argillaceous sediments. More recently, Fralick and others (1998) derived an age of 1878 ± 2 Ma for zircons found within the lapilli tuff at the Kaministikwia River gorge. The Animikie Group unconformably overlies diabase and gabbro dikes with a Rb–Sr isochron age of 1970 ± 80 Ma (Beck and Murthy 1982). Ash sediments from tuffs in the Virginia Formation, conformably overlying the Biwabik Formation, yielded Nd-isotopic ages of 1.86 and 1.99 Ga (Hemming et al. 1995).

We focus on the Lower Algal Chert Member from two sites, Whitefish Falls and the Schreiber Channel Provincial Nature Reserve (Fig. 1), where calcite and chert occur in stromatolites and ooids. Shegelski (1982, 1991) presented the relationships at both localities among the stromatolitic bioherms, isolated stromatolites, ooids, enclosing sediments, and basement. The relationships are superficially similar between localities; however, slight differences occur at Whitefish Falls, such as chert carbonate beds occurring between bioherms (Shegelski 1991), ooids rather than peloids being more common in the grainstone, and isolated columnar and columnar–branching stromatolites (up to about 10 cm in diameter) occurring in the grainstone.

The Schreiber Reserve locality is located along the north shore of Lake Superior, in Collingwood Bay (UTM grid reference 16U: 474 500 m E, 5 404 150 m N) within the Schreiber Channel Provincial Nature Reserve (Ontario Ministry of Natural Resources 1984). This is the classic locality and type locality of many of the Gunflint microfossils (Awramik and Barghoorn 1977; Barghoorn and Tyler 1965) and where the Gunflint chert was originally considered to be of primary origin. The sediments are relatively unmetamorphosed (Barghoorn and Tyler 1965) and are well preserved, as are the microbial fossils found in the chert. The Lower Algal Chert Member is well developed and character-

Fig. 2. Lithofacies relations amongst basement, grainstone, conglomerate, and stromatolites at the Whitefish Falls locality (schematic). Block indicates likely position of sample A. Modified after Shegelski 1982, 1991.



ized by bioherms up to a metre in diameter that formed on boulders of the Basal Conglomerate (often referred to as the Kakabeka Conglomerate; e.g., see Hofmann 1969). The bioherms consist of columnar-branching, columnar-layered, and stratiform stromatolites, with interspace- and interbiohermal-sediments dominated by ooids and peloids (Awramik 1976; Hofmann 1969; a view of a typical outcrop is shown in plate 5A, p. 309, of Hofmann 1998).

The Whitefish Falls locality (UTM Grid Reference 16U: 289 150 m E, 5 351 750 m N) is approximately 3 km west of Nolalu on Highway 588, about 30 m downstream from the bridge that crosses the Whitefish River. This locality has been referred to as "Whitefish River west of Hillside" (Moorhouse 1960, p. 8) and "Rapids, Whitefish River at Hillside" (Edhorn 1973, p. 66). Very low-grade metamorphism, greater than at Schreiber, has possibly affected the sediments, as evidenced by mineral and textural observations described further on. The Lower Algal Chert is well developed here. The Lower Algal Chert Member is characterized by larger bioherms than at Schreiber (over 1.5 m in diameter) that formed directly on the basement (Shegelski 1982, 1991. See Fig. 2) on what might have been topographic highs. These highs were either (*a*) still present and 'emergent' after the conglomerate was deposited or (*b*) the result of basement exposed after erosion of the conglomerate prior to or during deposition of the Lower Algal Chert. There is evidence for erosion of the conglomerate prior to Lower Algal Chert deposition, because granular chert was observed to downcut the conglomerate in one, and possibly two, areas at the locality. The bioherms consist of columnar-branching, columnar-layered, pseudocolumnar, and stratiform stromatolites with interspace- and interbiohermal-sediments dominated by ooids and peloids (Shegelski 1982, 1991).

Methods

Field relationships, hand specimens, slabs, and thin sections of samples from the Whitefish Falls and the Schreiber Reserve localities were examined and compared. Thin sections were examined optically with standard petrographic microscope and luminoscope. Cathodoluminescence was used to identify carbonates, and to attempt to distinguish any different phases of calcite and calcite cementation. Mineral identifications were made primarily using the petrologic microscope. In the case of selected Whitefish Falls samples, electron-microprobe backscattered-electron images, using energy dispersive X-ray analysis (EDA) to give qualitative element identification, was used to support the optical mineral determination.

Whitefish Falls material

The Lower Algal Chert at Whitefish Falls consists of a complex and variable array of chert in many colors, stromatolite morphologies, mineral assemblages, and textures. Hand specimens vary in color from pale-pink, almost translucent chert to green and black, with minor white, yellow, and red common. It is primarily the green and black material that contains a significant proportion of calcite. The stromatolites occur in two modes; (*a*) in bioherms and (*b*) as stratiform structures and individual- and branching- columns in grainstone. Their morphology has not been systematically described; however, many different shapes are present including stratiform, columnar, pseudocolumnar, columnar-layered, and columnar-branching forms (see also Shegelski 1982, 1991). Some of these shapes resemble those illustrated from the Schreiber locality (see Awramik and Semikhatov 1979, their figures 1 and 2; Cloud 1965, his figures 2A and B; Hofmann 1969, his forms A and B; and Lougheed 1983, his figures 1A and 1G). The preservation of laminae of the Whitefish Falls stromatolites is variable. Often they are not well preserved, and microfossils, when found (see Edhorn 1973) are also usually not well preserved (Awramik 1976).

Stromatolitic–oolitic Whitefish Falls material possesses a variable range of chert/calcite ratios. Chert predominates, making up 85–95% of most thin sections based on visual estimation (not including minor iron minerals). However, one particular sample (sample A) has preserved carbonate in about half of the stromatolite volume and in about 99% of ooid volume, leading overall to a roughly 1:1 chert:carbonate ratio observed in thin section. Also present are euhedral (hexagonal and diamond-shaped) crystals of hematite. Their relationship to the chert and the calcite plays a crucial role in understanding the sequence of mineralization in the Lower Algal Chert Member of the Gunflint.

Other minerals found within the Whitefish Falls samples include greenalite, pyrite, magnetite, and barite. Barite occurs as extremely small (0.5 μm), infrequent inclusions within megaquartz, and was only detected using the microprobe.

