Stromatolites and calcitized evaporite in a hypersaline playa lake: Rossport Formation (Mesoproterozoic, Ontario)

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Abstract
The Mesoproterozoic Rossport Formation of Ontario, Canada is generally interpreted as having been deposited in an intracratonic basin, most probably a rift-related lake. While the Rossport, overall, is dominated by sandstone and shale, the Middlebrun Bay Member, in the middle of the formation, is a carbonate unit. The Middlebrun Bay Member, in exposures on the Channel Islands and along the north Shore of Lake Superior, consists most commonly of cherty, dolomitic microbial laminites and low-relief columnar to conical forms. In contrast to typical outcrops, the Middlebrun Bay Member on Copper Island expresses as a massive, coarsely crystalline limestone unit, devoid of stromatolites or microbial laminae. Several features suggest dissolution and replacement of a primary, soluble phase such as an evaporite mineral. The top of the unit is marked by evidence of dissolution and collapse, including large sandstone clasts let down from the overlying bed. At petrographic scale, the Copper Island Carbonate comprises millimetre-scale anhedral spar with abundant stylolites and concentration of insoluble material at grain boundaries, indicating recrystallization from a previous phase. Geochemical data from Copper Island and from correlating stromatolitic carbonate on Channel Island and mainland Ontario are consistent with hypersaline conditions, with elevated concentrations of carbonate-associated sulphate, V and Ba. Based on these data, the massive carbonate exposed on Copper Island is interpreted as a calcitized evaporite, probably deposited originally as gypsum, and replaced by calcite during diagenesis. These data support previous work suggesting that the Middlebrun Bay interval was deposited during a period of increased aridity and low clastic influx, and further suggest that this restricted, hypersaline lake precipitated both carbonate and gypsum, comparable to modern arid playa lakes.

KEYWORDS
evaporite, lacustrine carbonate, Mesoproterozoic, stromatolite
1 | INTRODUCTION

The Proterozoic Eon, and particularly the Mesoproterozoic Era, preserves a rich record of epicontinental (Buick et al., 1995; Kah, 2000; Kah et al., 2012) and continental-margin (Maslov et al., 1997) carbonate platforms. A combination of high eustatic sea level, high sea water carbonate saturation (Bartley & Kah, 2004), and dynamic redox conditions (Gilleaudeau et al., 2016; Gilleaudeau & Kah, 2015; Wang et al., 2020) resulted in abundant and diverse stromatolites in nearly all Mesoproterozoic marine basins (Awramik & Sprinkle, 1999; Cantine et al., 2019; Kah & Bartley, 2021). The record of Proterozoic non-marine carbonates is less well-known, but recent work suggests that microbialite diversity in lacustrine settings is low compared to marine basins (Fedorchuk et al., 2016; Rogala et al., 2007). In addition, distinguishing Proterozoic shallow marine environments from lacustrine environments can be challenging, and several putative marine successions have been reinterpreted as lacustrine (e.g., Borden Basin: Gibson et al., 2019; Hahn et al., 2015; Kah et al., 2001) and vice versa (e.g., Midcontinent Rift succession: Fedorchuk et al., 2016; Jones et al., 2020), while others remain unresolved (e.g., Belt Supergroup: Frank et al., 1997; Winston, 1986; Winston et al., 1993). Indeed, most preserved successions in the Proterozoic have a high degree of ‘continuity’, and most are interpreted as structurally controlled lakes, epeiric seas, or epicratonic basins whose relationship to the global ocean was unknown. Many Proterozoic successions lack diagnostic facies or sufficient three-dimensional exposure to resolve the uncertainty with a high level of confidence. Where substantial three-dimensional facies reconstruction is possible, particularly when core is available, broad-scale environmental interpretations are more secure (Cheadle, 1986a; Rogala et al., 2005).

Proterozoic lacustrine successions, furthermore, are frequently clastic dominated, and carbonates are absent or present as subsidiary lithologies (Cheadle, 1986a, 1986b; Fedorchuk et al., 2016; Parnell et al., 2010). As a result, no generalised framework exists to help interpret Proterozoic stromatolites from these environments, nor is it yet known how the morphology and microstructure of Proterozoic lacustrine stromatolites relates to either modern lacustrine or ancient marine stromatolites. Precise modern analogues of Proterozoic stromatolites are difficult to find; the dominance of macroscopic biota in shallow, open water carbonate platforms of the modern ocean means that stromatolites are rare in normal marine settings. Indeed, of the two best-known occurrences of modern marine stromatolites, Shark Bay (Suosaari et al., 2016) and the Bahamas (Andres & Reid, 2006; Suosaari et al., 2019), only the Bahamian stromatolites grow in open marine waters of normal salinity (Dill et al., 1986; Reid et al., 1995). In contrast stromatolites occur in a wide variety of modern and Phanerozoic lakes (Chidsey et al., 2015; Gomez et al., 2014; Martin-Bello et al., 2019; Zeng et al., 2019) and may present opportunities as analogues for ancient stromatolites. For example, modern lacustrine stromatolites share textural features with Proterozoic stromatolites, including clotted micritic to microsparitic fabric, botryoidal texture and radial-fibrous fabric (Gomez et al., 2014; Keim et al., 2020), each of which are common in Proterozoic marine stromatolites (Bartley et al., 2000; Knoll et al., 2013) across a wide range of macroscopic forms. As both chemical sedimentary rocks and macroscopic fossils, stromatolite-bearing carbonate successions have the capacity to record palaeoenvironmental conditions and inform understanding of the conditions under which mineralizing microbial communities thrived (Grotzinger & Knoll, 1999); however, a general model describing the relationship between form and environment has proved to be elusive. Recent work on modern microbialites from a hypersaline lake in Argentina suggests that carbonate nucleated in extracellular polymeric substances exhibits a distinct microsparitic microstructure (Gomez et al., 2018; Mlewski et al., 2018). Work in a hypersaline lagoon in Brazil found that peloidal microsparitic texture can result from the intimate intergrowth of calcite crystals with different Mg content and grain size (Keim et al., 2020). Taken together, these observations of modern microbialites suggest that microbialite microspar and peloids are primary features resulting from carbonate growth in living and decomposing microbial consortia and may represent a robust microbialite textural signature (Mlewski et al., 2018).

