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Preservation of Organic Carbon in Dolomitized Cambrian Stromatolites and Implications for Microbial Biosignatures in Diagenetically Replaced Carbonate Rock

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ABSTRACT

Stromatolites have been a major focus in the search for ancient microbial life, however, the organic carbon biosignatures of dolomitized stromatolites have not yet been fully characterized or correlated with their dolomitizing conditions. Although dolomitization rarely preserves microbial morphology, the presence of organic carbon can provide valuable information for characterization of fossils' biogenicity, syngenicity, and indigeneity to their host rock. The Cambrian Allentown Formation in New Jersey, USA, is an excellent example of dolomitized stromatolites and thrombolites containing diagenetically modified microbial biosignatures. Based on XRD and EPMA data, the dolomite composition is typically stoichiometric, with varying degrees of cationic ordering. The outcrop underwent early dolomitization in a marginal-marine setting and later burial diagenesis resulting in multi-generational dolomite formation: (1) microspar dolomite formed by early diagenetic replacement at or near the surface, (2) zoned dolomite formed penecontemporaneously with the microspar phase as rhombohedral crystals by infilling primary pore spaces within the microspar matrix. The rhombic crystals continued to grow outward in alternating stages of Fe-enriched and -depleted fluids, which were preserved in zoned rims and revealed by cathodoluminescence, and (3) saddle dolomite formed during late stage deep burial with Fe- and Mn-rich fluids, and occurs as a void-filling, high-temperature phase. Organic carbon, characterized using confocal Raman microscopy, has an exclusive distribution within the microspar dolomite, and the D and G bands' characteristics reveal similar thermal alteration to the host rock, indicating that the mapped organic carbon is indigenous and syngenetic with the Cambrian carbonates. The findings presented in this study reveal organic matter found within microspar of various dolomitized facies deriving from different source pools of organic carbon. This study sheds light on biosignatures in secondary dolostones and may aid biosignature detection in older carbonate rocks on Earth and Mars.

Keywords: dolomitization, Cambrian stromatolites, organic carbon, biosignatures, burial diagenesis

1. INTRODUCTION

Stromatolites are microbially mediated sedimentary structures that record the oldest forms of life on Earth (Barghoorn and Tyler, 1965; Grotzinger and Knoll, 1999; Allwood et al., 2006). These ancient structures have drawn a significant focus of geobiology and astrobiology research because of their ability to archive the interactions of biological, physical, and chemical processes (e.g., Hoffman, 2013), providing an invaluable reference to Earth's past. A complication in the reconstruction of these structures derives from the fact that, as any other rock and fossil, stromatolites undergo diagenesis over time, which alters original biological signatures (biosignatures), including chemical (e.g., organic carbon) and physical (e.g., cellular morphology) evidence.

The most common diagenetic changes in stromatolites are silicification and dolomitization, which involve the replacement of original calcium carbonate ($CaCO_3$) by silica (SiO_2) during silicification and dolomite [$CaMg(CO_3)_2$] in dolomitization. Silicification during early diagenesis leads to the exceptional preservation of original textures, microfossils, and organic chemistry, which are leading indicators in the characterization of biogenicity, indigeneity (i.e., naturally occurring in the environment), and syngenicity (i.e., formed at the same time as the enclosing rock) (Knoll et al., 1988; Buick, 1990; Grotzinger and Knoll, 1999; Van Kranendonk et al., 2003; Sugitani et al., 2007; Schopf and Kudryavtsev, 2012; Braiser et al., 2015). Unlike silicification, dolomitization commonly results in the loss of microbial morphology (Schopf, 1999; Bartley et al., 2000), making the characterization of syngenetic and indigenous biosignatures more difficult (Grotzinger and Rothman, 1996). Dolomite [$CaMg(CO_3)_2$] may form during deposition (as primary dolomite) or post-deposition (secondary dolomite) from various fluid chemistries and temperatures (Machel, 1978, 2004; Guido et al., 2018). The fate of organic matter preserved under such a wide variety of conditions is yet to be properly evaluated.