Petrography of chert

Sample A

One sample (sample A) is of particular importance, as it contains the best evidence of primary carbonate in ooids and stromatolites. Sample A was collected as a loose piece a few metres downstream of the falls. It is an angular block (the corners being practically square) measuring 24 × 10 × 10 cm. Superficially it is indistinguishable from, and most likely originated from, the stromatolite-containing grainstone that was deposited on and encloses the bioherms at Whitefish Falls (see Fig. 2). There are portions within this sample that have sufficiently different textures to warrant differentiation into (1) stromatolite columns; (2) ooids; and (3) interooid areas.

1. In stromatolitic laminae, megaquartz in the range of 20–200 μm is dominant, with the size range of 20–40 μm being about average (Fig. 3A). Microquartz is present, but seldom smaller than 10 μm. All quartz crystals are randomly oriented. In general, there is no systematic pattern of arrangement or variation in crystal size. In some instances, crystal size seems to be related to the amount of 'impurities' (mostly iron minerals; the greater the impurities, the smaller the crystal size), which in turn is dependent on the original laminae (dark laminae contain more 'impurities'). Crystal boundaries can rarely be seen to crosscut stromatolite laminae. The poor preservational state of the laminae masks these crosscutting relations. In general, the finer the crystal size, the better preserved the laminae.

2. In ooids, megaquartz may be found in association with calcite (Figs. 3B, 3C), although in general there is little quartz in this subregion. At a minimum, ooids are over 60% calcite, with the remainder consisting of quartz (not including minor iron minerals). As with the stromatolite laminae, megaquartz found associated with ooid laminae crosscuts the laminae (Fig. 3B), as well as ooid boundaries, leaving inclusion trails marking the former grain edge (Figs. 3D, 3E).

3. Interooid areas contain microquartz and megaquartz. Occasionally, crystal size grades from fine to coarse from the rim of a pore space to the center. Most often megaquartz is "dirty," with numerous iron minerals (e.g., greenalite) and sometimes calcite present, usually along crystal boundaries, but occasionally as inclusions.

Other Whitefish Falls samples

Materials examined include samples from bioherms and grainstone units that occur between and on top of the bioherms. In contrast to sample A, the chert texture in these other Whitefish Falls samples is almost uniform across all three portions described above, with microquartz of ca. 6–20 μm in size predominating (Fig. 4A). In general, preservation of the stromatolite microstructure is better in these materials than in sample A, but poorer than that from the Schreiber Reserve. Again, this appears to be a function of crystal size, which is smaller on average (smaller = better preservation). The crystal size is small enough to mask crosscutting relations between the quartz crystal boundaries and the laminae of the stromatolites.

A few examples of length-slow chalcedony were observed. These examples occurred exclusively within fractures. The fibers have grown inward from both fracture walls and are in an 'S' shape, with a suture line from the two sides running down the middle between them.

Compared to sample A, ooids were observed to be siliceous as the rule, rather than the exception. Megaquartz is present in minor amounts, occasionally within stromatolite laminae, but primarily in ooids and interstices. Within ooids, quartz crystal boundaries crosscut the original growth laminae. Ghost structures of diamond-shaped laths (see below) were also observed in some of these ooids.

As above, quartz crystal size and orientation show no systematic pattern of arrangement or variation, except in occasional instances where it seems to be dependent on 'impurities'.

Petrography of carbonate

Sample A

The dominant carbonate is low-magnesium calcite. Crystals are large, 200–800 μm, and crosscut original ooid and stromatolite laminae (Fig. 4B). Calcite is most common in ooids and least common in interstices. In sample A, practically all ooids (~99%), and ~33%–50% of given stromatolite columns, are composed at least partially of calcite, whereas other Whitefish Falls material has less calcitic ooids (~10%) and less calcite in stromatolite columns (~5%).

Five textural types of calcite can be defined in Whitefish Falls samples, three of which are found in ooids and stromatolites and two in interooid areas. Summarized (see Table 1), the stromatolitic–oolitic types are (1) ochre-tinted, large-crystal (200–800 μm) calcite, with well-preserved, original ooid growth laminae crosscut by calcite crystal boundaries; (2) ochre, large-crystal (200–800 μm) calcite, with poorly preserved or obliterated ooid laminae also crosscut by calcite crystal boundaries; and (3) clear, large-crystal (200–800 μm) calcite, usually associated with opaque, euhedral iron minerals. In stromatolites, no trace of lamination is found in this last textural type, although in ooids there may be rare faint traces of lamination. The interooid textural types are (4) blocky calcite, often twinned and (5) fibrous calcite crystals. These two textures are also found in fractures.

Ooids with types 1 and 2 textures display partial to complete yellow-brown coloration under both plane-polarized and crossed-polarized light. Type 1 texture has well-preserved ooid laminae (Figs. 4B, 4C, 4D, 4E) that are crosscut by calcite crystal boundaries. These laminae are a yellow-brown color, which imparts a distinct ochre coloration to the calcite crystals. Type 2 textures exhibit the same coloration, but the pigment is disseminated to varying degrees throughout the calcite crystal, not concentrated in the form of well-defined laminae (Figs. 4C, 4E). In all cases of type 1 and 2 textures, the crystals conform to the outline of ooid grain edges, except in instances where quartz has intruded or otherwise crosscut the ooid boundary.

Other ooid- and most stromatolite-calcite are relatively colorless or untinted in plane-polarized light (type 3 texture; Figs. 3D, 4C, 4D, 4E) and possess numerous euhedral crystals of opaque iron minerals (described in the subsection below). Faint traces of original ooid lamination can be seen in some ooids with type 3 texture, with the iron minerals crosscutting the lamination (Fig. 5A). Ooids are not necessarily restricted to a single textural type. The majority of ooids possess type 3 texture. The remainder has a combination of two or all three textures. In many cases, type 1 textures grade laterally (along ooid laminae) into type 2 textures, with type 3 textures crosscutting both (Figs. 4C, 4D, 4E). Calcite crystals in all three textural types are large (200–800 μm), crosscut preserved ooid laminae, have irregular boundaries between one another, and exhibit weak pseudopleochroism. As with types 1 and 2, calcite crystals of type 3 texture do not extend past the ooid boundaries.