Connecting these field studies of modern microbialites to interpretations of Proterozoic stromatolites requires first documenting the environmental settings that produced stromatolites, across a wide range of basin types (Cantine et al., 2019), followed by more detailed work relating stromatolite morphology and microstructure to independent environmental indicators (Bartley et al., 2015; Grotzinger, 1989; Grotzinger & Knoll, 1999; Kah & Bartley, 2021; Kah et al., 2006, 2009). One important strategy for constraining the environmental conditions that produced ancient stromatolites is to evaluate the depositional conditions of the facies associated with stromatolite growth. For example, placing intervals of stromatolite growth into a stratigraphic framework (Grotzinger, 1989) or relating stromatolite morphology to distinct portions of a parasequence (Kah et al., 2009) permits macroscopic morphology to be connected with specific environmental conditions. Applying a consistent framework for stromatolite description (Grey & Awramik, 2020) at all scales allows identification of similar features across time and environments. Importantly, examination of correlative facies in a basin can help constrain the specific conditions under which stromatolites grew (Bartley et al., 2015), a strategy that is particularly important for ancient lacustrine settings in which stromatolites represent subsidiary or anomalous lithologies in the basin overall (Cheadle, 1986a, 1986b; Fedorchuk et al., 2016; Parnell et al., 2010), especially compared to Proterozoic marine successions where stromatolites...
represent a volumetrically significant portion of platform stratigraphy (Cantine et al., 2019).

At the same time, the Precambrian record of evaporite deposits, and more specifically, bedded sulphate deposits, reflects secular changes in global oxygenation, modified by local conditions. Palaeoproterozoic shallow marine successions rarely contain evidence of bedded evaporites, although a few sulphate-containing units have been described from Palaeoproterozoic units associated with the Great Oxidation Event and its aftermath (Blättler et al., 2018; Pope & Grotzinger, 2003; Schröder et al., 2008). Changes to sulphate availability in marine settings mark the establishment of the more familiar modern carbonate-evaporite successions (Kah et al., 2001, 2004), with bedded evaporite units occurring in restricted marine environments. The record of evaporites in Proterozoic lacustrine settings, however, need not follow this pattern, and Proterozoic lakes may have evolved water chemistries that departed from those of their marine counterparts, in the same way that modern lakes may exhibit anomalous chemistry (Witherow & Lyons, 2011). Nevertheless, as global oxygenation increased, sulphate, produced during oxidative weathering, would have become more abundant in both lacustrine and marine waters and sulphate evaporites probably would have increased in abundance in both restricted marine and hypersaline lacustrine settings (Kah & Bartley, 2011).

Proterozoic lacustrine stromatolites have been associated with restricted alkaline or hypersaline conditions (Cheadle, 1986a; Fedorchuk et al., 2016; Rogala et al., 2005, 2007); similar conditions of hypersalinity in Phanerozoic lacustrine (Awramik & Buchheim, 2015; Gallois et al., 2018; Martin-Bello et al., 2019), marine (Mercedes-Martín et al., 2014; Oliveri et al., 2010), and Recent (Gomez et al., 2014; Keim et al., 2020) lacustrine settings are associated with intervals of stromatolite growth and with bedded sulphate deposition (Gomez et al., 2014; Mlewski et al., 2018). The Mesoproterozoic Sibley Group, although dominantly clastic (Franklin et al., 1980) contains a thin horizon of stromatolites and microbial laminites interpreted as occurring under restricted, hypersaline lake conditions (Cheadle, 1986a; Rogala et al., 2005). Here, these microbial carbonates from the Middlebrun Bay Member of the Rossport Formation are described along with a previously undescribed laterally adjacent massive carbonate unit, in order to better constrain the conditions that produced stromatolites in this Mesoproterozoic lake.

2 | GEOLOGICAL SETTING

The Sibley Group is a clastic-dominated lacustrine succession present in outcrop and in the subsurface in the southern area of north-western Ontario (Figure 1; Rogala et al., 2005). The Sibley Group comprises five formations—in ascending order, the Pass Lake, Rossport, Kama Hill, Outan Island and Nipigon Bay formations (Figure 2). The Sibley Group crops out widely along the north shore of Lake Superior east of Thunder Bay, as well as in the vicinity of Lake Nipigon. In addition, Sibley Group strata have been intersected in drill core throughout this region (Rogala et al., 2005, 2007). The group is approximately 950 m thick and is dominated by terrigenous sediment, including shale, sandstone and conglomerate. Redbeds are common and most units were deposited in alluvial, fluvial or shallow lacustrine environments (Cheadle, 1986a, 1986b; Rogala et al., 2005).

