

Preservation of carbon isotopes in kerogen from thermally altered Mesoproterozoic lacustrine microbialites

Jeffrey T. Osterhout, Andrew D. Czaja, Julie K. Bartley, and Philip W. Fralick

Abstract: Stable carbon isotope geochemistry is a well-established and reliable tool for studying metabolisms of microbial communities in the Precambrian record; however, the isotopic effects of high-temperature alteration from igneous intrusions (i.e., contact metamorphism) have not been thoroughly explored. The Mesoproterozoic (~1.4 Ga) Middlebrun Bay Member of the Rosspport Formation, Sibley Group, in Ontario, Canada, is composed of carbonaceous stromatolites and microbial laminites preserved in an evaporitic, lacustrine chert–carbonate deposit and is cross-cut by an intrusive mafic sill at the studied locality. Sedimentary organic matter (kerogen) was investigated along two vertical stratigraphic transects to determine the spatial variability of its geochemical preservation. Thermal alteration of the preserved kerogen (as measured by Raman spectroscopy) increased toward the mafic sill, but the alteration was greater for kerogen preserved in carbonate mineralogies compared to that preserved in quartz (chert). Bulk $\delta^{13}\text{C}_{\text{org}}$ values fluctuate throughout each vertical section, with a total average of $-28.2\% \pm 0.8\%$; however, values are unexpectedly lower for samples near the mafic sill, approaching -30% , inconsistent with previously reported patterns. These measurements indicate that thermal alteration of sedimentary rocks does not universally result in ^{13}C enrichment and increased $\delta^{13}\text{C}_{\text{org}}$ values and suggests that ancient kerogen may be preferentially shielded from postdepositional heating effects due to micrometre-scale differences in mineralogy.

Key words: kerogen, carbon isotope geochemistry, thermal alteration, Raman spectroscopy, Precambrian, Rosspport Formation, Middlebrun Bay Member.

Résumé : Si la géochimie des isotopes stables du carbone est un outil bien établi et fiable pour l'étude des métabolismes de communautés microbiennes dans les roches précambriennes, les effets isotopiques de l'altération à haute température associée à des intrusions ignées (c.-à-d. métamorphisme de contact) n'ont pas été explorés en profondeur. Le membre mésoprotérozoïque (~1,4 Ga) de Middlebrun Bay de la Formation de Rosspport du Groupe de Sibley, en Ontario (Canada), est composé de stromatolithes carbonés et de laminites microbiennes préservés dans un dépôt évaporitique de chert et carbonates lacustres et est recoupé par un filon-couche mafique intrusif dans la localité à l'étude. La matière organique sédimentaire (kérogène) a été examinée le long de deux coupes stratigraphiques verticales afin de déterminer la variabilité spatiale de sa préservation géochimique. L'altération thermique du kérogène préservé (mesurée par spectroscopie Raman) augmente vers le filon-couche mafique, mais l'altération est plus grande pour le kérogène préservé dans les assemblages minéralogiques à carbonates que dans ceux à quartz (chert). Les valeurs de $\delta^{13}\text{C}_{\text{org}}$ globales fluctuent le long des deux coupes verticales, leur moyenne totale étant de $-28,2 \pm 0,8 \%$; cependant, contrairement aux attentes, ces valeurs sont plus faibles près du filon-couche mafique, s'approchant de -30% , ce qui ne concorde pas avec les motifs rapportés précédemment. Ces mesures indiquent que l'altération thermique des roches sédimentaires ne se traduit pas universellement par un enrichissement en ^{13}C et une augmentation du $\delta^{13}\text{C}_{\text{org}}$ et donnent à penser que le kérogène ancien pourrait être protégé préférentiellement des effets d'augmentations de la température après le dépôt en raison de différences minéralogiques à l'échelle du micron. [Traduit par la Rédaction]

Mots-clés : kérogène, géochimie des isotopes du carbone, altération thermique, spectroscopie Raman, Précambrien, Formation de Rosspport, membre de Middlebrun Bay.

Introduction

Reconstructing the composition of microbial ecosystems is of great importance to paleobiologists exploring the early evolution of Earth's biosphere. Ancient metabolic and biogeochemical processes are routinely investigated in sedimentary rocks using a combination of carbon isotope and organic geochemistry (e.g., Schidlowski et al. 1983; Eigenbrode and Freeman 2006; Marshall et al. 2009; Thomazo et al. 2009). However, the effects of thermal

alteration on the molecular structure and carbon isotope composition of insoluble organic matter (i.e., kerogen) remain poorly understood, particularly for Precambrian deposits (Des Marais 2001). Kerogen and organic carbon isotope compositions can serve as useful indicators of biogenic organic matter in unmetamorphosed sedimentary rocks, including that associated with fossilized microbial mats (e.g., stromatolites) and microorganisms (microfossils), and are regularly included in studies seeking to reconstruct ancient microbial ecosystems (Des Marais 2001;

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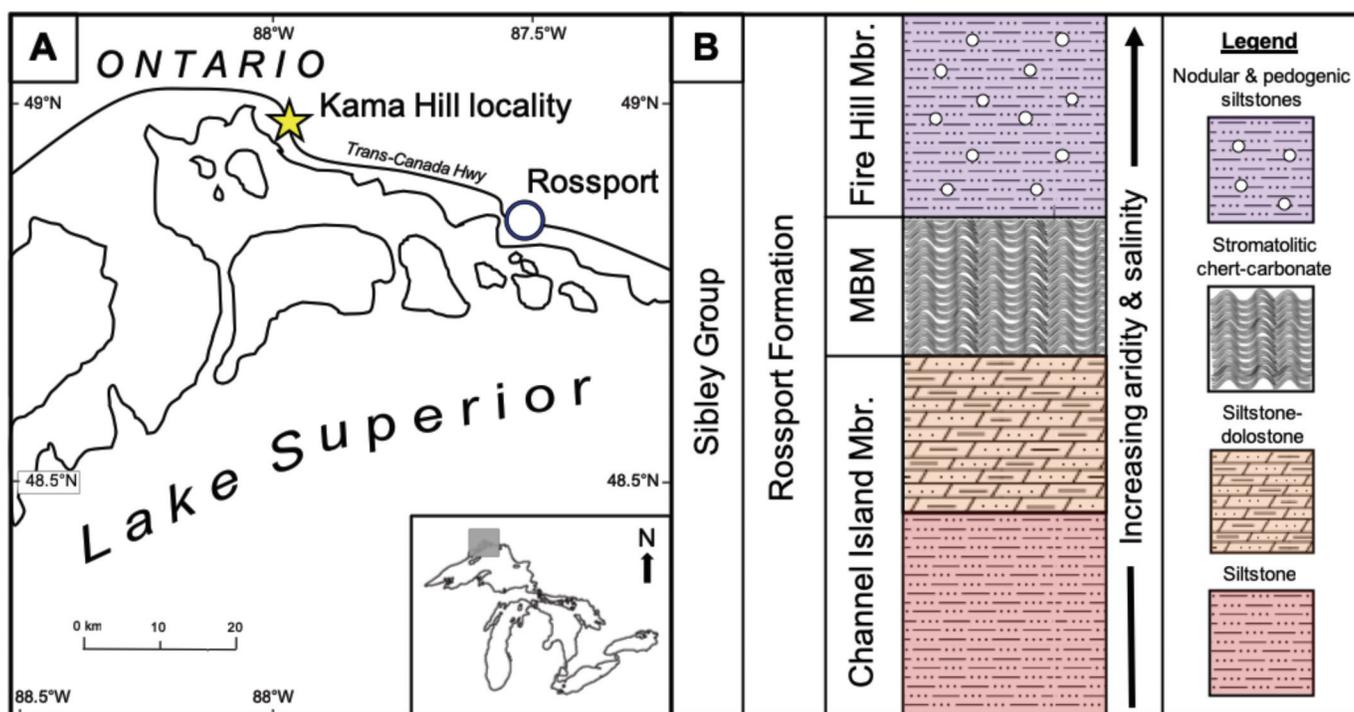
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Fig. 1. (A) Map of study area near the town of Rosspport, Ontario, Canada, on the north shore of Lake Superior (see inset) showing the location of the Kama Hill outcrop (yellow star), where samples of chert–carbonate from the Middlebrun Bay Member were collected. (B) Simplified stratigraphic section of the Rosspport Formation within the Sibley Group showing the relative position of the Middlebrun Bay Member (MBM) and the interpreted paleoenvironmental conditions. Abbreviations: Hwy., Highway; Mbr., Member. Adapted from Rogala et al. (2007). [Color online.]