Fig. 3. Chert and carbonate textures, and crosscutting relations (Whitefish Falls). (A) Quartz crystals in sample A stromatolite column. Megaquartz of 20–40 μm size dominates. Note calcite with euhedral hematite crystals in lower-left and upper-right corners. Crossed nicols, thin section MS-UUP. (B) Sample A ooid with partially silicified rim and calcite core with hematite crystals. a, quartz crystal boundaries cross cut ooid growth laminae; b, calcite extends to rim of ooid toward bottom of picture, with hematite crystals only in the calcite; c, quartz crystals cross ooid boundary. Crossed nicols, thin section MS-UUP. (C) Another sample A ooid with partially silicified rim (arrows). Plane polarized light, thin section SBO389. (D) Morphology of euhedral hematite crystals (hexagonal and diamond-shaped laths) within calcite (cal) ooid. Filled arrows, where hematite on border between quartz and calcite has been truncated; outlined arrows, trace of original ooid boundary, preserved as an inclusion trace in chert. Plane polarized light, thin section SBO389. (E) Quartz crystals (qtz) crosscutting ooid boundary. Notice calcite inclusions delineating original ooid boundary (arrows). Crossed nicols, thin section SBO389. Scale bar in A, B, C = 250 μm; in D = 100 μm; in E = 25 μm.

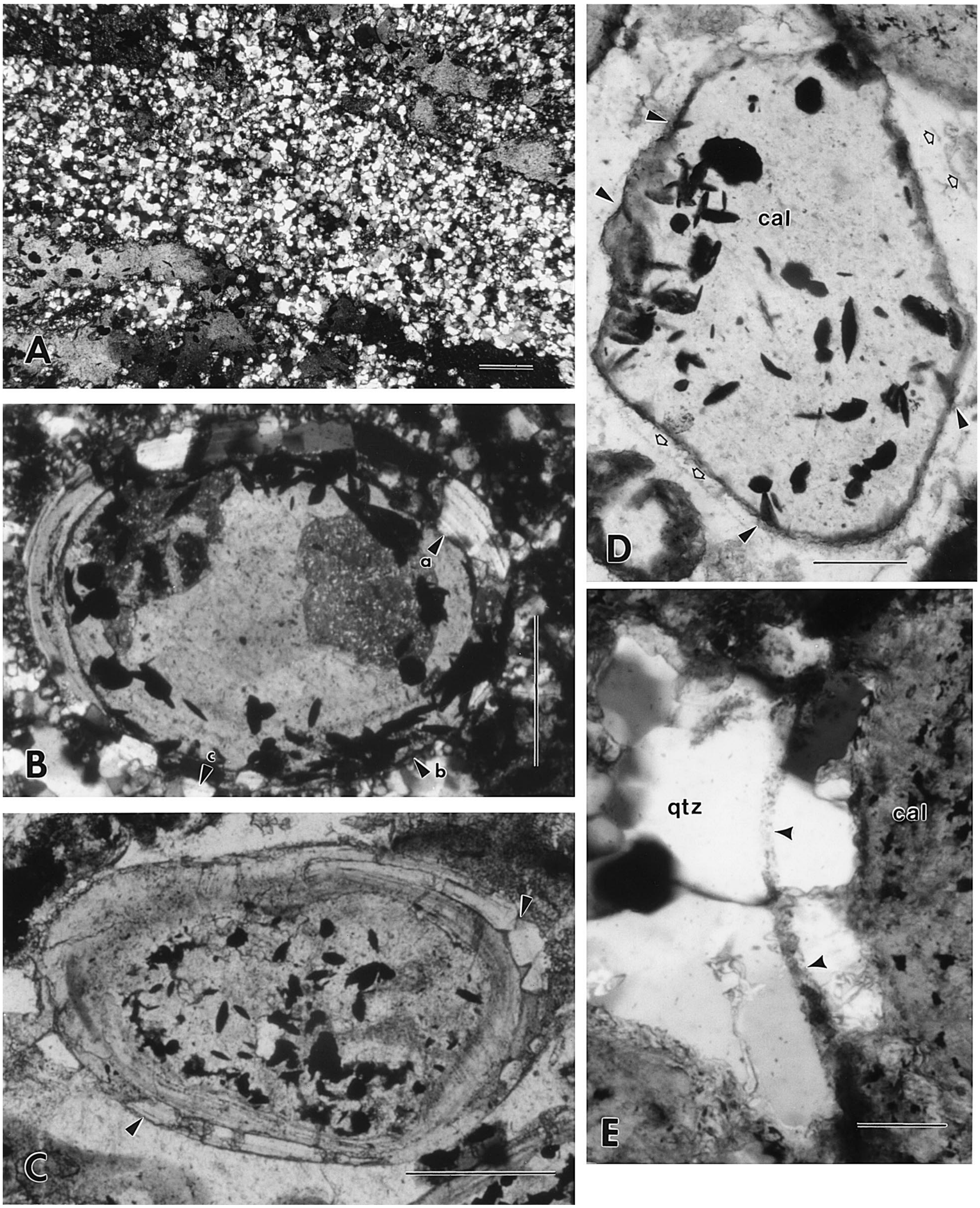


Fig. 4. Crystal sizes, textures, and crosscutting relationships in Whitefish Falls ooids and stromatolites. (A) Chert crystals, representative of stromatolites, found in samples other than sample A. Microquartz of 6–20 μm dominates. a, completely silicified ooids; b, partially silicified ooid, with megaquartz in outer rim. Crossed nicols, thin section MS-15. (B) Large calcite crystals in Sample A ooid. Note the preserved original growth laminae crosscut by calcite crystal boundaries. Crossed nicols, thin section SBO389. C) Crosscutting relations among the three textural types (1, 2, and 3) of calcite in sample A ooid. Type 1 (T1) grades laterally into type 2 (T2), which is crosscut by type 3 (T3). Crossed nicols, thin section SBO389. (D) Type 1 (T1) texture calcite crosscut by type 3 (T3) texture calcite in sample A ooid. Crossed nicols, thin section MS-12L. (E) Type 1 (T1) texture grading laterally into type 2 (T2) texture. Crossed nicols, thin section MS-12L. Scale bar in A, B = 250 μm; in C, D, E = 100 μm.