Deposition of the Sibley Group initiated (Figure 2) with coarse clastics of the Pass Lake Formation (Franklin et al., 1980) resting unconformably on the Palaeoproterozoic Rove Formation in the study area and on Archean basement elsewhere. The Loon Member of the Pass Lake Formation is a conglomerate that preserves basal debris flows and immature fluvial–alluvial deposits (Cheadle, 1986a). The overlying Fork Bay Member represents alluvial outwash and sand flats, containing planar crossbeds, dewatering features and evidence for subaerial exposure (Cheadle, 1986a). The Pass Lake grades into the Channel Island Member of the Rossport Formation (Figure 2), consisting mainly of siltstones that grade upward into dolomitic siltstones and dolostones. Dolostones of the Channel Island member contain calcium sulphate nodules and bladed crystals (Rogala et al., 2007) and are interpreted as representing deposition near the lake margin during highstand of a playa lake (Cheadle, 1986a). The Channel Island Member coarsens upward, with sandstone dominating near the top of the unit. The overlying Middlebrun Bay Member (Figure 3), the subject of this study, is a thin (ca 1 m) chert-carbonate unit bearing microbially laminated and low-relief columnar to conical stromatolites (Cheadle, 1986b). White, grey and black chert occur throughout the Middlebrun Bay Member but are particularly prominent in a chert breccia at the base of the member and a grey chert unit at the top. The uppermost cherty horizon of the Middlebrun Bay Member contains calcite pseudomorphs after displacive halite (Cheadle, 1986a, 1986b). Deposition of the Middlebrun Bay Member occurred during an interval of high aridity in the playa lake, resulting in cessation of clastic input, evaporative concentration of lake waters, and initiation of stromatolite development (Cheadle, 1986a; Rogala et al., 2005). Above the Middlebrun Bay Member, the Fire Hill Member records re-initiation of clastic influx, consisting of mudstone, siltstone and sandstone, with subsidiary dolostone and evaporites, and is interpreted as representing continued deposition under hypersaline conditions with intermittent exposure. (Rogala et al., 2007). The Fire Hill Member contains an intraformational conglomerate at its base, sulphate nodules, and abundant shrinkage cracks that may be either desiccation or syneresis cracks (Cheadle, 1986b). Above the Rossport Formation, clastics of the Kama Hill and Outan Island formations represent deposition in a prodelta to fluvial environment (Rogala et al., 2005, 2007). The Nipigon Bay Formation, with dune-form cross-stratified sandstones, unconformably
overlies the Outan Island Formation and records an interval of aeolian deposition (Rogala et al., 2005, 2007).

The age of the Sibley Group is broadly constrained to be lower Mesoproterozoic. The Sibley Group overlies and may be interbedded with (Davis & Sutcliffe, 1985) a granite–rhyolite complex with a U–Pb age of 1,536.7 ± 10/−2.3 Ma (Davis & Sutcliffe, 1985). The Sibley Group is overlain by the late Mesoproterozoic Osler Group (1,097 ± 3.7 Ma; Davis & Sutcliffe, 1985) and is cross cut by Keweenawan age dikes and sills. Notably, the Kama Bay locality has a prominent sill intruding the top of the Middlebrun Bay Member (Osterhout et al., 2019). Channel Island and Copper Island localities lack intrusions within the Middlebrun Bay Member. Two palaeopoles from the Sibley Group are consistent with early Mesoproterozoic Laurentian apparent polar wander paths and suggest that the Sibley Group is coeval with the Belt Supergroup at 1,400–1,450 Ma (Elston et al., 2002).

3 | METHODS

3.1 | Field collection

Samples for petrographic and geochemical analysis were collected from surface exposures of the Middlebrun Bay Member of the Rossport Formation on Channel Island, Copper Island,
and from roadcut exposures near Kama Bay, on the mainland (Figure 3). Samples for geochemical analysis were obtained on interior, less weathered samples, avoiding areas with cracks, roots, or other evidence of surface alteration.

3.2 | Petrography

Field samples were cut using a water saw to obtain paired thin sections and polished slabs. Petrographic features were discerned using a combination of optical microscopy (Nikon polarizing microscope) and cathodoluminescence (Reliotron III CL instrument). In some cases, carbonate texture could be visualised more readily when a white card was placed below the thin section, in the plane-polarized light path. Images were acquired using a Canon Digital Rebel T2i, either attached to a low-power binocular microscope or with a macro lens to acquire cathodoluminescence images of polished slabs.

3.3 | Geochemistry

Subsamples of individual carbonate elements were obtained from powdered whole rock (indicated as whole rock in Table 1) or from cut slabs using a drill press fitted with a 0.5 mm drill bit (indicated as drilled in Table 1). When drilling, recognisable carbonate phases, including micrite, cement, and anhedral calcite, were identified on polished slabs by CL and reflected light microscopy, supplemented by optical microscopy of paired thin sections. Individual phases were targeted during drilling, taking care to avoid undesired phases for each sample, such as stylolites, highly silicified layers, late-stage cements, and insoluble residues between grains or layers. This technique is widely used in Proterozoic carbonate analysis and has been shown to be effective at minimising contamination by non-carbonate phases (Bartley et al., 2001; Kaufman & Knoll, 1995; Saltzman et al., 1998). In addition, this technique permits specific primary or early diagenetic carbonate phases, such as microspar or microbial texture, to be targeted while others, such as late-stage cement or stylolites are avoided (Kaufman et al., 1993; Kaufman & Knoll, 1995). Approximately 1 mg of powder was dissolved in 10 ml 2% HNO3 containing 100 ppb internal standard (Li, Sc, Y, In, Tb, Bi) and analysed using an Agilent 7700 quadrupole ICPMS. Elemental concentrations were calculated using measured concentrations of Ca$^{2+}$ and Mg$^{2+}$ and assuming substitution into stoichiometric calcite or dolomite. Precision and reproducibility, determined by repeat analysis of standards and replicate samples, is better than 5% for all elements.