Schidlowski 2001; Oehler and Cady 2014). However, the great antiquity of many Precambrian units has led them to be too physically and (or) geochemically altered to preserve any morphological biosignatures. Therefore, of particular importance for establishing the biogenicity and paleoecology of Precambrian systems is the characterization of well-preserved kerogen having primary, unaltered stable carbon isotope compositions and the measurement of related geochemical changes across a thermal metamorphic gradient.

Thermal alteration of sedimentary rocks can affect both the molecular structures and carbon isotope compositions of maturing kerogen. As sediments undergo diagenesis and lithification, organic biomolecules (i.e., lipids, carbohydrates, proteins) experience transformation processes resulting in polymerization and formation of thermally immature, macromolecular kerogen (Durand 1980). Subsequent thermal alteration of kerogen in sedimentary deposits can change its molecular structure, typically through the removal of functional groups associated with aromatization and condensation reactions (Vandenbroucke and Largeau 2007), eventually leading to graphitization, such as occurs in high-grade metasedimentary rocks (e.g., Mojzsis et al. 1996; Rosing 1999; Ohtomo et al. 2014). As a result, average carbon isotope compositions of sedimentary kerogen that would otherwise reflect the original isotopic fractionation due to biological carbon fixation can be modified by thermal alteration (Des Marais 2001; Schidlowski 2001). Carbon isotope compositions of organic matter ($\delta^{13}\text{C}_{\text{org}}$) in Precambrian rocks have average $\delta^{13}\text{C}_{\text{org}}$ values of roughly -25‰ and range from approximately -60‰ to -10‰ (e.g., Schidlowski 2001; Thomazo et al. 2009). The range of Precambrian $\delta^{13}\text{C}_{\text{org}}$ values includes units with relatively high (i.e., less negative) values (e.g., McKirdy and Powell 1974; Schidlowski et al. 1979, 1983; Hayes et al. 1983). These higher values are generally attributed to thermally altered kerogen or graphite produced through burial and regional metamorphism. However, in most cases, it is

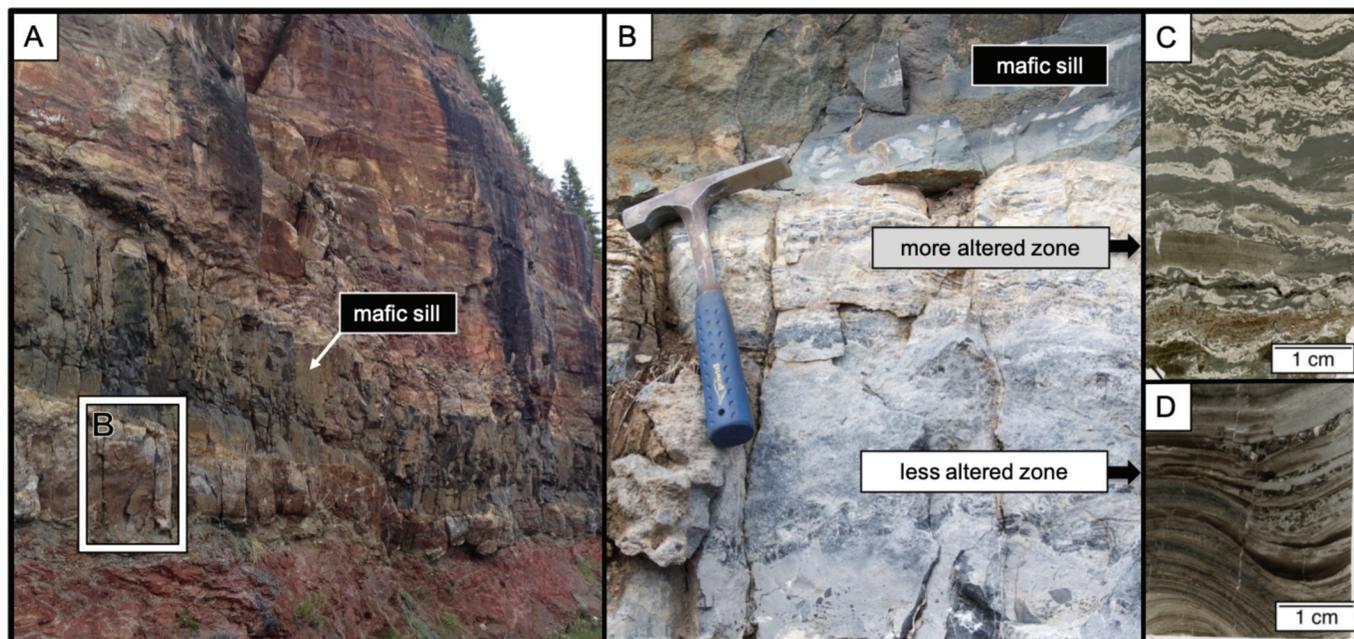
impossible to compare the $\delta^{13}\text{C}_{\text{org}}$ values of thermally mature organic matter to those of coexisting, well-preserved kerogen from the same sedimentary deposit.