Although the dolomitization process may be destructive to original stromatolitic textures and compositions, studies of microfossils in dolomitic stromatolites have been reported. These studies have interpreted the investigated dolomitic stromatolites as formed by primary dolomite precipitation (Rao et al., 2003; Ayllón-Quevedo et al., 2007; Sanz-Montero et al., 2008; Calça et al., 2016). The microfossils characterized in these primary dolomitic structures are preserved exclusively in silica (Ayllón-Quevedo et al., 2007; Sanz-Montero et al., 2008; Calça et al., 2016) and sulfur-rich mineral phases (Lindtke et al., 2011). In contrast, the effects of secondary dolomitization on the preservation of organic material remain largely unexplored. Secondary dolomitization may occur in a wide range of environments from the surface to deep burial (several km depths) settings (Machel, 1978), under different temperatures and pressures, and as such provides a range of settings that could be conducive to the long-term preservation of organics. Characterizing the effects of secondary dolomitization on microbial fossil preservation is critical for interpreting traces of early life in the geological record. The syngenicity and indigeneity of this type of fossilization in the geologic record can only be comprehensively examined after the degree of alteration of the host rock has been characterized and evaluated against that of the biologic remains (Buick, 1990; Braiser et al., 2004).

The need for detailed insight into the preservation processes of organic matter, or biosignatures in general, within dolomitized carbonate lithologies is also relevant to astrobiology. Carbonate lithologies are a recognized astrobiology target for Mars exploration (Cady et al., 2003; Summons et al., 2011; D'Elia et al., 2017). The primary science goal of the Mars 2020 mission is to determine whether life existed on Mars by seeking signs of extinct life in the rock record (Mustard et al., 2013; Williford et al., 2018). In February 2021, the Mars 2020 Perseverance rover will land in Jezero Crater, an ancient paleolake (~4.0-3.5 Ga) with a diverse suite of carbonate-bearing terrains, including those with Mg/Ca compositions similar to dolomites on Earth (Horgan et al., 2020). Although the origin of the magnesium carbonates identified is still uncertain (Ehlmann et al., 2008; Goudge et al., 2015), the crater may contain lacustrine carbonate deposits, which are habitable environments on Earth that provide the potential for biosignature preservation (Horgan et al., 2020). Therefore, investigating organic matter preservation in ancient dolomites on Earth can facilitate future searches for potential biosignatures in Martian magnesium carbonates.

In this paper, we contrast the host rock alterations with the organic carbon contained within. The measurements of whole rock and high-resolution in situ analysis of the three dolomite mineral phases from the Cambrian Allentown Formation are used to characterize the dolomitization setting. Confocal Raman spectroscopy is used to determine the spatial association of organic carbon to minerals and their alteration. Finally, the results are used to evaluate the level of diagenetic alteration that has affected the outcrop, and the effect that such alteration had on the preservation of the organic carbon.

2. GEOLOGIC SETTING

2.1. Regional geology and sedimentology

The Late Cambrian (515-500 Ma) Allentown Formation (Weller, 1903; Howell, 1945; Harris et al., 1995; Dalton et al., 2014), commonly referred to as Allentown Dolomite, is part of the Kittatinny Supergroup (542-443 Ma). The Kittatinny Supergroup is a northeast trending lithostratigraphic unit (Fig. 1) that records the formation of the eastern Laurentian (North America) passive margin, when the deposition of shallow-water carbonates prevailed. Paleoreconstruction of the area shows Laurentia positioned below the equator and rotated approximately 90° clockwise from its current orientation (Blakey, 2016). During the Cambrian, sediments from eroding inland rocks were transported by streams to the coast and deposited on the shallow shelf (Miller, 1941; Dalton et al., 2014). The paleoenvironment has been interpreted as shallow subtidal to supratidal resulting in the deposition of limestones that have been subsequently dolomitized (Miller, 1941; Stead and Kodama, 1984; Dalton et al., 2014).

In the 1950s, the Allentown was divided into two members: the Limeport (bottom) and Allentown Members (top) (Drake Jr., 1965). This distinction was made in older literature because the lower Limeport Member contains numerous ‘cryptozoan’ features (hereafter referred to as stromatolites) of various morphologies, including large domes with convex-shaped laminae, wavy beds, and small domes of laterally linked laminae (Drake Jr., 1965). Previous geologic mapping of the Allentown Formation reveals cyclic bedding (from oldest to youngest) as follows: textureless dololutite (<0.0039 mm grain size), dolarenite (0.0625-2 mm), oolitic dolarenite (0.0625-2 mm), dolorudite (>2 mm), cryptozoan (stromatolitic) dolomite, and desiccation dolorudite (>2 mm) (Drake Jr., 1965). These inversely graded bedding cycles suggest a regression sequence. Individual bedding cycles range in thickness from ~2 to 10 m, and the entire formational sequence measures up to 580 m thick (Drake Jr., 1965; Monteverde, 1992).