Whole-rock samples for determination of carbonate-associated sulphate (CAS) were processed according to the procedure given by Hurtgen et al. (2004) and Kah et al. (2016). Samples were obtained by crushing rock taken from the unweathered interior of field samples and milling in a clean ceramic ball mill. The CAS was extracted by first soaking 40–100 g of carbonate powder in 5.5%–6.0% sodium hypochlorite solution for >24 h, followed by an ultrapure water (18.2 MΩ.cm) rinse to remove metastable sulphides, organic sulphur compounds, and sulphates not bound to carbonate. Remaining carbonate was dissolved slowly in 3 M HCl, monitoring pH during acid addition to maintain pH as close to neutral as possible, but always >3 (Kah et al., 2016). Insoluble residue was removed by filtration through 0.5 μm filters. The pH was raised to >9 using 6 M NaOH, then centrifuged to remove precipitated iron oxides, if any formed. Sulphate released into solution was precipitated as BaSO$_4$ by addition of 150 ml of saturated BaCl$_2$ solution and allowing precipitate to form overnight. Solid BaSO$_4$ was filtered onto oven-dried and weighed glass fibre filters. Precipitate was then dried overnight in a 90°C oven and weighed.

4 | RESULTS AND INTERPRETATION

4.1 | Stromatolites

Middlebrun Bay Member stromatolites occur within a ca 1 m bed (Figure 4A) and are stratiform to columnar, with synoptic relief between 0.1 and 5 cm. Millimetre-scale lamination (Figure 4B,C) is commonly preserved, with locally
| Sample   | Locality   | Sample type and description           | CAS | Mg/Ca | Na  | K   | V   | Mn  | Fe  | Sr  | Ba  |
|----------|------------|---------------------------------------|-----|-------|-----|-----|-----|-----|-----|-----|-----|
| SB13-02  | Copper Island | Drilled; clean sparry calcite         | —   | 0.01  | <   | <   | 0.4 | 86  | 43  | 81  | 29  |
| SB13-02-1W | Copper Island | Whole rock; massive coarse carbonate  | 75  | 0.01  | 150 | 804 | 1.9 | 370 | 36,907 | 12 | 3,512 |
| SB13-02-2W | Copper Island | Whole rock; massive coarse carbonate  | —   | 0.00  | 170 | 295 | 0.5 | 64  | 9,776 | 7  | 486 |
| SB13-03  | Copper Island | Drilled; recrystallized sucrosic sparry calcite | —   | 0.00  | <   | <   | 2.4 | 1,181 | 435 | 995 | 62,635 |
| SB13-03-1W | Copper Island | Whole rock; coarse sucrosic calcite   | 387 | 0.01  | 162 | 203 | 2.2 | 944 | 52,336 | 6  | 6  |
| SB13-03-2W | Copper Island | Whole rock; coarse sucrosic calcite   | —   | 0.00  | 282 | 402 | 2.0 | 957 | 62,946 | 6  | 10 |
| SB13-04  | Channel Island | Drilled; micritic microbial laminite | —   | 0.60  | <   | 981 | 53.4 | 828 | 903 | 900 | 21,567 |
| SB13-06  | Channel Island | Drilled; micritic microbial laminite | —   | 0.27  | <   | 2,778 | 74.8 | 1,499 | 638 | 1,305 | 28,269 |
| SB13-08  | Channel Island | Drilled; micritic laminite            | —   | 0.36  | <   | 1,380 | 75.3 | 1,411 | 585 | 1,348 | 34,900 |
| SB13-10  | Channel Island | Drilled; micritic microbial laminite | —   | 0.72  | <   | 156 | 19.6 | 859 | 352 | 1,358 | 39,565 |
| SB13-10-1W | Channel Island | Whole rock; microbial laminite        | 661 | 0.26  | 495 | 658 | 8.5 | 1,032 | 52,938 | 37 | 10,401 |
| SB13-10-2W | Channel Island | Whole rock; microbial laminite        | —   | 0.26  | 766 | 1,219 | 6.2 | 942 | 36,859 | 130 | 53,577 |
| SB13-11  | Channel Island | Drilled; micritic microbial laminite | —   | 0.32  | <   | 31  | 12.7 | 1,853 | 356 | 1,214 | 21,429 |
| SB13-28  | Kama Bay      | Drilled; micritic silica-rich microbial laminite | —   | 0.87  | <   | <  | 21.6 | 1,345 | 6,875 | 123 | 233 |

*Note:* Concentration values in ppm. Dash indicates analysis not performed. ‘<’ indicates concentration was below detection limits. See Table S1 for full dataset.
oversteepened laminae (Figure 4D,E). Stromatolites from the Channel Island locality are typically stratiform, with maximum synoptic relief around 1 cm (Figure 4B,D). A few stromatolites have moderately well-developed apical zones, giving them coniform character (Figure 4E). Synoptic relief is probably constrained by limited accommodation, perhaps no more than a few centimetres of total depth. Stromatolites from the Kama Bay locality exhibit locally higher relief and display both stratiform and low domal morphologies (Figure 4C,E). The greater synoptic relief, up to about 5 cm, indicates somewhat greater accommodation compared to Channel Island.

Stromatolites probably experienced episodes of water energy and subaerial exposure, as evidenced by delamination of structures (Figure 4C) and disruption of laminae (Figure 4B,D). Breccias (Figure 4F) composed of both chert and carbonate clasts are prominent on the east side of Channel Island near the top of the Middlebrun Bay Member, suggesting exposure of early-lithified microbialites. The top of the unit is deeply weathered, and the base of the Fire Hill Member has previously been interpreted as an interval of soil development (Cheadle, 1986b).