To investigate changes in the molecular structure and carbon isotope composition of Precambrian kerogen across a natural thermal gradient, this study examined a Mesoproterozoic (~ 1.4 Ga) organic-rich, lacustrine chert–carbonate deposit in Ontario, Canada, that was intruded by a diabase sill (~ 1.1 Ga) in contact with the unit. Comparisons between thermal alteration and carbon isotopic compositions of sedimentary organic matter have not been examined in detail for nonmarine rocks of Precambrian age on the spatial scales of this study. The close proximity of an ancient microbialite unit (containing stromatolites and microbial laminites) to a mafic sill provides a unique opportunity to investigate the thermal alteration of biogenic kerogen and organic carbon isotope signatures across a vertical temperature gradient via combined in situ Raman spectroscopic analyses and bulk (whole-rock) carbon isotope analyses.

Geologic setting

The studied material is from the Mesoproterozoic (~ 1.4 Ga) Middlebrun Bay Member of the Rosspport Formation, part of the Sibley Group in western Ontario, Canada (Fig. 1). Franklin et al. (1980) and Cheadle (1986) described the sedimentology and lithostratigraphy of the Sibley Group, and Rogala et al. (2007) further revised the stratigraphic nomenclature to its current form. The Sibley Group is composed of fluvial and lacustrine siliciclastic and chemical sedimentary rocks deposited within the Sibley Basin, which formed as the result of an evolving rift or intracratonic extension during the Mesoproterozoic (Franklin et al. 1980; Cheadle 1986; Fralick et al. 2000) and is now exposed between the northwest shore of Lake Superior and Lake Nipigon.

Fig. 2. Roadcut outcrop at the (A) Kama Hill locality with the (B) Middlebrun Bay Member exposed near Rosspport, Ontario, and representative thin sections showing (C) microbial laminite and (D) stromatolite textures. The unit undulates slightly and is cross-cut by an intrusive mafic sill. **Figure 2A** faces southeast and the gray sill above the Middlebrun Bay Member is approximately 1.4 m in thickness. Note rock hammer for scale in panel B is ~28 cm long. [Colour online.]



The Pass Lake Formation, the lowermost of the Sibley Group, contains bedrock-confined fluvial conglomerates and an overlying strandline to shallow lacustrine deposit, with siliciclastics originating from the Trans-Hudson Orogen to the northwest (Rogala et al. 2007). The overlying Rosspport Formation is divided into three members (Fig. 1B), together comprising a shallowing-upward sequence of lacustrine sediments exposed to increasingly arid conditions and elevated salinity (Rogala et al. 2007). The basal unit of the Rosspport Formation, the Channel Island Member, records a saline, alkaline (pH ~9–10) (Cheadle 1986) playa lake system (Rogala et al. 2007). The middle unit, the Middlebrun Bay Member (MBM) (this study), was deposited during a time of low siliciclastic input or rapidly in a shore-proximal position (Cheadle 1986; Rogala et al. 2007), and the uppermost Fire Hill Member exhibits typical subaerial weathering profiles in saline, gypsiferous mudflats with intervening ponds (Rogala et al. 2007). Thus, the MBM separates largely subaqueous units from overlying subaerial sediments deposited during a period of locally increasing desiccation and salinity. These stratigraphic relationships imply an evaporitic, strandline playa-sabkha setting for the stromatolites and microbial laminites of the MBM that were deposited diachronously across the basin as the lacustrine system shrank (Rogala et al. 2007).

Depositional ages of the Sibley Group are moderately well constrained within the Mesoproterozoic. The lower age of the Rosspport Formation is constrained by a ≤ 1.77 Ga U–Pb detrital zircon age in the underlying Pass Lake Formation (Rogala et al. 2007), and a Rb–Sr isochron age of 1339 ± 33 Ma from dolomitic mudstones in the Rosspport and Kama Hill Formations is consistent with detrital zircon constraints (Franklin 1978; Franklin et al. 1980). These ages are also compatible with paleomagnetic correlations between the Sibley Group and the ~1.45–1.40 Ga Missoula Group of the Belt Supergroup that indicate that the paleopole positions are correlated with the Apparent Polar Wander Path of North America (Robertson 1973; Elston et al. 1993, 2002). These combined lines of evidence place the deposition of the Rosspport Formation within the middle Mesoproterozoic.

Sampling locality

Microbialite samples were collected from the Kama Hill outcrop ($48^{\circ}59.86'N$, $88^{\circ}1.37'W$), which is accessible along a ~100 m road cut 50 km west of the town of Rosspport in Ontario, Canada (Fig. 1A). Cheadle (1986) first recognized stromatolites and microbial laminites from the MBM, describing the laminites as cryptalgal *Stratifera* sp. and the columnar stromatolites as *Conophyton metula*. Microbialite textures are more silicified and stromatolitic at the base of the unit and transition into more calcareous microbial laminae upsection. The upper and lower portions of this unit appear to be separated by a brecciated section that likely formed as a result of dissolution and collapse of overlying rocks. Thus, for the purposes of this study, the MBM is separated into three distinct facies: (1) the lowermost chert-rich stromatolites, (2) the middle brecciated unit, and (3) the uppermost calcareous (and dolomitic) microbial laminites.

The Kama Hill outcrop also exposes a mafic sill ~2 m thick that intruded along the top of the MBM (Figs. 2A and 2B). A zone of alteration with a thermal gradient radiating outward from the intrusion is evident in the overall appearance of the MBM (Fig. 2B), representing a region of contact metamorphism surrounding the igneous intrusion that likely contributed to localized carbonate dissolution and brecciation. This sill and other intrusions into the Sibley Group are likely related to dynamic activity associated with the Midcontinental Rift ca. 1.1 Ga (Rogala et al. 2007).

Materials and methods

Samples of chert-carbonate were collected from two vertical stratigraphic sections (~30–35 cm) of the MBM at the Kama Hill locality separated by ~50 m along strike. These sections were divided into subsamples by stratigraphic position relative to the overlying mafic sill, creating two vertical transects. Samples of chert-carbonate were prepared for petrographic, isotopic, and Raman spectroscopic analyses. Thin sections were made from rocks every 5–7 cm along each transect to study the effect of thermal alteration via petrography and Raman spectroscopy.

Samples were also sectioned every 2 cm along each transect for bulk carbon isotope analyses of extracted kerogen. Following the acquisition of Raman spectra, isotope ratio mass spectrometry was used to measure $\delta^{13}\text{C}_{\text{org}}$ values along each vertical transect to compare the degree of thermal maturity with corresponding carbon isotope compositions of kerogen.