2.2. Study area

The study area in Hamburg, New Jersey, USA, includes 40 m of uplifted dolostone (dolomitic carbonate rock), tilted 44° NW. Exposure along the southwestern side of the outcrop (Figs. 2, 3) allows for measurements of bedding thickness that are elsewhere inexact due to glacially polished rock surfaces. Along the longest transect, the outcrop is 100 m long with extensive vegetation cover that limits correlation between the northeast and southwest parts of the outcrop (Fig. 3A). The southwest side of the outcrop does not contain microbial structures (Fig. 3B), but the transect analyzed in the middle of the outcrop (Fig. 3A) contains stromatolites and thrombolites. The bottom of transect A is ~13 m of fine-grained, grey dolosiltite intercalated with iron oxidized dissolution seams that are weathered black in outcrop (Fig. 2B). The occurrence of thrombolites (microbially mediated clotted structures) is marked by a brown wavy layer of ~1 cm thick laminae (Fig. 2C). The thrombolites are overlain by small (≤5 cm). round stromatolite heads (Fig. 2D, E) that occur periodically in overlying strata for ~20 m. Massive oolitic dolarenite (Fig. 2F) is situated above the stromatolite heads for ~11 m. The oolitic grainstone is overlain by ~13 m of dolosiltite with numerous beds of high energy, storm deposit features of rip-up clasts (linearly stratified features) (Fig. 2G), edgewise conglomerates (Fig. 2H), and jumbled intraclasts (non-linearly stratified and randomly dispersed features) (Fig. 2I). These beds co-occur with coarse-grained dolomite-filled vugs (≤9 mm) (Fig. 2J). Large (≤30 cm) domal stromatolites, as well as intraclasts and collapse breccia are observed at the top of the formation (Fig. 2K). The northeast side of the outcrop reveals the convex up structure of the domes (Fig. 2L). Mudcracks (continuous polygonal morphology) are situated above the large domal stromatolites (Fig. 2M) at the top of transect A, and syneresis cracks (discontinuous sinuous morphology) are observed southwest of the stromatolites at the top of transect B (Fig. 2N). Transect B and sampling point marked by an asterisk (*) (Fig. 3) are dominated by oolitic facies. Wavy stylolites parallel to bedding are found throughout the formation (Fig. 2O). Chert occurs as black lenses or thin layers (~1 cm) throughout the formation (Fig. 2P). This bedding sequence corresponds to a peritidal marine regression (Wilson, 1975; Flügel, 2004) (Fig. 1C).

3. MATERIALS AND METHODS

3.1. Sampling strategy

Samples (n = 22) were collected from 2017 to 2020 in Hamburg, New Jersey, USA. The sampling strategy included twenty-two different sampling points, from bottom to top of the formation, while targeting obvious stromatolitic morphologies and significant changes in strata texture or appearance (Fig. 3). Sampled transects are marked A and B (Fig. 3) and the starting letter of each sample name (Table 1) corresponds to the transect where the sample was collected, samples labeled *12b-d are not part of either transect but rather the samples that exhibited characteristic textures and were collected at sides of the transects. Table 1 lists samples from bottommost (*12d) to the topmost bedding layers (A18) and what samples were included in which analyses in this study. Hand-sized samples were collected in an organically clean manner to avoid contamination by using gloves to handle samples that were wrapped in sterile aluminum foil and placed in canvas bags. Subsampling was performed in the laboratory using a diamond blade saw and deionized water to cut away outer rock layers from the interior areas that were later used for analyses.

3.2. Petrographic and mineralogical analyses

Petrographic analyses of 14 texturally different layers were used to describe the stromatolites and associated dolostones. The petrographic study involved plane polarized and cross polarized light inspection of thin sections for textural and mineral identification, as well as to target regions of interest for further spectroscopy. The detection of minor mineral phases was performed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) at Rutgers

University using a Hitachi S-4800 operating at 15 to 20 kV and 12 to 15 uA, equipped with an Apollo X EDAX.

Powder X-ray diffraction (XRD) of whole rock samples was used to determine dominant mineral assemblages in 21 samples. The equipment used at Rutgers University was a Bruker D8 with a Cu-Kα radiation. Operational settings were 40 kV, 25 mA. XRD spectra were collected over the 2Θ range of 5-75° and with a step size of 0.02° or 0.04° and a count time of 48 or 115 s per step, respectively. Identification of peak patterns was performed in DIFFRAC suite. Eva V3.1 software using the International Center for Diffraction Data database (version PDF2013). Backgrounds were subtracted before calculating d-spacing values. Stoichiometry was calculated by taking the 2Θ value of the d_{104} peak, and converting the 2Θ to d-spacing using Bragg's Law (Bragg and Bragg, 1913), and lastly, using the equation in Lumsden (1979) which relates the d-spacing of the d_{104} peak to mol% of $CaCO_3$. The equation derived by Lumsden (1979) can result in $\leq$ 3 mol% $CaCO_3$ inaccuracies (Reeder and Sheppard, 1984), and therefore this stoichiometric data was checked by electronprobe microanalysis data. The degree of cation ordering was calculated by the intensity ratio of the d_{015} and d_{110} peak (Graf and Goldsmith, 1956; Goldsmith and Graf, 1958). Reported values of dolomite stoichiometry and degree of cation order represent bulk sample averages only (Table 2).