At mesoscale to microscale, Middlebrun Bay stromatolites have textures characteristic of precipitated stromatolites. Carbonates are fine-grained, micritic to microsparitic and dolomite is largely fabric retentive (Figure 5A,B). Micritic carbonate is arranged into laminae 1–10 mm thick in outcrop that vary in thickness across the microbialite structure (Figure 4B,C). A typical microbialite exhibits strong layering in outcrop, with laminae ranging from 1 to 10 mm in thickness (Figure 4B through E). Laminae most commonly thicken across topographic highs (Figure 4D, arrow 1), but they may also thicken in troughs (Figure 4D, arrow 2), or display a crinkled texture with slope and thickness variation across a horizon. Laminae are frequently oversteepened (Figure 4D, arrow 3; Figure 5A through C) and are occasionally overturned. In thin section, most mesoscale lamination is composed of finescale, micron to millimetre-thick layers distinguished by subtle differences in grain size and by varying amounts of organic material (Figure 5A through D). Stromatolites have filmy to micritic microstructure that is locally peloidal (Figure 5F; cf. Grey & Awramik, 2020). Laminated carbonate displays uniform moderate luminescence with no crystal zonation evident (Figure 5E). Late-stage carbonate and void-filling cements are typically more brightly luminescent and more coarsely crystalline. This combination of micritic microstructure with irregular laminae typically results from production of carbonate within microbial mats during mat growth and/or decomposition (Gomez et al., 2014; Mlewski et al., 2018), resulting in an early-lithified microbialite that nevertheless may have possessed some ductility, leading to small-scale wrinkling and slumping.

The Channel Island and Kama Bay stromatolites are variably silicified, and chert is cryptocrystalline to microcrystalline. Silica in Kama Bay stromatolites (Figure 5C,D) is somewhat coarser and more pervasive throughout microbialites than silica from the Channel Island locality (Figure 5A,B).
Where present, silica is concentrated along laminae, preserving mesoscopic lamina structure, or replacing several laminae (Figure 5B). Chert frequently cuts across laminae and does not preserve original microscale carbonate fabric (Figure 5F) as it does in many early silicified carbonates (Bartley et al., 2000; Knoll et al., 2013) and microfossils are absent. Post-lithification brecciation and cracking is evident in thin section as well as at outcrop scale. Taken together, these features suggest that at least some of the silicification may have occurred relatively late in diagenesis, and it is probable that both syndepositional and later silica are present in Middlebrun Bay carbonates.

Overall, field and petrographic evidence suggests that stromatolites grew in a shallow subaqueous environment. Their textures indicate that laminae accreted via carbonate precipitation rather than trapping and binding. Stromatolites were intermittently exposed, with significant exposure and brecciation occurring at the top of the unit, below the Fire Hill Member (Figure 4F; Cheadle, 1986a, 1986b).

4.2 | Copper Island carbonate

The stratigraphy of Copper Island is dominated by shoreline exposures of the distinctive redbeds of the Fire Hill Member, which are dominated by fine-grained clastics, many of which contain shrinkage cracks (cf. Cheadle, 1986b). The base of the Fire Hill Member at this locality is marked by a basal intraformational conglomerate with large, subrounded clasts encased within the upper portion of a bright white limestone bed (Figure 6A) or resting with sharp, karst-like contact on the underlying limestone (Figure 6B,D). This limestone, situated below the Fire Hill Member, lies in the same stratigraphic position as the Middlebrun Bay Member on Channel Island, just to the north-west of Copper Island (Figure 1C), but differs lithologically from the common expression of this unit as observed on Channel Island and in numerous localities on the mainland (Cheadle, 1986a, 1986b; Rogala et al., 2005). While typical exposures of the Middlebrun Bay
Member are characterised by cherty, dolomitic stromatolites, microbial laminites and intraformational breccia (Cheadle, 1986b; Rogala et al., 2005), the Middlebrun Bay Member on Copper Island is a coarsely crystalline limestone, lacking internal lamination (Figure 6) and with a crystalline texture characterised by insoluble material concentrated at grain boundaries (Figure 6C) and stylolites.

In thin section, samples from this unit have large anhedral to subhedral crystals (Figure 7A,B), abundant stylolites, and zoned crystals, which are particularly evident by
cathodoluminescence (Figure 7C). Both stylolites and crystal boundaries contain accumulations of insoluble residue (Figure 7B).

The Copper Island carbonate is best interpreted as possessing a secondary texture, with diagenetic calcite replacing a primary mineralogy and fabric. The unit was probably deposited in very shallow water and subsequently exposed, as evidenced by the nature of the contact with the overlying Fire Hill Member. Loss of volume during dissolution and precipitation is evidenced by the presence of sandstone blocks derived from the overlying beds within the upper portions of the unit, producing a collapse breccia (Figure 6A). The coarse limestone with insoluble residue at grain boundaries produces a texture reminiscent of chicken-wire evaporite (Figure 6B,C).

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**FIGURE 8** Geochemical data from Middlebrun Bay Member carbonates. Unfilled bars represent whole-rock samples; filled bars are single-phase drilled samples (see text for details). (A) Potassium content (ppm), showing elevated [K] in samples from Channel Island and an overall pattern in which [K] is higher in whole-rock samples compared to single-phase subsamples of the same rock (brackets). (B) Barium content (ppm), with overall high [Ba] across all three localities and showing an overall pattern in which [Ba] is comparable or higher in single-phase samples than in whole-rock samples. (C) Vanadium content (ppm), showing elevated [V] at all localities with an overall pattern in which [V] is comparable or higher in single-phase samples than in whole-rock samples. The highest [V] occurs in stromatolitic samples. (D) Carbonate-associated sulphate (CAS), in ppm, for three whole-rock samples. The sample from Channel Island and one of the Copper Island samples have elevated CAS relative to Proterozoic marine carbonates (Gellatly & Lyons, 2005; Kah et al., 2004)

**FIGURE 9** Relationship between [Mn] and [Sr], from single-phase, drilled sub-samples of Middlebrun Bay Member carbonates, showing elevated [Sr] in Channel Island carbonates.