Optical microscopy

Samples of chert-carbonate from each vertical transect were cleaned and prepared as $\sim 150\ \mu\text{m}$ thick sections and moderately polished to a finish of $30\ \mu\text{m}$. Thin sections were viewed using an Olympus BX53 microscope and were typically covered with a thin layer of fluorescence-free immersion oil (Olympus Type-F) to improve image clarity. Photomicrographs were captured under transmitted white light using a 20 \times objective and an Olympus DP73 digital camera.

Raman spectroscopy

Raman spectra were obtained from the same thin sections described above by use of a Horiba T64000 Raman spectrometer in the Department of Geology at the University of Cincinnati. The system was operated in single mode and coupled with an Olympus BX41 microscope using a 50 \times long working distance objective (NA = 0.50) and a Coherent Innova 90C FreD Ar⁺ laser. A laser excitation of 457.9 nm was used, and point spectra were collected for 60 s and processed using the software LabSpec (v.5; Horiba, Inc.). Spectra were collected from points below the surface to avoid possible alteration to the molecular structure of kerogen that can be caused by polishing (Beyssac et al. 2003; Nasdala et al. 2004; Kouketsu et al. 2014). Spectra were first corrected for the wavelength-dependent system response function using a calibrated light source; spectra were then baseline subtracted and normalized to the G-band ($\sim 1600\ \text{cm}^{-1}$) of each kerogen spectrum.

To compare the degree of thermal alteration experienced by kerogenous materials in this study relative to previously described Precambrian deposits, multiple spectra of kerogen embedded in both carbonate and chert (i.e., quartz) were measured along each vertical section. The Raman spectra obtained for all samples were characterized quantitatively according to their Raman index of preservation (RIP) using the equation outlined by Schopf et al. (2005):

$$(1) \quad \text{RIP} = \frac{\alpha}{\gamma} = \frac{\int_{1100}^{1300} I(v)dv}{\int_{1300}^{1370} I(v)dv}$$

wherein the RIP is calculated by determining the ratio of α (the integrated area under the spectral curve between 1100 and $1300\ \text{cm}^{-1}$) to γ (the integrated area under the spectral curve between 1300 and $1370\ \text{cm}^{-1}$). Schopf et al. (2005) defined the RIP value as the ratio of these two variables (α/γ) normalized to a set of thermally altered microfossils, with RIP values ranging from 1 (most altered) to 9 (least altered). To fit Raman spectra of kerogen from the MBM on this scale, a regression was applied to the RIP and integrals for the original data, generating the equation (Czaja et al. 2016)

$$(2) \quad \text{RIP} = \left(\frac{\alpha}{\gamma}\right) \times 7.6866$$

The determination of RIP values allows for direct comparison with previously reported Raman spectra of biogenic kerogen in

other Precambrian sedimentary and metasedimentary deposits, and resulting values can be plotted according to their relative grade of thermal maturity.

Raman geothermometry calculations were also performed to provide an estimate of peak metamorphic temperatures. All Raman spectra measured for each lithology at each level throughout the individual sections were averaged (Tables S1 and S2, Supplementary Material¹). Backgrounds were subtracted from these averaged spectra using a linear baseline between 950 and $1800\ \text{cm}^{-1}$. Backgrounds were relatively minor and using a polynomial fit was unnecessary (did not affect the results). These processed spectra were then deconvoluted by use of the method described by Kouketsu et al. (2014), i.e., by use of the software package PeakFit (v.4.12; SeaSolve Software Inc., Massachusetts, USA) and using their "fitting F". From these deconvoluted spectra, peak metamorphic temperatures were calculated using the equation

$$(3) \quad T\ (^{\circ}\text{C}) = -2.15(\text{FWHM-D1}) + 478$$

where FWHM-D1 represents the full width at half maximum for the D1 Raman band of carbonaceous matter (i.e., kerogen) centered around $1350\ \text{cm}^{-1}$. This calculation is reliable for temperatures measurements below $400\ ^{\circ}\text{C}$ with an error of $\pm 30\ ^{\circ}\text{C}$ (Kouketsu et al. 2014).

Organic carbon isotope ($\delta^{13}\text{C}_{\text{org}}$) analyses

Samples of unweathered rock interiors were cut and crushed to millimetre-sized chips and acidified for bulk stable carbon isotope analyses of the extracted organic material, following procedures outlined by Durand (1980) and further adapted from Grey (1999) and Grey and Sugitani (2009). To avoid any modern organic contaminants, the rock chips were washed in ethanol and rinsed with distilled, deionized (DDI) water ($18.2\ \text{M}\Omega$). Approximately 25 g of rock chips was weighed out for each sample and transferred to 50 mL conical-bottomed Falcon tubes. The samples were covered with 5 mL of DDI water and then the tubes were filled with a solution of 36%–38% hydrochloric acid to remove carbonate. Samples were monitored daily, decanted, and refreshed with additional DDI water and hydrochloric acid. This process was repeated at room temperature until the carbonate-acid reaction ceased. To remove silicate materials, the samples were decanted, rinsed with DDI water, and filled with a solution of 48%–51% hydrofluoric acid. Samples were monitored daily, decanted, and refreshed with additional DDI water and hydrofluoric acid. This process was repeated at room temperature until the mineral matrix was fully dissolved. The samples were then decanted, rinsed in DDI water, and dried overnight in an oven at $100\ ^{\circ}\text{C}$.

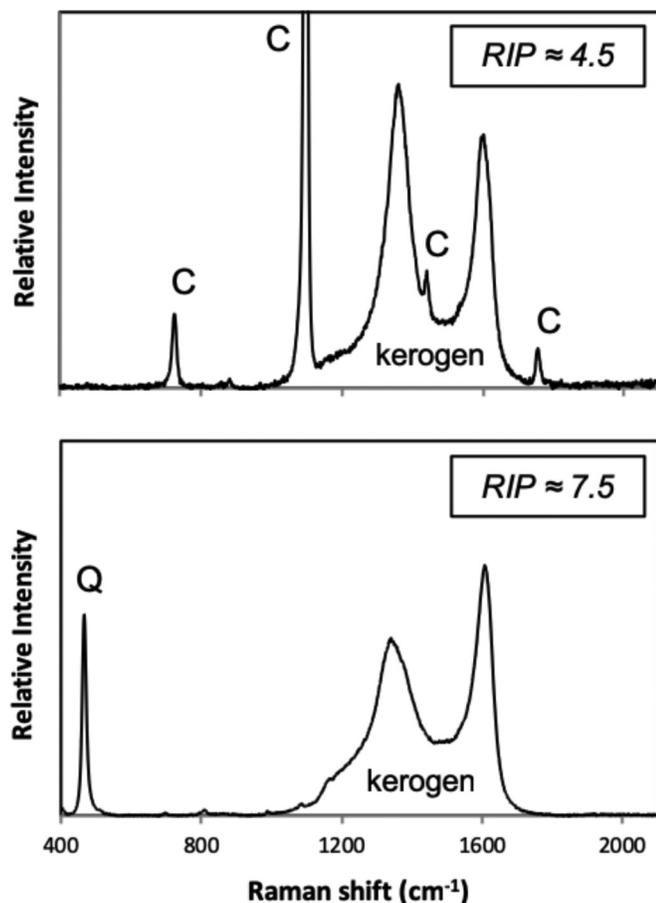
Acid-insoluble kerogen residues were placed in tin capsules and loaded into an autosampler for EA-IRMS analysis. Following combustion, the organic carbon isotope composition of the volatilized CO_2 gas was analyzed using a Costech elemental analyzer coupled with a Thermo Delta V Advantage isotope ratio mass spectrometer in the Department of Geology at the University of Cincinnati. The samples were run under 0% or 78% He dilutions. Results are reported in delta notation ($\delta^{13}\text{C}_{\text{org}}$ in units of per mil (‰)) relative to the internationally recognized Vienna Pee Dee Belemnite (VPDB) reference standard.