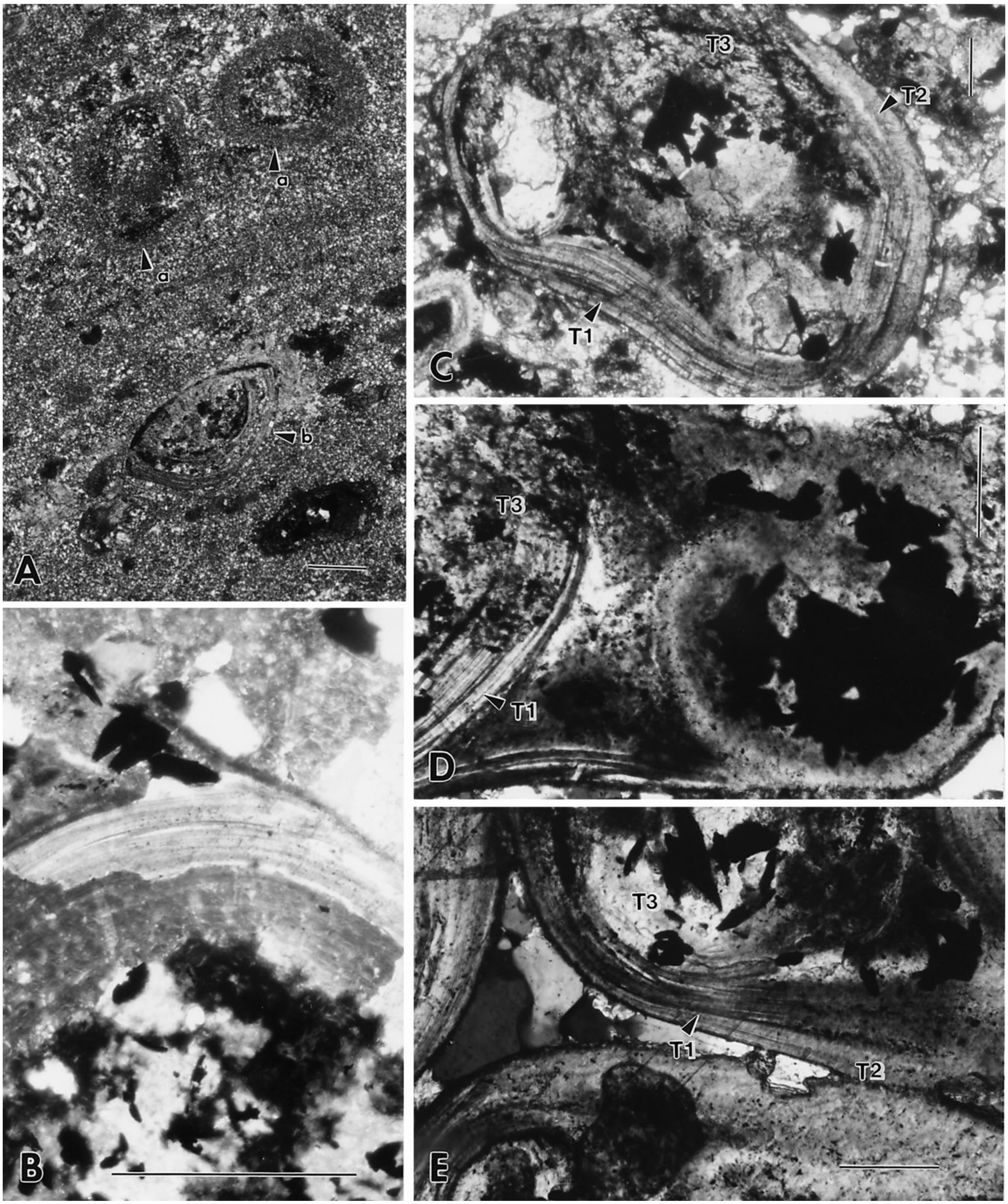


Table 1. Textures and relationships of calcite in Whitefish Falls ooids and stromatolites.

Calcite textural type	Description	Crosscutting relations	Interpretation
Type 1	Ochre-colored. 200–800 μm crystals, contains preserved	Crystals crosscut ooid growth laminae; grades laterally into type 2; crosscut by type 3	Neomorphic calcite after aragonite; closest to original texture
Type 2	Ochre-colored. 200–800 μm crystals. Found in stromatolites and ooids. Ooid laminae are diffuse, if present. No laminae present in stromatolites	May grade laterally into type 1. Crosscut by type 3	Neomorphic calcite, after aragonite in ooids. Secondary alteration after type 1 calcite
Type 3	Clear colored. 200–800 μm crystals, in ooids and stromatolites. Specular hematite crystals abound. Rare laminae remnants may be present in ooids	Crosscuts types 1 and 2. Hematite crystals crosscut by quartz at calcite–quartz boundaries	Calcite affected by very low grade metamorphism. Post-dates types 1 and 2. Hematite indicates calcite was before quartz

The calcite in the stromatolites shows a systematic pattern of arrangement. Patches of the calcite are almost always seen to occur in curvilinear trends that mimic the general trend of the preserved stromatolite laminae. In addition, these curvilinear trends of calcite are usually interrupted and made discontinuous by patches of quartz–chert (Figs. 5B, 5C). Although the chert also seems to occur in the same curvilinear trends, these chert trends display more tendency to deviate from the overall trend of the preserved laminae and also extend past the stromatolite column edges, whereas the calcite does not.

Textural types 4 and 5 are found outside of ooids and stromatolite columns in interstices and fractures. Calcite found in interstices are either large, untinted, blocky-and-twinned crystals (type 4) or clean, fibrous-bladed crystals (type 5; Fig. 5D). Blocky crystals have predominately straight crystal boundaries. Where type 4 crystals do not have straight boundaries, these calcite crystals occur along boundaries of, and intrude into, crystals of megaquartz. Both types 4 and 5 can be found with portions of or entire ooids incorporated within their crystal boundaries. Under cathodoluminescence, both types 4 and 5 luminesce much brighter than types 1–3. Calcite found in fractures tends more to be type 5 than 4.

Calcite crystals in both ooids and stromatolite columns were examined by electron microprobe for strontium concentration. In all cases, no strontium was detected above the limits of the microprobe, which was 7 ppm.

Other Whitefish Falls samples

Low-magnesium calcite is dominant. Only rare ooids are found, with calcite displaying textural types 1 and 2, as described from sample A. Crystal size can be quite large, up to 2 mm. Crystals are untinted, and euhedral iron crystals are absent. Boundaries of the calcite crystals are usually straight and regular, often exhibiting rhombohedral morphology. Where associated with ooids, they crosscut the grain boundaries (Fig. 5E). Other crystals occur in long (cm plus) or narrow (mm or less) tracks that resemble veins. Original texture of the rock is less-well preserved in these ‘veins’ when compared to texture in chert immediately adjacent to the calcite. Aside from this ‘vein’ feature and the lack of observed twinning, the calcite here possesses (and is considered) type 4 texture, as described above.