3.3. Geochemical analyses

$\delta^{13}C_{dolo}$ and $\delta^{18}O_{dolo}$ were analyzed via acidification of each powdered sample at 60°C using 85% H_3PO_4. Analyses were carried out on a GasBench II System (Thermo) coupled to a Delta V Plus isotope ratio mass spectrometer (IRMS) (Thermo) at NASA Goddard Space Flight Center. Bulk (n=16) samples were chosen based on texture and mineralogy differences and were

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analyzed to determine the isotope ratios of dolomite. Micro-drilled (n=7) samples were sampled from thin-section billets at Rutgers University using a Medenbach micro-drill in order to isolate microspar and saddle dolomite phases for comparison to the bulk rock, and to target the minimum and maximum temperature of formation. The bulk samples were analyzed in triplicate, and micro-drilled samples were analyzed in, at minimum, two replicates. Standards were run before, in the middle of, and after each run. Precision is based on reproducibility of NIST reference standard NBS-19 at ±0.05‰ for $\delta^{13}C_{dolo}$ and ±0.15‰ for $\delta^{18}O_{dolo}$. Isotopic values are reported relative to the Vienna Pee Dee Belemnite (VPDB) (Table S1 in supplementary material).

Organic carbon abundance, nitrogen abundance, and $\delta^{13}C_{org}$ were determined using an Elemental Analyzer (Costech) coupled to a Delta V Plus IRMS (Thermo) at NASA Goddard Space Flight Center. Powdered samples were placed in ashed (500°C) glass vials. Sedimentary organic material was separated via dissolution in 6N HCl for approximately 48-96 hours. Insoluble material was allowed to settle before samples were carefully decanted and then left to dry. The complete dissolution of carbonates was verified using SEM/EDS microscopy. Dry insoluble material was scraped out of glass containers, weighed, and packed into tin capsules for analyses. Standards were analyzed periodically during each run to assess the precision of the measurements. Precision is based on reproducibility of reference standard USGS40 (glutamic acid) at ±0.07‰ for $\delta^{13}C_{org}$. Isotope values are reported relative to VPDB standard and total organic carbon as wt% (Table S1 in supplementary material). To calculate wt% organic carbon, the analyzed sample’s weight was divided by its total weight (pre-dissolution) and multiplied by

100%. The residual % of organic carbon measured was then converted to total organic carbon (TOC) by the following equation:

TOC = ((organic carbon measured) * (analyzed sample weight / initial sample weight)).

Qualitative elemental X-ray mapping (n=2) and cathodoluminescence (CL) mapping (n=9) was performed on thin sectioned samples with the JEOL Superprobe JXA-8200 at Rutgers University. Samples were chosen based on texturally different microscale features. Operating conditions were 15 kV accelerating voltage, 14 nA beam, focused beam diameter (~1 micron), a step size of 1 µm, and a dwell time of 30 ms. The Kα X-ray maps and CL maps were processed with the xCLent software at Rutgers University to create red, green, and blue (RGB) colored composite maps of the sample.

Quantitative electronprobe microanalyses (EPMA) of mineral composition were obtained on 7 samples with the JEOL Superprobe JXA-8200 at Rutgers University, to isolate each phase of dolomite. Operating conditions were 15 kV accelerating voltage, 15 nA beam current, and a beam diameter of 5 microns. Analytical standards were well-characterized synthetic oxides and minerals including strontianite (Sr), orthoclase (Si), fayalite (Fe), rhodonite (Mn), calcite (Ca), ZnO (Zn), and dolomite (Mg). Data quality was ensured by analyzing secondary standard materials as unknowns. Average detection limits (in oxide wt%) are SrO = 0.03; MnO, SiO_2, FeO = 0.02; CaO, MgO = 0.01; and ZnO = 0.17. The average analytical errors for elements above detection limit are: Ca ~0.25%; Mg ~0.47%; Fe ~5.36%; and Mn ~46%. Stoichiometry (Mg/Ca) was calculated for each phase of dolomite. Stoichiometry was determined by converting the average elemental wt% of Mg and Ca for each dolomite phase to mol% Mg and Ca, where total percentage of Mg and Ca was normalized to 100. Results are reported in Table 2 and Table S2 in supplementary material.