Inorganic carbon isotope ($\delta^{13}\text{C}_{\text{carb}}$) analyses

Carbon isotope analyses of inorganic carbon ($\delta^{13}\text{C}_{\text{carb}}$) in carbonates were performed at Applied Petroleum Technology (Oslo, Norway). The samples were combusted in a EuroVector Elemental Analyser EA3028-IRMS at $1700\ ^{\circ}\text{C}$, and the CO_2 is flushed into a Horizon Isotope Ratio mass spectrometer (IRMS) from NU-

¹Supplementary data are available with the article through the journal Web site at <http://nrcresearchpress.com/doi/suppl/10.1139/cjes-2018-0309>.

Fig. 3. Representative Raman spectra of kerogen within carbonate from the uppermost altered zone in contact with the mafic sill (top) and kerogen in quartz from the lower, less altered zone (bottom) of the Middlebrun Bay Member. Note average Raman index of preservation (RIP) values at the top right of each spectrum showing lower values and thus increased thermal alteration of kerogen upsection. C, carbonate; Q, quartz.



Instruments. A standard (NGS NSO-1, topped oil) is analyzed every 10 samples. The $\delta^{13}\text{C}$ value obtained for this standard is -28.61% (VPDB). The variation in the isotopic values for the standard by repeated analysis over a period of three years is $\pm 0.09\%$.

Results

Raman spectra confirmed the presence of macromolecular carbonaceous matter (kerogen) within individual laminae (Fig. 3) as well as field observations that the upper portion of each section contained more thermally altered kerogen and the lower portions were dominated by less altered kerogen (Figs. 3 and 4). Petrographic and Raman analyses of individual laminae show micrometre-scale mineralogical differences between alternating layers of chert (quartz peak $\sim 465\text{ cm}^{-1}$) and carbonate (calcite peak $\sim 1085\text{ cm}^{-1}$, dolomite peak $\sim 1100\text{ cm}^{-1}$) (Figs. S3 and S4, Supplementary Material¹). Raman spectra also revealed differences in the carbonate mineralogy throughout each stratigraphic section, with increasing dolomitic compositions upsection, closer to the mafic sill (Table S1; Fig. S4, Supplementary Material¹).

The RIP values calculated from kerogen spectra show characteristic differences within individual stratigraphic layers depending on the type of mineral matrix hosting the kerogen (Fig. 4). RIP values for all measured kerogen from both sections range from a maximum of 8.3 to a minimum of 3.6 with an average of 6.6 ± 1.1 (1 SD) (Tables S1 and S2, Supplementary Material¹). For Section 1

($n = 69$), RIP values for kerogen preserved in chert range from 7.5 ± 0.2 near the base to 6.4 ± 0.2 near the top ($\Delta\text{RIP} \approx 1.1$), whereas values for kerogen preserved in carbonates range from 7.8 ± 0.3 to 4.9 ± 0.9 ($\Delta\text{RIP} \approx 2.9$), respectively. The data for Section 2 ($n = 70$) show a very similar trend with RIP values for kerogen preserved in chert ranging upsection from 7.1 ± 0.3 to 5.5 ± 0.7 ($\Delta\text{RIP} \approx 1.6$) and values for kerogen preserved in carbonates that range from 7.6 ± 0.4 to 4.4 ± 0.5 ($\Delta\text{RIP} \approx 3.2$) (Fig. 4; Tables S1 and S2, Supplementary Material¹). Each section records an overall decrease in RIP values upward toward the mafic sill (Fig. 4).