Petrography of the euhedral iron minerals

Both sample A and other Whitefish Falls samples

The euhedral crystals can be bright translucent-red, translucent-brown, or opaque-black in transmitted light. They range in size from 10 to more than 200 μm. The morphology of these minerals includes hexagonal plates and elongated diamond-shaped laths (Fig. 3D). When examined by EDA, iron was the only significant, detectable component (elements lighter than Fluorine being nondetectable).

In sample A thin sections, the euhedral opaque crystals are found within calcite, not in quartz. Often a crystal found at a boundary contact between calcite and quartz has been truncated (Fig. 3D), or has been ghosted. Figure 6A shows such ghosting of the tip of one of the diamond-shaped laths, as the crystal passes from a calcite matrix into quartz within sample A material. In samples other than sample A Whitefish Falls sections, ghost outlines of these iron minerals can be found in siliceous ooids (Figs. 6B, 6C, 6D).

Schreiber Channel Provincial Nature Reserve

Our observations generally match those described previously (e.g., Barghoorn and Tyler 1965; Cloud 1965; Dimroth and Kimberly 1976; Hofmann 1969; Lougheed 1983; Markun and Randazzo 1980; Simonson and Lanier 1987) and are summarized as follows. Chert is fine microquartz (4–10 μm in size), with megaquartz and uncommon chalcedony present in interstices. Chalcedony was observed in both the length-slow and length-fast states. In all cases, it occurred in small pores. Also, of particular note is that quartz crystals within ooids are often larger (megaquartz-size) than interooid quartz, the crystals are randomly oriented, and crystal boundaries crosscut original ooid growth laminae. Ooids are siliceous (aside from dark iron minerals) with carbonate a minor constituent (<1%). Where carbonate is present, it usually occurs as euhedral rhombs that crosscut the chert and ooid laminae or is fracture fill. Closer inspection of ooids reveals the rare occurrence of remnant calcite and calcite inclusions within ooids (Fig. 6E). None of the ghosted, diamond-shaped structures found in Whitefish Falls material ooids were observed.

Fig. 5. Hematite crosscutting relationship, calcite in stromatolites, and replacement calcite textures. (A) Specularite (hematite) crystals crosscutting traces of ooid growth laminae (arrows). Plane-polarized, but using non-Kohler illumination to show laminae better, thin section SBO389. (B) Calcite (gray areas, arrows) showing curvilinear trends mimicking original laminae within sample A stromatolite column. These trends are cut by quartz that does not show any systematic pattern of arrangement. Transmitted light, thin section MS-UUP. (C) Close up of area between arrows of (B). Transmitted light, thin section MS-UUP. (D) Fan of fibrous calcite (texture type 5). Crossed nicols, thin section MS-CP. (E) Unpigmented, blocky calcite (texture type 4). Note how the crystals are subhedral and do not conform to ooid grain outlines. Crossed nicols, thin section MS-15. Scale bar in A = 50 μm; in D = 500 μm; in E = 100 μm. Scale in B, C in mm.