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occurred after the overlying Fire Hill Member was deposited, as evidenced by collapse of the basal Fire Hill Member into the top of the Middlebrun Bay Member (Figure 6A).

4.3 | Trace element patterns

Elemental patterns in carbonates reflect the chemistry of the waters in which they precipitated, modified by diagenetic and metamorphic processes. Thus, examination of trace element patterns can elucidate components of both depositional and post-depositional processes. Carbonate geochemistry is summarised in Figures 8 and 9 and Table 1. A complete set of geochemical analyses is included in Table S1.

Stromatolite-bearing carbonates from Channel Island and Kama Bay localities are dolomitic, with Mg/Ca mass ratios between 0.27 and 0.72 for Channel Island samples and 0.87 for the Kama Bay sample. Copper Island carbonates are calcitic, with low Mg/Ca ratios (Table 1). Trace element patterns can be divided into three categories (Table 1; Figure 8): (a) elements with higher concentration in whole-rock samples than in drilled samples (Figure 8A)—Na, K, Fe, Rb, Zn, Mo, Pb and U; (b) elements whose concentrations in drilled samples are similar to or higher than in whole-rock samples (Figure 8B,C)—Mn, V, Sr and Ba; (c) elements with a different pattern in stromatolitic carbonate from Channel Island compared to Copper Island carbonate—Cu and Cr. Elements in the first category may be leached from insoluble phases, such as clays, or may be more abundant in non-targeted carbonate phases, such as late-stage cements. For example, Na concentrations are below detection limits for all drilled samples, and K concentrations range from below detection limits to 2,778 ppm, with drilled samples lower than whole-rock samples. In contrast, elements in the second category concentrations are not enriched in whole-rock samples, suggesting that their concentrations are not driven by leaching of non-carbonate phases; further, they may be enriched in the carbonate phases targeted by microdrilling, such as microsparitic carbonate (Channel Island) and spar interiors (Copper Island). The final category is more difficult to interpret but may represent elemental enrichment in stromatolitic dolomites compared to Copper Island calcite with a distinct diagenetic history.

The trace elements Mn, Sr and Fe are typically used as indicators of diagenesis (Banner & Hanson, 1990) in Proterozoic carbonates. Of these, only Mn and Sr belong to the first category of trace element pattern above. Iron concentrations appear to be substantially affected by contributions from non-carbonate phases or non-targeted carbonate phases. In drilled samples, Mn and Sr lack the negative correlation (Figure 9) expected to occur during meteoric diagenesis and dolomitization (Banner & Hanson, 1990) However, several individual samples, mostly whole-rock samples, have high Mn and low Sr (Table 1) as predicted for a diagenetic signal, which may indicate a diagenetic fingerprint in late-stage phases not targeted for drilling.

Carbonate-associated sulphate concentrations were determined for three samples—two from Copper Island and one from Channel Island (Table 1, Figure 8D). The CAS concentrations ranged between 75 and 661 ppm.

5 | DISCUSSION

5.1 | Deposition and diagenesis of Middlebrun Bay stromatolites

Previous stratigraphic and sedimentological analyses suggest that the Middlebrun Bay Member was deposited in a shallow lacustrine setting, during a time of increased aridity, low lake levels, and reduced clastic influx to the basin (Cheadle, 1986a, 1986b; Rogala et al., 2005, 2007). Mesoscale and microscale observations of the stromatolites on Channel Island and at Kama Bay are consistent with this interpretation and additionally suggest in situ carbonate precipitation and rapid lithification of microbialite structures, stabilising steep laminae during stromatolite growth. Low synoptic relief of stromatolites is also consistent with shallow water microbial growth.

The diagenetic history of the Middlebrun Bay Member is complex but bears similarity to other Proterozoic chert-dolomite successions. The primary phase produced within stromatolites was probably calcite or aragonite, rather than dolomite. Although syndepositional or primary dolomite can occur, particularly in modern hypersaline lakes, such as the Coorong Lakes of South Australia, where it is mediated by sulphate reducing bacteria (Wright & Wacey, 2004), the relationship of this microbial dolomite to Proterozoic rock-forming dolomite has not been firmly established. In addition, relatively high Sr content in stromatolitic samples, particularly from Channel Island (Table 1), suggests a calcite or aragonite precursor (van Smeerdijk Hood & Wallace, 2018).

The fabric-retentive nature of the dolomite suggests dolomitization occurred relatively early in diagenesis, which commonly preserves robust, interpretable trace element signatures, particularly for samples that have been screened and selected via microdrilling (cf. Kaufman & Knoll, 1995). In single-phase, drilled samples from Channel Island, Mn/Sr and Fe/Sr values are uniformly low, with Mn/Sr <1.2 and Fe/Sr <1. Relatively high Sr values, coupled with overall low Mn and Fe concentrations (Table 1) suggests that typical meteoric diagenesis, which would enrich Mn and Fe while depleting Sr (Banner & Hanson, 1990), is not a dominant signal in these carbonates. In contrast, the Kama Bay sample has high Mn and Fe and lower Sr concentration. A sill intrudes the top of the unit at the Kama Bay locality (Osterhout et al., 2019), making it likely that this location experienced some
thermal alteration, a conclusion supported by evaluation of organic matter maturity trends that indicate alteration close to the intrusions (Osterhout et al., 2019). For Channel Island samples, trace element chemistry is likely to have been only modestly affected by more distal thermal events, as intrusions were not observed in the vicinity of the Middlebrun Bay Member on Channel Island. Early dolomitization may even have acted to stabilise trace element chemistry, as has been observed in other Proterozoic dolomites (Bartley et al., 2001; Halverson et al., 2010). Therefore, while it is not argued that the Middlebrun Bay stromatolites are unaltered, the petrographic and geochemical data support a conclusion that a relict depositional signal has been preserved in these carbonates.