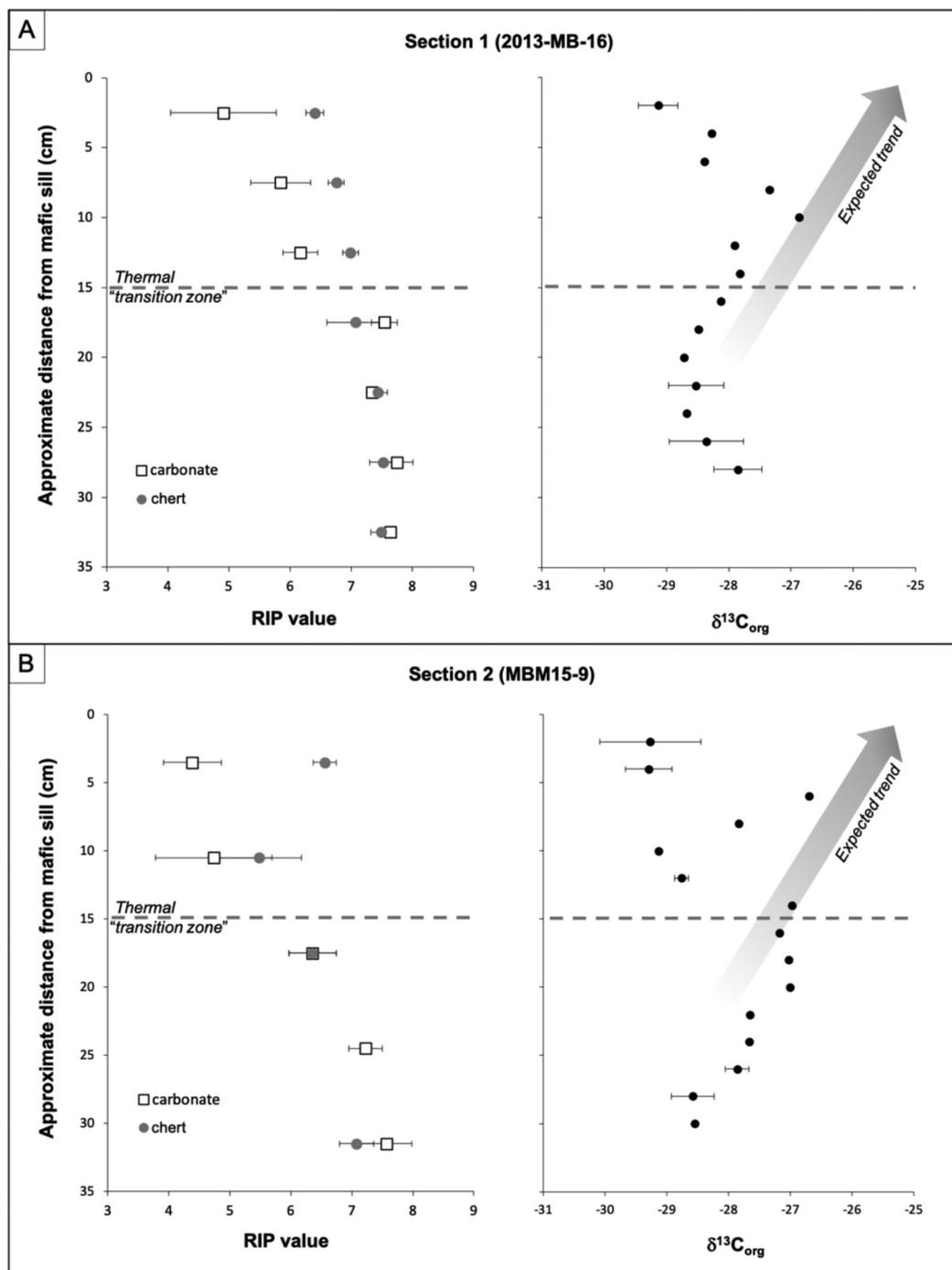
Raman geothermometry measurements show an overall increase in peak metamorphic temperature for kerogen upsection toward the mafic sill, particularly within carbonate lithologies. For Section 1, temperature estimates of kerogen within chert range from $226 \pm 30\text{ }^\circ\text{C}$ near the base to $237 \pm 30\text{ }^\circ\text{C}$ near the top; however, the values range from 214 ± 30 to $263 \pm 30\text{ }^\circ\text{C}$ within the section. For kerogen in carbonates from Section 1, values range from $231 \pm 30\text{ }^\circ\text{C}$ near the base to $298 \pm 30\text{ }^\circ\text{C}$ near the top, showing a strong relationship with position within the section. For Section 2, there appears to be no correlation between the distance from the sill and peak temperature for kerogen in chert; however, for kerogen in carbonate, there is a strong relationship, ranging from $262 \pm 30\text{ }^\circ\text{C}$ near the base to $316 \pm 30\text{ }^\circ\text{C}$ at the top of the section (Tables S1 and S2; Fig. S5, Supplementary Material¹). For kerogen in carbonate in each section, there is also a strong negative linear relationship between RIP and peak metamorphic temperature, but for kerogen in chert, there is no significant relationship in either section (Fig. S2, Supplementary Material¹).

Bulk carbon isotope values of extracted kerogen from the MBM have a range of $\delta^{13}\text{C}_{\text{org}}$ values between approximately -30% and -26% with an average of $-28.2\% \pm 0.8\%$ (Fig. 4; Tables 1 and 2). $\delta^{13}\text{C}_{\text{org}}$ values from Section 1 ($n = 14$) have an average of $-28.2\% \pm 0.6\%$ and values from Section 2 ($n = 19$) have a comparable average of $-28.1\% \pm 0.9\%$. These values are consistent with previously reported average $\delta^{13}\text{C}_{\text{org}}$ values from bulk samples of the Rosspport Formation of -26.4% (Strauss and Moore 1992) and -29.7% (Strauss et al. 1992a). In the samples studied here, $\delta^{13}\text{C}_{\text{org}}$ values fluctuate throughout both vertical stratigraphic sections, but each section has an interval of lower values ($\sim 2\%$ relative to mean) at the uppermost level of the section (Fig. 4). Two subsamples from Section 1, including sample 2013-MB-16-1-1 (thermally altered, near the mafic sill) and sample 2013-MB-16-4-3 (least altered, at maximum distance from the mafic sill) yielded $\delta^{13}\text{C}_{\text{carb}}$ values of -1.8% and -1.5% , respectively (Table 1).

Discussion

As described above, sedimentological and geochemical evidence suggests that the Mesoproterozoic MBM microbialites represent a phototrophic microbial community deposited on the shorelines of an ancient ($\sim 1.4\text{ Ga}$) lacustrine, playa-sabkha environment. Raman spectroscopic and carbon isotope data collected from samples of chert-carbonate for two vertical transects reveal a higher level of thermal alteration in kerogen near the mafic sill that roughly correlates with decreasing $\delta^{13}\text{C}_{\text{org}}$ values (Figs. 3 and 4). Raman spectra also show an apparent decoupling between the chert and carbonate lithologies, with kerogen in carbonates showing an overall wider range of RIP values ($\sim 7.8\text{--}4.4$) compared to kerogen in quartz-rich cherts ($\sim 7.5\text{--}5.5$). The variability in the RIP values for each transect, both for chert and carbonate, is much greater than 5%, which is the typical maximum variation for ancient organic matter within a single unit (Schopf et al. 2005). The differences in thermal alteration are more evident when examining each section individually, as the stratigraphic change of RIP values (ΔRIP) is at least two times greater for kerogen in carbonates compared to kerogen within quartz (see Results) (Tables S1 and S2, Supplementary Material¹). This suggests that the organic matter preserved within carbonates was more geochemically sus-

Fig. 4. Mean and standard deviations of Raman index of preservation (RIP) values and bulk $\delta^{13}\text{C}_{\text{org}}$ values from (A) Section 1 and (B) Section 2 of the Middlebrun Bay Member. RIP values are shown for Raman spectra of kerogen from both chert (circles) and carbonate (squares) lithologies in each thin section (Tables S1 and S2, Supplementary Material¹). Note that RIP and $\delta^{13}\text{C}_{\text{org}}$ values show a similar decrease with increasing proximity to the overlying mafic sill in both sections, and RIP values are particularly low for carbonate lithologies.



ceptible to thermal alteration, whereas kerogen preserved in quartz was altered to a lesser degree when exposed to the same thermal gradient. Interestingly, bulk organic carbon isotopes from stratigraphically equivalent samples yield values depleted in ^{13}C relative to the mean (up to 2‰) near the mafic sill (Fig. 4; Tables 1 and 2). This trend is unexpected because it is contrary to most previously described theoretical expectations and experimental results, which suggest that sedimentary organic matter becomes enriched in ^{13}C with increasing thermal maturity,

consistently resulting in higher $\delta^{13}\text{C}_{\text{org}}$ values (Hayes 1993; Schidlowski 2001; Galimov 2006). Based on the data reported here, there are dynamic thermal and mineralogical controls involved in the preservation of ancient organic geochemical signatures and consequently many challenges to interpreting these data within their proper geologic context.