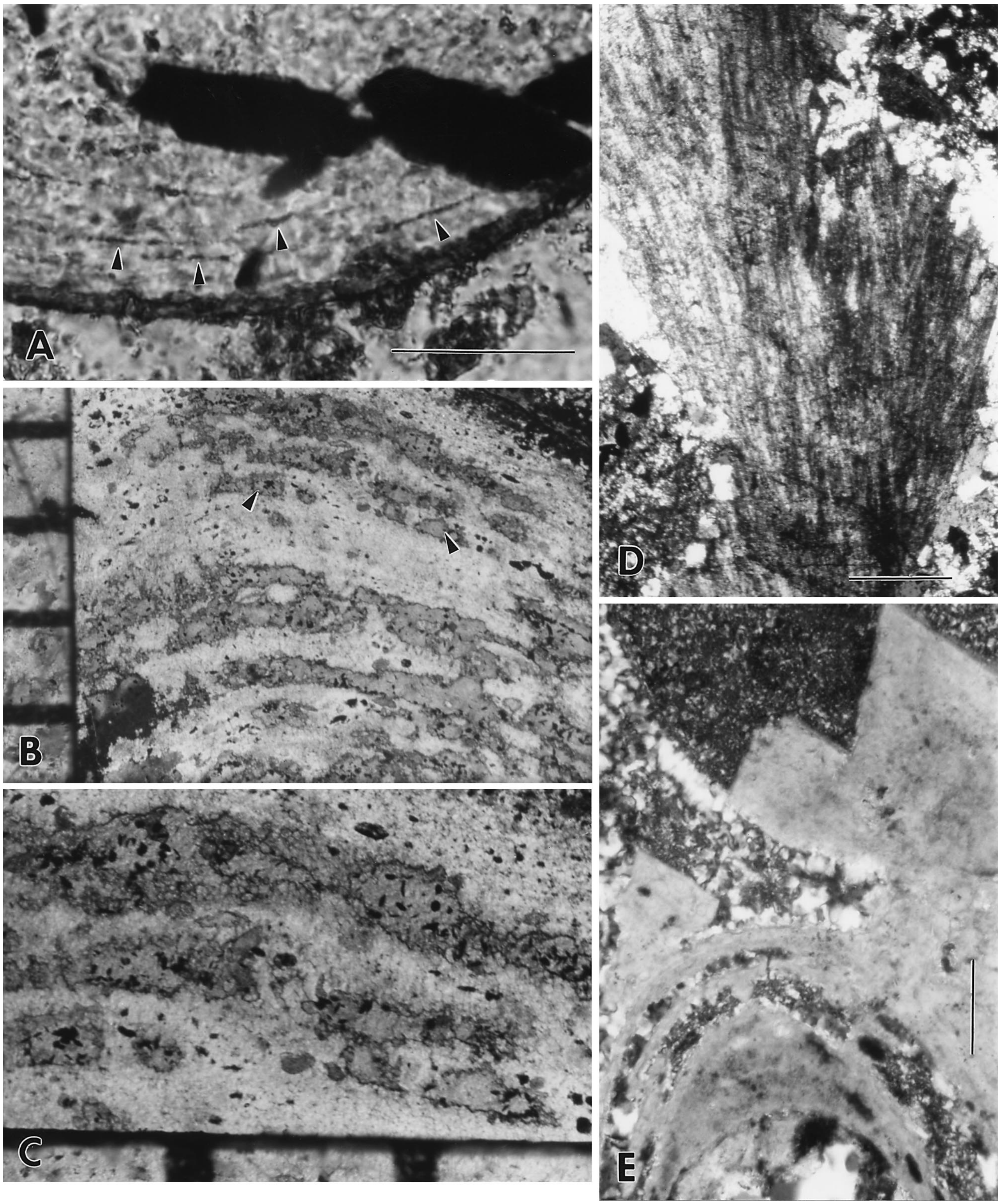
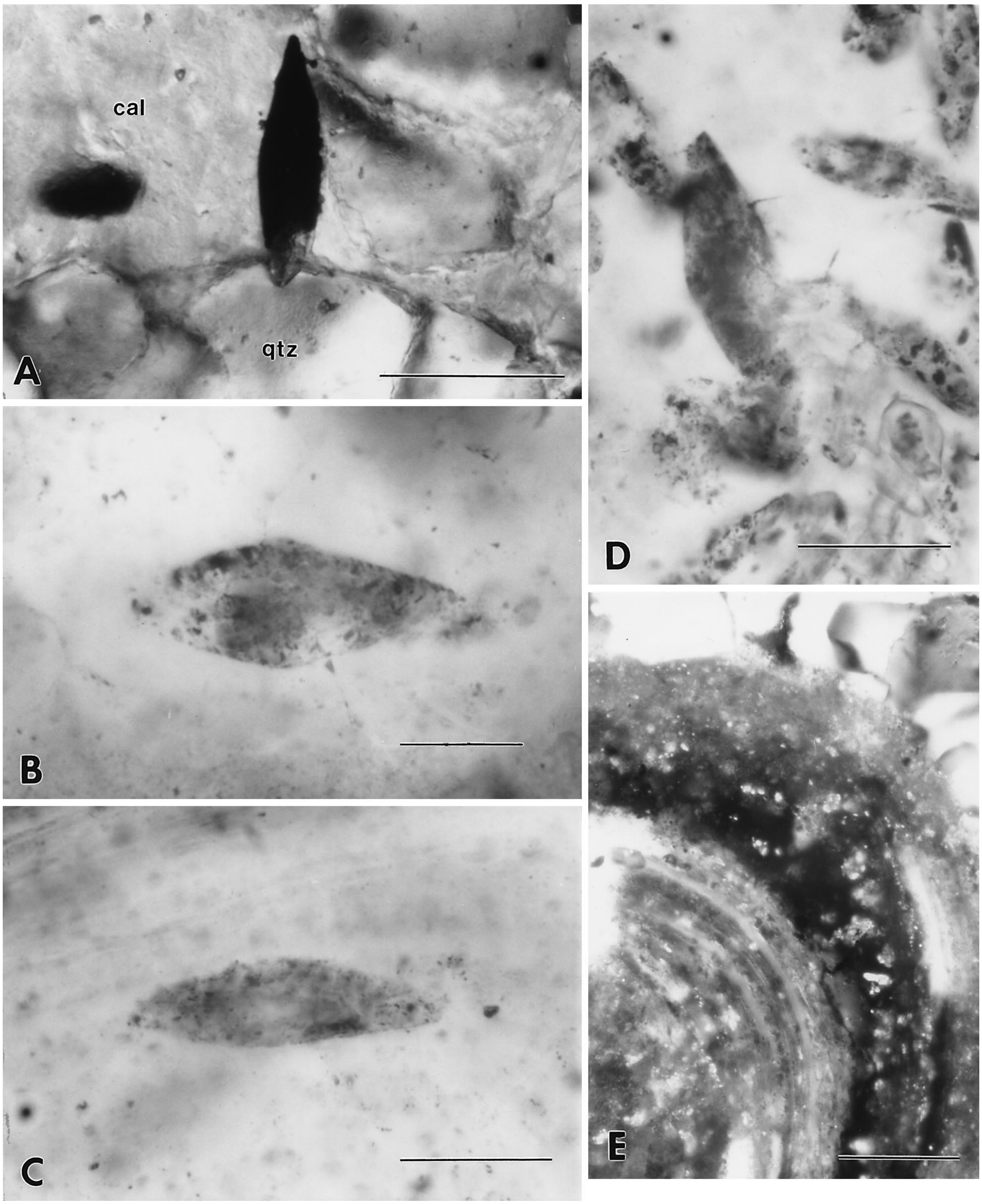


Fig. 6. Ghosted hematite crystals in Whitefish Falls stromatolite and ooids, and calcite remnant in Schreiber ooid. (A) Specularite crystal tip crosscut and ghosted by quartz (qtz) replacing calcite (cal) in sample A stromatolite column. Since the quartz did not entirely replace the calcite, the specularite crystal remains mostly intact within the remaining calcite while the tip in the quartz is corroded and ghosted. Plane polarized light, thin section SBO389. (B) and (C) Corroded ghosts of specularite crystals in Whitefish Falls ooids that are completely silicified. Plane polarized light, thin sections MS-15 (B) and MS-13 (C). (D) Cluster of corroded specularite ghost crystals in Whitefish Falls ooid. Plane polarized light, thin section MS-15. (E) Calcite remnants (bright spots) within Schreiber Reserve ooid. Crossed nicols, thin section SMA-223. Scale bar in A, C, D, E = 50 μm; in B = 25 μm.



Discussion and conclusions

Several published papers argued for the replacement nature of silica in iron formations in general (Dimroth and Kimberly 1976; Lepp 1987; Lepp and Goldich 1964) and for the Gunflint in particular (Lougheed 1983; Markun and Randazzo 1980). These works all are based on indirect, and (or) comparative, evidence (i.e., geochemical, mineralogical, and (or) textural) and are largely dismissed by workers who favor the primary silica interpretation (e.g., "most investigators interpret the algal unit to represent...silica sedimentation," Kimberly 1983, p. 228). Markun and Randazzo (1980) suggested that the ooids of the Gunflint were originally carbonate, possibly aragonite, based on comparison between Gunflint ooids and silicified ooids of the Upper Cambrian "State College" oolite (central Pennsylvania) along with modern ooids.