Silica represents a third mineralogical phase in the Middlebrun Bay microbialites, post-dating dolomitization. Unlike syndepositional to early diagenetic cherts that are common in Proterozoic fossil-bearing marine successions (Knoll et al., 2013), the silica in the Middlebrun Bay member is fabric-obliterative. Silica cross cuts (Figure 5D) or follows laminae, comprising coarser-grained layers within the finer-grained dolomicrospar (Figure 5B). Silica is frequently discontinuous (Figure 5F) and slightly nodular (Figure 5E). At the petrographic scale, some silica exhibits spherulitic growth within the dolomitic matrix, a relationship associated with later silica growth, rather than syndepositional silicification (Dunham, 2018).

This paragenetic sequence is broadly similar to other well-preserved Proterozoic dolomites but differs from many of the well-known fossiliferous chert-bearing Proterozoic units, in that the silica appears to be later and does not preserve either the primary textures or microfossils (Bartley et al., 2000; Knoll et al., 2013) that can be preserved during penecontemporaneous silification.

5.2 | Hypersalinity and evaporite deposition

Previous work in the clastic portions of the Sibley Group suggests that this succession is characterised by intervals of hypersalinity (Cheadle, 1986a; Rogala et al., 2007) that resulted in deposition of evaporite minerals, both as sulphate nodules within fine-grained clastic units, and as moulds of gypsum and halite crystals (Rogala et al., 2007), particularly in the Fire Hill Member of the Rossport Formation, where sulphate nodules are abundant. The Mesoproterozoic was an interval where marine sulphate concentrations were likely low (Canfield, 1998) relative to modern sea water but higher compared to previous intervals, resulting in CAS <200 ppm for carbonates deposited in marine settings (Gellatly & Lyons, 2005; Kah et al., 2004) and development of widespread bedded evaporites, such as those observed in the peritidal Angmaat Formation of arctic Canada (Kah et al., 2004). Against this limited understanding of Mesoproterozoic marine sulphate content, sulphate concentrations of Mesoproterozoic non-marine settings are unconstrained. Hence CAS concentrations may be useful in reconstructing the composition of depositional and early diagenetic fluids responsible for carbonate production (Gill et al., 2008; Marenco et al., 2008), and might provide some constraint on sulphate behaviour in ancient lacustrine systems, such as the Rossport Formation. The CAS content in the Middlebrun Bay Member at Channel Island is elevated (661 ppm) compared to Proterozoic marine carbonates (Figure 8), and similar to inferred calcitized evaporites from the Mesoproterozoic Atar Group (Manning-Berg, 2014). Although CAS content has not been evaluated from other Proterozoic non-marine carbonates, the relatively high concentration in these carbonates suggests high sulphate concentration in the depositional environment of the Middlebrun Bay carbonates and is consistent with deposition under hypersaline conditions with elevated sulphate content.

Trace element chemistry is also consistent with, but does not require, an interpretation of hypersalinity. Several laboratory studies affirm that carbonates incorporate many trace elements in proportion to their concentration in the fluids from which they precipitate (Allen et al., 2016; Bertlich et al., 2018; Ishikawa & Ichikuni, 1984), although other factors may also influence trace element incorporation (Allen et al., 2016). Thus, elevated trace element concentrations in carbonate, compared to average (marine or freshwater) values, may indicate hypersaline depositional conditions. Although trace element chemistry has not been shown to be a robust tool for detailed water mass reconstruction, some trace element patterns have shown promise for constraining fluid compositions (Bertlich et al., 2018; Veizer et al., 1978). Middlebrun Bay carbonates have markedly elevated Ba and V concentrations compared to normal marine carbonates (Figure 8), but unremarkable Na, Sr, Zn, Rb, Mo, Pb and U content (Table S1). In addition, Ba and V concentrations do not appear to be strongly driven by leaching of non-carbonate phases (see discussion above). Further, the extremely high [Ba] in one single-phase sample from Copper Island may suggest that Ba was introduced during diagenesis rather than deposition of carbonates. It is reasonable to posit that potassium content was high in lake waters as well, but the high mobility of potassium, particularly via leaching of K from clays during sample preparation (Veizer et al., 1978) makes that conclusion tentative. Higher concentrations of K in whole-rock compared to single-phase (drilled) samples (Table 1) further support the notion that K leaching during preparation may be a contributing factor. Notably, Na concentrations are not elevated in this unit (Table 1), suggesting low concentrations of Na in depositional fluids or post-depositional loss of sodium. Overall, it is reasonable to
posit that Middlebrun Bay stromatolites preserve elevated V, Ba and sulphate concentrations inherited from hypersaline depositional conditions.