Comparing the MBM to other nonmarine Precambrian deposits, the earliest organic evidence for a terrestrial biosphere comes from organic matter in 2.6 Ga carbonaceous paleosols of South

Table 1. Carbon isotopic data for Middlebrun Bay Member, Section 1 (2013-MB-16).

Sample ID	Distance from sill (cm)	$\delta^{13}\text{C}_{\text{org}}$ (‰VPDB) ^a	Average (‰)	SD (‰)	$\delta^{13}\text{C}_{\text{carb}}$ (‰VPDB) ^b
16-1A	2	-29.4			-1.8 ^c
Duplicate		-28.9	-29.2	0.3	
16-1B	4	-28.3			
Duplicate		-28.3	-28.3	<0.1	
16-1C	6	-28.4			
16-2A	8	-27.3			
16-2B	10	-26.9			
16-2C	12	-27.9			
Duplicate		-27.9	-27.9	<0.1	
16-3A	14	-27.8			
16-3B	16	-28.1			
16-3C	18	-28.5			
Duplicate		-28.5	-28.5	<0.1	
16-4A	20	-28.7			
16-4B	22	-28.2			
Duplicate		-28.8	-28.5	0.4	
16-4C	24	-28.7			
16-4D	26	-27.9			
Duplicate		-28.8	-28.4	0.6	
16-4E	28	-27.6			-1.5 ^c
Duplicate		-28.1	-27.9	0.4	
Average		-28.2		0.6	

^aInternal error for each measurement = ~0.3‰.^bInternal error for each measurement = ~0.1‰.^cApproximate stratigraphic equivalent.**Table 2.** Carbon isotopic data for Middlebrun Bay Member, Section 2 (MBM-15-9).

Sample ID	Distance from sill (cm)	$\delta^{13}\text{C}_{\text{org}}$ (‰VPDB) ^a	Average (‰)	SD (‰)
9-1A ^b	2	-28.6		
Duplicate		-30.2		
Duplicate		-29.1	-29.3	0.8
9-1B	4	-29		
Duplicate		-29.6	-29.3	0.4
9-1C ^b	6	-26.7		
9-1D	8	-27.8		
9-2A	10	-29.1		
9-2B	12	-28.7		
Duplicate		-28.8	-28.8	0.1
9-3A	14	-26.9		
9-3B	16	-27		
9-3C	18	-27.2		
9-3D	20	-27		
9-3E	22	-27		
9-3F	24	-27.7		
9-3G	26	-27.8		
Duplicate		-27.7		
Duplicate		-27.5	-27.7	0.2
9-3H	28	-27.6		
Duplicate		-28.1	-27.9	0.3
9-3I	30	-28.6		
9-3J	32	-28.4		
Duplicate		-28.7	-28.6	0.3
Average		-28.1		0.9

^aInternal error for each measurement = ~0.7‰.^bSamples powdered instead of crushed.

Africa (Watanabe et al. 2000, 2004). The reported $\delta^{13}\text{C}_{\text{org}}$ values for this unit are relatively high, ranging from -17.4‰ to -14.3‰, and the paleosols have been exposed to zeolite and lower greenschist facies metamorphism (i.e., $T < \sim 300^\circ\text{C}$) (Martini 1994; Watanabe et al. 2000). Sedimentary rocks that form within restricted basins

(e.g., evaporitic lakes) typically yield higher $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ values (up to +5‰ each) compared to shallow subtidal and deep marine deposits, largely reflecting differences in biological communities and physicochemical environments (Hayes 1993; Des Marais 2001). Thus, in addition to ecological and metamorphic effects, the organic matter present within Archean paleosols likely experienced a complex history in connection with the atmosphere and possible groundwater circulation, making the isotopic compositions more difficult to interpret. Kerogen and carbon isotopes have also been described from other Precambrian paleosols and lacustrine deposits, but they have so far provided little information regarding thermal isotopic alteration (e.g., Elmore et al. 1989; Price et al. 1996; Rye and Holland 2000).

Additional insight may instead be gained from highly metamorphosed Archean deposits containing crystalline graphite, such as those of the Isua and Nuvvuagittuq Greenstone Belts (e.g., Schidlowski et al. 1979; Rosing 1999; Ueno et al. 2002; Papineau et al. 2011; Ohtomo et al. 2014; Tashiro et al. 2017). Carbon isotope analyses of graphite from these units have displayed a wide range of values (approximately -50‰ to -5‰); however, the original isotopic composition of kerogen precursors cannot be accurately determined for rocks of this age and metamorphic grade (Des Marais 2001). It has been shown that ^{13}C - ^{12}C isotopic exchange can occur between sedimentary organic matter and coexisting carbonate during high-grade metamorphic processes (Valley 1986). Thus, progressive thermal alteration of carbonaceous material within carbonate-bearing sedimentary rocks is thought to produce higher $\delta^{13}\text{C}_{\text{org}}$ values (and lower $\delta^{13}\text{C}_{\text{carb}}$ values) as the organic matter is graphitized and the isotopic difference between the inorganic and organic species approaches thermodynamic equilibrium (Valley 1986; Schidlowski 2001). The role of hydrothermal circulation associated with postdepositional alteration of carbon isotopes is another possibility worth considering, yet it has been demonstrated that isotopic exchange with CO_2 -rich fluids or mantle-derived carbon typically results in increased $\delta^{13}\text{C}_{\text{org}}$ values and potentially decreased $\delta^{13}\text{C}_{\text{carb}}$ values (Summons and Hallman 2014). For younger Proterozoic rocks, thermal alteration of kerogen has been described in more detail and has consistently shown that kerogen maturation can increase $\delta^{13}\text{C}_{\text{org}}$ values by ~3‰-10‰ (McKirdy and Powell 1974; Strauss et al. 1992a, 1992b). Such observations have provided the basis by which isotopic alteration of Precambrian organic matter is generally understood.