Markun and Randazzo (1980) also suggested evaporitic–intertidal conditions for Gunflint deposition based on cracks in the ooids (interpreted to be the result of desiccation) and also by the presence of length-slow chalcedony in ooid interstices (cf. Folk 1971 and Pittman). Lougheed (1983) interpreted evaporative conditions in the Biwabik Formation based on euhedral opaque minerals of similar morphology to those found at Whitefish Falls. Based only on comparisons with illustrations in the literature, he described them as pseudomorphic replacements after gypsum.

The complete diagenetic history of the Gunflint Formation can best be discerned through the careful study of the mineralogical and textural relationships of all the separate lithofacies, not simply the Lower Algal Chert Member alone, as reported here. Our observations, however, lead us to suggest that carbonate was the primary phase for ooids and stromatolites in this lithofacies, that they have been silicified, and that the euhedral iron minerals are specular hematite, probably a result of low-grade metamorphism and not pseudomorphs. This would preclude them from being used as evidence for evaporative conditions in the Gunflint. It is important to understand that our observations do not require that 100% of the sediments of the Lower Algal Chert were primary carbonate. Nor are the conclusions intended to extend to the other members of the Gunflint.

There is no doubt that a large proportion of the calcite present in the Lower Algal Chert is replacement of quartz, evidenced by textural types 4 and 5. Additionally, we do not rule out the possibility of any primary silica within the Member, especially silica cements. However, the crosscutting relationships evident in sample A, with megaquartz crystals replacing calcite in ooids (Figs. 3B, 3C), especially crosscutting ooid grain boundaries (Figs. 3B, 3D, 3E), and other ooids being almost or entirely calcite (Figs. 4C, 4D, 4E), clearly show that carbonate was the initial mineral species present in ooids and that the ooids were later partially- to wholly-replaced by silica. These crosscutting relationships are not seen in Schreiber ooids. Most Schreiber Reserve ooids have little or no calcite in them whatsoever. Where calcite is found in Schreiber Reserve samples, it can usually be shown to postdate quartz. However, the size, random orientation, and crosscutting relationships of quartz crystals to the growth laminae within ooids, along with the calcite remnants and inclusions in Schreiber Reserve ooids (Fig. 6E), combine to indicate that quartz is not primary and suggest that carbonate was.

It is less likely that the combination of textures and crosscutting relationships described above shows a pattern of calcite replacing primary silica ooids, followed by a replacement of some of this calcite by quartz. First, quartz repeatedly crosscuts ooid grain boundaries, whereas only unpigmented and relatively textureless (type 4) calcite occasionally does so in ooids. Second, the laminae within the type 1 texture calcite ooids are the best preserved of any ooid laminae, carbonate or silica. Also, the calcite in type 1 and 2 textures have irregular boundaries between crystals, yet conform perfectly to the outlines of ooids. Both of these features are not found in replacement calcite textures (e.g., types 4 and 5).

The Whitefish Falls ooids are now composed of low-Mg calcite. It is possible, however, that they were originally composed of aragonite based on the disrupted texture of the original growth laminae crosscut by calcite crystal boundaries (Sandberg 1985). The preservation of the original growth laminae can be observed within the neomorphic calcite and this suggests that the ooids may have had a tangential fabric, as those found in the Bahamas. The mode of the fine preservation of the original texture (shown in type 1), crosscut by neomorphic calcite crystals, indicates that the calcite precipitation took place via a thin-film alteration front by diffusion (Pingitore 1982). Also, the irregular boundaries between the neomorphic calcite, weak pseudo-pleochroism of the calcite crystals, as well as the original ghosted structure suggest the texture now observed was produced by the replacement of former aragonite by calcite during early diagenesis (Bathurst 1975). Similar textural observations and conclusions were made about Mesoproterozoic ooids of the Belt Supergroup of Montana by Tucker (1984).

Strontium analysis of neomorphic calcite shows the relative low concentration (below the detection limit of 7 ppm). It is accepted that relatively high strontium content within neomorphic calcite may well indicate former aragonite mineralogy (Sandberg 1985). However, calcitized aragonite will retain the original high strontium content within neomorphic calcite only if the diagenetic system is closed and the diagenetic process is isochemical, and (or) the neomorphic calcite contains numerous aragonite crystal relics (Maliva and Dickson 1992). In other words, the strontium content of neomorphic calcite is dependent upon the diagenetic system (open vs. closed). Thus, low strontium concentration in the neomorphic calcite within Whitefish Falls ooids in this study does not exclude the possibility of an original aragonite mineralogy. Previous studies have shown that the strontium content of calcitized aragonitic mollusks can be quite low (e.g., Maliva and Dickson 1992; Woo et al. 1993).

The evidence for the original mineral species of the stromatolites being carbonate is less convincing. It can be demonstrated, though, that the calcite now present predates the quartz. No lamination is preserved within the stromatolitic calcite, while it is preserved in the chert. This could ordinarily suggest that the calcite replaced the chert. The calcite found in the stromatolites (as well as ooids) is predominantly type 3, which generally has been observed not to preserve lamination in the ooids (although type 3 textures may be found crosscutting types 1 and 2, where ooid lamination is preserved). Specular hematite crystals are found in the type 3 calcite in the stromatolites. The crosscutting relations with respect to the specular hematite and the quartz (Figs. 3D, 6A) show that the quartz postdates the hematite. If we accept the probability of the specular hematite postdating the calcite, a conclusion derived further below, then it follows the calcite predates the quartz, but does not necessarily indicate it was the primary mineral.

Additional (albeit, less convincing) evidence for carbonate predating quartz in the stromatolites comes from the systematic arrangement in which the calcite occurs in the stromatolite columns. The calcite usually is found as discrete bands trending in arcuate, curvilinear fashion across the column, mirroring the laminae preserved in the chert (Figs. 5B, 5C). These calcite bands are often interrupted in their cross-column continuity by chert that, as described in the petrographic section, surficially appears similar (in terms of arrangement), but has more tendency to not follow the overall profile of the stromatolite laminae and also extends past column edges. This crosscutting relationship suggests that the calcite was present before the chert, but again does not demonstrate that calcite was the original mineral.