3.4. Confocal Raman microscopy

Confocal Raman microscopy and spectroscopy was used for spot analyses and mapping of 14 thin sections and 8 unprocessed rock samples, to determine the organic carbon spatial distribution, associations with minerals, and to analyze the D and G bands (~1350 and 1600 cm^{-1}, respectively) characteristic Raman signal for the organic matter. Five thin sections were chosen for the final high-resolution analysis. These representative layers ranged across the top, middle, and bottom areas of the outcrop and include all lithological textures observed (Fig. 3, Table 1). This work was performed at Rutgers University with a WITec alpha300 equipped with a frequency-doubled Nd:YAG (532 nm) excitation laser. Operational settings were as follows: a 1 mV average laser intensity (range from 1-3 mV) to minimize laser-induced heating and to avoid structural modification of the samples, and a depth of 1-5 μm below the surface was used to avoid surface contamination. Mapped areas were visually inspected by transmitted and reflected light microscopy for holes and cracks in the samples that may contain polishing grit, epoxy, or other contaminants related to sample handling that may interfere with the D and G band spectra. Samples that could not be unambiguously identified as unaffected by this type of contamination or were too friable for thin sectioning were not included in the final Raman data sets.

D and G bands were analyzed in two ways for data quality assessment, using (1) WITec Project FIVE+ software cluster analysis, and (2) WITec Project FIVE+ software Gaussian fitted background subtraction. The cluster method identifies variations in D and G band phases within a map, averages it, and displays a distribution map. Ten clusters of spectral variations were calculated from each map, and one to three were chosen from each mapped area after quality evaluations (signal-to-noise ratio, surface contamination, and interference bands from hematite were avoided after being inspected both visually and spectrally). The Gaussian fit method uses a Savitzky-Golay filter to smooth the graph before applying background subtraction using a Gaussian fit for both the G and D bands. The average D and G band peak centers are displayed on a distribution map where one to three spectral points, representative of different spectral trends, were hand selected. Maps were inspected for visual and spectral interferences as listed above in the cluster analysis method.

The D and G band cluster results were deconvoluted into five peaks (D1, D2, D3, D4, and G) using PeakFit 4.12 software and following the methodology for peak fittings F and E in Kouketsu et. al. (2014). The numeric table exported from the PeakFit software was used to report all peak parameters including the full width at half maximum (FWHM) used to determine temperature of alteration (Table 4, and Tables S3c, S3d in supplementary material). Organic carbon first-order bands of Raman spectra (D and G bands at ~1350 and 1600 cm^{-1}, respectively) record the host rock’s maximum temperature and can be used as an organic paleothermometer (Pasteris and Wopenka, 1991; Wopenka and Pasteris, 1993; Marshall et al., 2001, 2012). The G band represents the ordered, graphitic structure of carbon, and the D band represents the disordered carbon structure. Variations in the bands, related to differing amounts of thermally induced rearrangement, can be used to determine structural order of the carbon and associated temperature setting required for such level of crystallinity (Pasteris and Wopenka, 1991; Beyssac et al., 2002). Thermometry was calculated using the D1 band geothermometer from Kouketsu et al. (2014):

$$T(°C) = -2.15 * (FWHM\text{-}D1) + 478 (\pm 30°C)$$

This widely used geothermometer was chosen due to the consistency of FWHM with temperature (Kouketsu et al., 2014). A two-tailed, two-sample *T*-test (p=0.05) was applied to D1 and D2 spectral data to determine if variations within the bands and derived temperatures were statistically different (Figs. S1, S2 in supplementary material).

4. RESULTS

4.1. Allentown petrology and mineralogy

4.1.1. Bulk mineralogy

Based on powder X-ray diffraction (XRD) (Fig. S3 in supplementary material) the mineralogy of the Allentown Formation is predominantly dolomitic with few 1-40 cm thick, greyish-black chert lenses (Fig. 2P), and ~1 cm brown colored feldspathic carbonate layers (Fig. 2C) (samples A15, B15b, and A6, respectively). The feldspathic (orthoclase and microcline) carbonate layers occur as thin wavy layers or disk-shaped forms and are commonly observed along fractured bedding surfaces or at the top of microbial macrostructures. Results for stoichiometry and cation ordering are presented in Table 2. The average d-spacing of the dolomite d_{104} peak is 2.889 Å and ranges 2.854 – 2.894 Å ($1\sigma = 0.009$) for (n=20) samples. These d-spacings indicate that the stromatolite (A16) and thrombolite (A5) are stoichiometric (50.0 and 49.7 mol% $CaCO_3$, respectively). The sample B11 has low Mg-excess (49.3 mol% $CaCO_3$), and the cherty outlier (B15b) is 39.3 mol% $CaCO_3$, and the remaining samples range from 51-53 mol% $CaCO_3$ (Table 2). The 14 samples show low Ca-excess of <53 mol% $CaCO_3$, and 2 samples are 52.7 mol% $CaCO_3$. Reported values are derived from bulk rock measurements