5.3 Deposition and diagenesis of the Copper Island carbonate

Several elements of the field, petrographic and geochemical features of the Middlebrun Bay Member on Copper Island suggest that this locality underwent a diagenetic pathway distinct from that of the Middlebrun Bay stromatolites at Channel Island, despite their relative proximity to one another (Figure 1). The Copper Island carbonate is a massively recrystallized limestone, rather than dolostone, and all primary fabric has been obliterated. Evidence of post-depositional volume change is evidenced by the presence of collapsed blocks from the overlying unit. At the outcrop scale, the uniform mineralogy, recrystallized texture, and lack of internal lamination or fabric suggest that the rock deposited at this locality was markedly different from the stromatolitic carbonate deposited at Channel Island, Kama Bay and elsewhere in the basin.

Given that dolomite replaced Middlebrun Bay carbonates elsewhere in the basin, the primary rock at this locality was probably not composed of calcite at the time of the dolomitization event. In addition, Copper Island carbonate samples have lower K, Sr, V, Ba and CAS concentrations compared to stromatolitic carbonate from Channel Island, also consistent with calcite precipitation from a distinct fluid. Given the distinct field, petrologic and geochemical character of this carbonate, it is suggested that the original mineralogy was an evaporite mineral, possibly gypsum, given the elevated CAS concentrations in Middlebrun Bay stromatolites and inferred hypersaline character of the environment. The evaporites would have been lateral equivalents to the stromatolites, in a relationship similar to some modern hypersaline lakes, in which stromatolites grow where conditions are favourable for microbial growth and carbonate precipitation, while evaporite minerals form in other portions of the lake (Gomez et al., 2014; Mlewski et al., 2018). The original evaporite mineralogy would have persisted through deposition of subsequent layers of clastic material in this alluvial-playa lake system (Cheadle, 1986a), even as laterally adjacent stromatolite facies were dolomitized and silicified. Post-burial changes in porewater chemistry to carbonate-saturated, but sulphate-undersaturated, composition resulted in dissolution of the evaporite phase and replacement by calcite, producing coarse, zoned crystals, with insoluble material pushed to crystal boundaries, and resulting in local collapse of overlying, lithified strata into the Middlebrun Bay Member, where volume loss was significant.

Few calcitized evaporites have been identified in the Proterozoic record, and none from lacustrine settings. It is believed that only the unusual carbonates of units I-6 and I-7 of the Atar Group (Oued Tarioufet and Tawaz formations) have been described as calcitized evaporites (Manning-Berg & Kah, 2013). Manning-Berg (2014) develops a generalisable set of criteria for recognising an ancient calcitized evaporite: (a) Massive to nodular fabric; (b) karst and collapse features; (c) pytgmatic folding within beds; (d) coarse spar consisting of anhedral, zoned crystals; (e) displacement of insoluble residues to crystal edges; (f) abundant stylolites; (g) elevated concentrations of salinity-associated trace elements, including CAS. The Middlebrun Bay exposure on Copper Island displays most of these features (it lacks pytgmatic folding, as it does not preserve internal structure) and is thus best interpreted as a calcitized evaporite. These criteria are largely independent of depositional environment and would not be expected to differ dramatically between a marine and lacustrine calcitized evaporite, although details of trace element chemistry would be expected to differ, according to the peculiar characteristics of the depositional and diageneric environments.

5.4 Model for basin evolution

The features of the massive carbonate facies of the Middlebrun Bay Member on Copper Island suggest a model for trace element and CAS evolution in these rocks during deposition and diagenesis. In this model, trace elements, including sulphate, were concentrated by evaporation in a restricted water body during a period of regional aridity (Cheadle, 1986a; Rogala et al., 2005). Precipitation of stromatolitic carbonate under hypersaline conditions resulted in trace element enrichment, which was retained during early diagenesis. Coeval deposition of sulphate evaporites would also have resulted in high trace element concentrations; however, the dissolution and recrystallization process that resulted in calcification of the evaporite also resulted in a loss of trace elements. The final calcitized evaporite retains lower, and variable, trace element and CAS concentrations compared to stromatolites deposited in the same basin.

6 CONCLUSION

The Mesoproterozoic Sibley Group was deposited in an alluvial-playa lake environment across the southern area of north-western Ontario (Cheadle, 1986a). Although there is little disagreement that the Rosspport Formation represents a restricted, hypersaline environment, the carbonates of the Middlebrun Bay Member afford an unusual window onto the particular environmental conditions that resulted in carbonate precipitation in this continental basin. The Middlebrun Bay Member, a ca 1 m thick carbonate unit, affords a window into chemical sedimentary deposition during an arid interval of lake evolution (Rogala et al., 2007). Low-relief stratiform and columnar stromatolites
dominated this shallow, hypersaline environment, preserving evidence of hypersalinity in trace element content of early diagenetic dolomite. Evaporites, perhaps gypsum, were deposited in laterally adjacent areas. Subsequent diagenesis caused calcite to replace original evaporite minerals, producing a calcitized evaporite, which preserves evidence of its origins, in the form of elevated trace element concentration and diagnostic secondary carbonate textures. Calcitized evaporite in the Middle brun Bay Member crops out on Copper Island along the north shore of Lake Superior. The overall depositional environment during Middle brun Bay Member deposition is interpreted as similar to modern playa lakes that contain coeval stromatolites and evaporites, such as Laguna Negra in the high Andes of Argentina (Gomez et al., 2014). Evaporite deposition in a Mesoproterozoic non-marine environment is consistent with the overall pattern of increasing oxidative weathering through the Proterozoic and the increased abundance of marine sulphate evaporites beginning in the mid-Mesoproterozoic (Kah et al., 2001; Manning-Berg, 2015). The presence of a calcitized evaporite in the Middle brun Bay member provides an important data point for understanding the evolution of the global sulphur cycle.

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CONFLICT OF INTEREST
The authors have no conflict of interest.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

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