For the original composition of the interstitial cement, we have uncovered no evidence of primary carbonate. The gradational nature (fine-to-coarse grained) of the quartz in some of these spaces is interpreted as either cements filling dissolution porosity (cf. Dimroth and Kimberly 1976) or primary pore-filling cement (cf. Simonson and Lanier 1987). The presence of numerous mineral inclusions in the interstitial quartz indicates that it is a replacement product; however, it could well have been an amorphous silica gel, as suggested by Simonson and Lanier (1987). The calcite found in the interstices is often replacement of quartz along grain boundaries and did not occur simultaneous with (or precipitate from the same fluid as) the calcite of the ooids and stromatolites, as indicated by the different cathodoluminescence of these calcites. The evidence weighs in favor of the cement having been silica.

The specular hematite crystals occur in exclusive association with calcite, specifically textural type 3. Type 3 calcite cuts across types 2 and 1, which preserve (to varying degrees) the growth laminae. Type 2 may often be seen grading laterally (parallel to growth laminae) from type 1. Calcite types 1 and 2 are also ochre tinted, presumably from hydrated iron oxide, while type 3 is untinted (the iron comprising the hematite in type 3 may have derived at least partially from the oxy-hydroxides found in types 1 and 2). Combined, these observations indicate that type 3 calcite postdates types 1 and 2, and type 2 postdates type 1. Thus, type 2 is a secondary calcite texture after type 1, and type 3 is tertiary. This is important, because it demonstrates that the hematite postdates calcite in both ooids and in stromatolite calcite, where there are no preserved laminae.

Also, as a result from the exclusive co-occurrence of the specular hematite crystals with carbonate, we can infer that there have been multiple stages of silicification. We see occasional siliceous ooids in Whitefish Falls materials that have ghost remnants of euhedral hematite crystals in them. We also see areas in all Whitefish Falls and Schreiber Reserve samples where ooids and (or) stromatolites have been silicified without any trace of euhedral hematite. This has to mean there were at least two silicification stages. The first silicification stage occurred early and was practically complete in the vicinity of Schreiber Reserve, but less so in the Whitefish Falls area. This left patches of carbonate remaining within some Whitefish stromatolite columns and left the Whitefish ooids as mostly carbonate. After the event that caused the specular hematite crystals to form in the carbonate, a second silicification stage occurred, during which the hematite crystals in the affected carbonates were also mostly replaced by quartz, leaving only ghosts behind. This second silicification stage was much less pervasive than the first, possibly because the first may have greatly reduced permeability. This allowed a large proportion of the remaining carbonate in sample A to be preserved.

The possibility exists that the specular hematite crystals are pseudomorphic replacements, perhaps after gypsum. We found no calcium or sulfur signatures in microprobe analyses on the specularite. The minute quantities of barite found show that there was at least some sulfate in the system; however, this does not necessarily mean that it is or was associated with gypsum. The euhedral, diamond-shaped, opaque laths are consistent with gypsum (cf. Truc 1980, Plate 76, figs. 3–4). The hexagonal crystals are superficially similar to selenite (cf. Hardie and Eugster 1971); however, the hexagons in Whitefish Falls material are flat disks, whereas those of selenite would be cross-sections of hexagonal prisms. In addition, many of the elongated, diamond-shaped laths at Whitefish Falls are cross-sections of the flat, hexagonal disks. Specularite is a natural form of hematite consistent with flat hexagonal plates and diamond shapes. We, therefore, conclude that the specularite crystals are a "primary" iron-oxide and not replacement of gypsum. These forms of hematite crystals are not unexpected in rocks that have undergone very low-grade metamorphism (W. Wise, personal communication, 1998). Alternatively, Dimroth (1979) interpreted specularite as an early diagenetic alteration of "hematite dust." However, the interpretation of very low-grade metamorphic conditions would help explain the larger quartz crystal sizes, lack of chalcedony, and poorer preservation of stromatolite laminae and microfossils compared to Schreiber.

Put together, these observations serve to indicate that the sedimentary and diagenetic history of the Lower Algal Chert of the Gunflint Formation is quite complicated. First, there is evidence for primary carbonate ooids and stromatolites, cemented by silica. Next, a silicification event occurred that almost completely replaced all the carbonate in ooids and stromatolites in the Schreiber Reserve area and to a lesser degree at Whitefish Falls. Following that, diagenesis changed presumably aragonitic ooids to calcite, and a very low-grade metamorphic event at Whitefish Falls produced the specular hematite crystals. A second silicification stage took place after that, which accounts for the occasional specularite crystal relicts found in some Whitefish Falls samples. Finally, there were episodes of later calcite replacement of silica as evidenced by type 4 and 5 calcite textures, and perhaps more silicification.

On the face of it, the implications of our findings may seem to challenge the long-held notion of the silica-supersaturated Archean–Paleoproterozoic ocean (e.g., Siever

1992). But, it is necessary to remember that our results are relevant only toward some of the sediments (ooids and stromatolites) of one member of one iron formation. In fact, we feel that a silica-supersaturated ocean could actually support our interpretations, as what better way to account for the extensive and pervasive silicification of the Lower Algal Chert? Based on our evidence and its interpretation, and incorporating models that invoke chemically-stratified reservoirs (e.g., Carrigan and Cameron 1991; Winter and Knauth 1992) and sea-level change (e.g., Simonson and Hassler 1996), could the Gunflint have been deposited in a chemically stratified basin with transgression playing an important role? The suggestion is that nearshore, shallow, marine waters were precipitating carbonate ooids and stromatolites, much as we may expect in the Phanerozoic. With major transgression (which happened at least twice during Gunflint time, Goodwin 1960), these shallow-water carbonate deposits were covered with the deeper waters, which either caused or triggered silica cementation and (or) diagenesis and replacement by silica. This would help account for Simonson's (1987) interpretation of early silica cementation that occurred very near the sediment–water interface.

Summary

We have concluded that in the Lower Algal Chert Member of the Gunflint Formation (1) the ooids and the stromatolites were originally carbonate and not silica as has been previously interpreted; (2) there is suggestive evidence that the ooids were originally aragonitic; (3) the possibility of evaporitic conditions during basal Gunflint times, suggested by possible hematite replacement of gypsum crystals, is not supported by our evidence; and (4), there were multiple stages of both calcitization and silicification, and at the Whitefish Falls locality, at least, very low-grade metamorphism.

The Gunflint microbiota, therefore, did not exist in a radically different environment (silica precipitating, at least of ooids and stromatolites) than that of most other known Proterozoic microbiota. The fact that they are found with such high fidelity of preservation does help indicate that silicification probably took place during very early diagenesis. High fidelity of preservation does not always indicate that the mineral entombing the microbes was the primary mineral precipitated from the aqueous solution.

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