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and therefore represent sample averages, which may include an error of up to 3 mol% $CaCO_3$ due to the Lumsden (1979) calculation used (Reeder and Sheppard, 1984). The average degree of cation order calculated by the d_{015}/d_{110} intensity ratio is 0.67 and ranges 0.36 – 0.99 ($1\sigma = 0.16$) for (n=18) samples (Table 2). The range of cationic ordering ratios represent poorly- to well-ordered dolomite, respectively (Kaczmarek and Sibley, 2011; Pina et al., 2020). Most samples (n=13) are ≥0.60 which is indicative of relatively well ordered dolomite (Kaczmarek and Sibley, 2011). Cherty and feldspathic carbonate samples did not exhibit d-peaks of (015) or (110) in XRD, and therefore these samples were not included in the stoichiometry and cation ordering averages. Since these analyses are bulk sample measurements, the reported values represent sample averages and are not characteristic of the individual dolomite phases. Stoichiometry for individual dolomite phases was conducted using EPMA spot analyses.

4.2. Microscale textures and mineralogy

4.2.1. Multi-phase dolomite characterization

Composite Red-Green-Blue (RGB) cathodoluminescence maps with Red = 450-500 nm, Green = 400-450 nm, and Blue = 350-400 nm reveal three distinct phases of dolomite in all analyzed samples (Figs. 4, 5). Dolomite phases vary in crystal size, shape, and intercrystalline boundaries. The three phases of dolomite are classified and characterized by increasing grain size, as microspar, zoned, and saddle, respectively (Fig. 4). The microspar (M) dolomite is nonplanar, and has closely packed anhedral crystals with irregular, intercrystalline grain boundaries (Fig. S4 in supplementary material). The crystals average 20 microns and range 5-40 microns in size. Zoned (Z) dolomite is planar, subhedral to anhedral medium grained (10-100 microns) with straight compromised boundaries (Fig. 5B). The crystals are concentrically zoned in CL, but not in plane polarized light, and are characteristically pore lining or void-filling (Figs. 4E, 5). Saddle (S) dolomite is nonplanar, medium (10-100 microns) to coarse grained (>100 microns) saddle-shaped, void-filling, and exhibits undulatory extinction in cross polarized light (Fig. 6D, E). The three observed CL colors, by increasing wavelength, are blue, grey, and gold, and are found throughout the microspar and zoned dolomite phases; the saddle dolomite only exhibits a dull bluish color in CL (Fig. 4E). Throughout each phase of dolomite, two CL spectral peaks are present at 389 nm and 650 nm (Fig. 4D).

4.2.2. Porosity types and dissolution features

Open porosity is absent in the studied samples, but occluded pore types of primary and secondary origins were observed. Primary fenestral porosity (≤1 mm in size) is ubiquitous in stromatolite samples and infilled with zoned and saddle dolomite (Fig. 7A-C). Vugs are large (2 - 9 mm in average) secondary pores that are at least two times greater in size than the microspar matrix, and are infilled with zoned and saddle dolomite (Fig. 2J). Vugs occur predominately in layers with rip-up clasts and are absent from the lowermost finer grained facies. Secondary microfractures occur in two stages. The first stage includes vertical microfractures (<1 mm wide), infilled with zoned and saddle dolomite, that are present in limited layers of microspar dolomite, and crosscut horizontal laminae and fenestrae in the domal stromatolite (Fig. 7E). The second stage includes randomly oriented microfractures (<1 mm wide) that are present in the oolitic dolosiltite sample B14 and are only infilled with saddle dolomite (Fig. S5 in supplementary material).

Dissolution structures of numerous solution seams occur on fresh surfaces as brownish, irregular streaks but appear black on weathered surfaces, and are abundant in the lowermost outcrop layers of finely crystalline, microspar dolomite samples (Fig. 6F). The seams are Fe oxidized-stained but composed of dolomitic material. Microstylolites that parallel the laminae occur throughout sample A3 (Fig. 6G). Stylolites are either dolomitic in composition or, when found along fractured bedding planes, are infilled with quartz, feldspars, and iron oxides.