The measurement of carbon isotopes in thermally altered organic matter compared to its original, unaltered composition is rarely achievable in natural settings. Most geologic samples from the Precambrian have experienced widespread regional metamorphism and higher degrees of thermal alteration, which occurred on longer timescales than those encountered in this study. Several other studies have investigated the relationship between thermal maturity and carbon isotopes of organic matter in close proximity to an igneous intrusion (e.g., Simonet et al. 1981; Galimov and Simoneit 1982; Retallack and Jahren 2008), but the samples analyzed therein have come from relatively young deposits. Recent sediments in the Gulf of California show an isotopic shift towards lower $\delta^{13}\text{C}_{\text{org}}$ values for samples exposed to alteration at high temperatures (~300°C) near a basaltic sill (Galimov and Simoneit 1982; Galimov 2006). This situation closely resembles the geologic setting of the MBM, and the findings are seemingly consistent with those of this study; however, the samples are much younger, more immature, and of a different lithology and therefore serve only as an indirect reference. In comparison, Barghoorn et al. (1977) performed similar bulk carbon isotopic analyses of Precambrian rocks at nearby Flint Island, approximately 50 km from the Kama Hill locality of this study, on carbonaceous shales from the lower Gunflint Formation (~1.9 Ga). However, carbon isotopes were only measured in one section at four distances from a diabase sill ~1 m thick, and $\delta^{13}\text{C}_{\text{org}}$ values were shown to increase

near the sill (Barghoorn et al. 1977), consistent with previously reported theoretical expectations and in contrast with the findings of this study. It should be noted, however, that the relative thermal maturity of organic matter was not determined for the samples analyzed from the Gunflint Formation (Barghoorn et al. 1977).

The relationship between thermal maturity and $\delta^{13}\text{C}_{\text{org}}$ values reported here is unexpected and previously unreported for Precambrian rocks. Lower $\delta^{13}\text{C}_{\text{org}}$ values near the mafic sill do not appear to be the result of paleoenvironmental changes or regional metamorphism, but there remain several plausible explanations. For example, rapid geothermal heating of organic matter over a relatively short duration may result in carbon isotope compositions becoming depleted in ^{13}C relative to their initial value. This pattern has been observed in laboratory pyrolysis studies during the initial stages of thermal alteration in kerogen (e.g., Lorant et al. 1998; Tocqué et al. 2005); however, such studies are not directly applicable to natural systems and many other experiments are consistent with geologic evidence that the thermal alteration of organic matter results in an overall enrichment in ^{13}C (e.g., Peters et al. 1981; Lewan 1983). The full extent of isotopic alteration from rapid heating is unknown and the chemical reactions governing this phenomenon are poorly understood. Nonetheless, it has been proposed that rapid isotopic shifts towards lower $\delta^{13}\text{C}_{\text{org}}$ values during the early stages of kerogen cracking (i.e., low transformation) are possibly due to unknown precursors in immature kerogen (Galimov 2006) or residual carbon enriched in ^{12}C due to oxidation (Mojzsis et al. 1996; Eiler et al. 1997; Kump et al. 2011), yet the underlying chemical mechanisms require further investigation. Secondary ^{13}C depletion could be responsible for false-positives of organic biogenicity and metabolic identity if significant isotopic shifts were able to progress, although this is a highly unlikely scenario. Based on data from this study and those described above, the amount of isotopic alteration is minimal (i.e., not exceeding -5%), but additional studies of kerogen alteration under similar geologic conditions may provide further constraint.

The most notable pattern emerging from this study is that the organic matter of the MBM appears to have been preserved differently between the chert and carbonate-rich lithologies. It has been suggested that the recrystallization of quartz is capable of preventing extreme isotopic exchange between carbonaceous materials and the surrounding inorganic carbon, which is known as the “armoring effect” (Wada and Suzuki 1983). Although this effect is not understood in detail and requires further investigation, it could possibly be due to simple steric hinderances based on the mineralogy of the matrix. However, the greater thermal conductivity of quartz relative to carbonate minerals challenges such a direct explanation. Ueno et al. (2002) reported ion microprobe measurements that showed graphite surrounded by quartz had slightly lower $\delta^{13}\text{C}_{\text{org}}$ values than coexisting, unarmored graphite, indicating better preservation of the original isotopic composition from preexisting kerogen. Ion microprobe measurements of carbon isotopes in high-grade metasedimentary rocks have also been reported for graphitic inclusions in apatite and zircon, which have significantly lower $\delta^{13}\text{C}_{\text{org}}$ values relative to coexisting, unprotected graphite-bearing minerals (e.g., Mojzsis et al. 1996; McKeegan et al. 2007; Bell et al. 2015). Despite these findings, scientific consensus regarding the biogenicity of such carbonaceous materials remains elusive (e.g., Papineau et al. 2011). These studies, in addition to the data reported here, suggest that organic geochemical properties of sedimentary organic matter and its graphitic counterpart may be preferentially preserved within different lithologies and partially shielded from the effects of high-temperature metamorphism and that increased $\delta^{13}\text{C}_{\text{org}}$ values are not universally associated with thermally altered organic matter. The present study represents the first time such a direct comparison of thermal alteration and carbon isotopes has been made for Precambrian kerogen of a known biological origin in assorted

chert-carbonate samples, furthering our understanding of thermally altered organic matter and aiding our exploration of the early geobiological record.

Conclusions

The relationship between thermal maturity and organic carbon isotope compositions observed in thermally altered microbialites from the 1.4 billion year old lacustrine MBM is contrary to most theoretical expectations. Kerogen in chert-carbonate samples from this unit shows increasing levels of thermal maturity in closer proximity to the overlying diabase sill. Also, the kerogen embedded in quartz is apparently less susceptible to thermal alteration, and the kerogen embedded in carbonate is relatively more susceptible. Organic carbon isotope compositions from the same samples are more variable and overall lighter (^{13}C -depleted) closer to the sill, suggesting that thermal alteration of kerogen could under at least some circumstances produce lower, as opposed to higher, $\delta^{13}\text{C}_{\text{org}}$ values. These inconsistencies are best explained by a combination of two processes that operated independently: (1) silicification partially shielded kerogen from the effects of thermal alteration, whereas carbonates were less effective at “armoring” organic matter, although the underlying molecular mechanism is not well understood and (2) rapid heating of kerogen in close proximity to the mafic sill produced lower $\delta^{13}\text{C}_{\text{org}}$ values as opposed to higher values commonly associated with gradual burial or regional metamorphism.

Bulk carbon isotope analyses (this study) are useful for reconstructing the general paleoecology of ancient microbial ecosystems; however, they require samples to be acidified and measure a mixture of all insoluble carbon sources present within the extracted organic matter. This assortment of source material provides an average isotopic composition for the extracted kerogen but does not account for mixing or isotopic heterogeneity of carbon between different mineralogies in each sample. This limitation could be addressed in future studies by investigating carbon isotopes of kerogen in the carbonate and chert fractions separately. Using conventional bulk analysis methods, such as those used in this study, more material would be required to generate sufficient sample size. While these ensuing analyses may not elucidate the underlying chemical mechanism of carbon isotopic alteration, they would provide added clarity regarding the differential preservation of organic matter. Nevertheless, the effects of thermal alteration on stable carbon isotopes of Precambrian kerogen appear to be more dynamic than previously expected, and the implications of these findings extend back to the earliest records of biogenic organic matter on Earth.

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