4.2.3. Thrombolites

The thrombolites exhibit clotted, irregular microtextures (Fig. 6B, C). Rounded microcline and orthoclase, and sub-rounded quartz occur throughout the sample, with small amounts of peloids and ghost grains. SEM/EDS reveals minor mineral components of Fe-oxides and pyrite grains. The detected metal oxide morphologies range from euhedral to highly deformed in shape, and the pyrite has round to sub-round edges (Fig. S6 in supplementary material).

4.2.4. Ooids

The oolitic dolomite layers exhibit nonmimetic replacement (Sibley, 1978) where little or no original texture (radial or tangential) visible except for a dark-colored ooid outline and relics of concentric layers near the nucleus of the ooid (Fig. 8). Ooids vary in size from ~0.25 to 1 mm in diameter.

4.2.5. Stromatolites

The microtexture of the domal stromatolites consists of three distinctly colored layers, as follows: dark grey thinly layered convex-shaped laminae (<1 mm thick), light grey thinly layered convex-shaped laminae (≤1 cm thick) (Fig. 7F, G), and black, very thin (<1 mm) laminae (Fig. 7G). The dark and light grey layers alternate throughout the stromatolites, and the black layers occur predominately in the lower half (Fig. 7G) of the large domal stromatolites. EDS showed no differences in composition between dark and light grey bands of laminae. However, the black laminae are enriched in felsic material (Fig. S7 in supplementary material). Primary fenestral porosity (≤1 mm thick) in the domal stromatolite is parallel to laminae and infilled with zoned and saddle dolomite (Fig. 7A, E). Very fine-grained, rounded intraclast rip-ups are situated on the topmost layer (Fig. 7H), which also contains large (<0.5 mm in diameter), rounded feldspars of microcline and orthoclase, and sub-rounded quartz grains. The orthoclase minerals exhibit overgrowth rims (Fig. 7I). The SEM/EDS reveals Ti-oxides, Fe-oxides, pyrite and apatite as minor mineral components (Fig. S6 in supplementary data).

4.3. Geochemistry

4.3.1. Multi-phase dolomite high-resolution elemental analysis

Each phase of dolomite was targeted for microanalyses by electron probe after identification with CL. All three phases of dolomite contain Zn and Mn, and the microspar and zoned dolomite phases have Si (Fig. 4F). The zoned dolomite exhibits dark banding associated with Fe concentrations of 0.4 wt% or higher (Fig. 4G). A compositional trend is observed in the microspar and zoned dolomite phases by a covarying increase in Si with a decrease in Ca and Mg. A decrease in Si abundance and an increase in Fe and Mn abundance is observed across the phases of dolomite (Fig. 4F). No Sr is detected in any phase. The average mol% Ca is 49.3% (n=116 spots analyzed), 49.2% (n=130 spots analyzed), 50.8% (n=131 spots analyzed) for microspar, zoned, and saddle dolomite, respectively (Table S2 in supplementary material). These low Mg- and Ca-excess values translate to Mg/Ca ratio averages of 1.03, 1.03, and 0.97 for microspar, zoned, and saddle dolomite phases, respectively (Table S2 in supplementary material). These values represent stoichiometric microspar and zoned dolomite, and Ca-excess saddle dolomite. The EPMA error for Ca is 0.25% and Mg is 0.47%, so reported values may be closer to stoichiometric than shown.

4.3.2. Carbonate $\delta^{18}O$ and $\delta^{13}C$ composition

Isotope analysis reveals relatively low values of $\delta^{18}O_{dolo}$ (‰ VPDB) and $\delta^{13}C_{dolo}$ (‰ VPDB). Oxygen isotopes ($\delta^{18}O_{dolo}$) range from -18.23‰ to -6.05‰ referenced to VPDB ($1\sigma = 2.79$‰) (Fig. 9, Table S1 in supplementary material). Inorganic carbon isotopes ($\delta^{13}C_{dolo}$) range from -6.54‰ to -0.84‰ referenced to VPDB ($1\sigma = 1.39$‰).

4.3.3. Total organic carbon and organic $\delta^{13}C$ composition

Elemental analysis shows that nitrogen abundance is below detection limits, and organic carbon abundance ranges from 0.025 to 0.484 wt% ($1\sigma = 0.142$ wt%) (Fig. 10, Table S1 in supplementary material). Values of $\delta^{13}C_{org}$ for organic compounds range from -28.25‰ to -25.73‰ referenced to VPDB ($1\sigma = 0.81$‰).

4.4. Confocal Raman microscopy

Raman mapping of thin sections reveals that organic carbon, identified by D and G spectral bands, is exclusively associated with the microspar dolomite and commonly situated at or near grain boundaries (Fig. 11). The D and G peaks show slight variations among peak intensity, peak area, and peak position (Fig. 12, Tables S3a and S3b in supplementary material). D and G peak shifts within spectral maps are observed in samples A5 and A16, respectively (Fig. 11C, Figs. S8a, S8b in supplementary material). *T*-test results reveal a statistical difference ($p<0.05$) in D1 band positions between stromatolite and thrombolite samples compared to oolitic samples (Fig. S1b in supplementary material). The peak shifts in the thrombolite (in D band) and stromatolite (in G band) samples A5 and A16, spatially overlap and occur within the same mapped areas

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(Figs. S8aC-E in supplementary material), suggesting there are co-occurrences of different degrees of the organic matter crystallinity within the same analyzed area.

Data quality assessment was done by comparing the computer-fitted cluster method to the more commonly used manually-fitted Gaussian method. Comparison shows that the results from the two methods are in overall good agreement, but the Gaussian fit method causes a broader range and relative standard deviation (Table 3). Cluster analysis shows D/G peak intensity ratios average 1.00 ± 0.05; D-FWHM averages 68 ± 34; and D-position averages 1334 ± 12. Gaussian fit analysis shows D/G peak intensity ratios average 1.02 ± 0.75; D-FWHM averages 47 ± 57; and D-position averages 1335 ± 26. All peak parameter results from the cluster and Gaussian fit methods are presented in the supplementary material (Tables S3a, S3b).

Temperatures derived from Raman geothermometry average 293 ± 61°C, and D1 band variations show distinct grouping within samples in both peak position (rel cm^{-1}) and FWHM (Fig. 12). The sample grouping corresponds to different temperature ranges: temperature average of 314 ± 25°C for oolitic samples; temperature average of 313 ± 18°C for stromatolite samples; and temperature average of 271 ± 27°C for thrombolite samples (Table 4). *T*-test results for fitting E method reveal a statistical difference ($p<0.05$) among the temperature groups of stromatolite (A16), oolitic (A7, B11, B12a) and thrombolite (A5) samples, while fitting F method shows no statistical difference between facies (Figs. S2a, S2b in supplementary material).

5. DISCUSSION

Characterization of the dolomitization process (including fluid composition and temperature) is fundamentally important when attempting to decipher the origins and alteration levels of organic matter within the host rock. The following sections characterize the depositional environment and conditions for subsequent dolomitization based on outcrop observations (structural and textural features), petrological (microtextural and cross-cutting relationships), geochemical data, and Raman spectroscopy.

5.1. Sedimentary facies and paleoenvironment

Exposed stratigraphy displays a regression sequence where subtidal high energy ooid shoals transition to intertidal low energy silty lagoonal waters that progress to a supratidal mudcracked tidal flat (Fig. 1C). The dolomitized oolitic grainstone beds were likely ooid shoals that inhibited the incursion of marine waters and formed lower energy lagoons in which overlying finer, silt-sized deposits were formed. On top of the lagoonal deposits are finely laminated domal stromatolites in the beds which also include mudcracks, collapse breccias, and tidal channel deposits, indicative of nearshore, subaerial exposure (Fig. 2). The presence of edgewise conglomerate rip-up clasts, jumbled intraclasts, and torn laminae in small stromatolite domes (Fig. 2E) suggest occurrences of high energy storms in nearshore and shallow water. Some layers of lagoonal dolosiltite contain sparse ooids, referred to as oolitic dolosiltite (Table 2). At the top of the outcrop, on the southwest side and adjacent to the large domal stromatolites, are extensive syneresis cracks (Fig. 2N). Syneresis cracks form subaqueously (Plummer and Gostin, 1981), indicating that water levels may have been deeper within the same stratigraphic layer (southwest from the stromatolites). The Allentown Formation’s sedimentological features are consistent with a shallowing peritidal lithological sequence from a transitional marginal-marine setting (Wilson, 1975; Flügel, 2004).

5.1.1. Microtexture and mineralogy

The dark-to-light grey and black stromatolite laminae are characteristic features formed as a result of different mineral assemblages. The data indicate that the black laminae are enriched in silicate minerals, such as detrital quartz and feldspars (Fig. S7 in supplementary material). The black laminae (<1 mm thick) may have formed during the periods of minor marine flooding when only the smallest particles were carried by low energy waters across the microbial mats (Wilson, 1975). Additionally, scattered siliceous fine grains are found along some dark and light grey stromatolitic laminae, a feature characteristic in regression carbonate evaporitic cycles (Wilson, 1975). Previous Allentown studies (Buie, 1932; Miller, 1941) have attributed the dark-to-light grey color variation to laminae with different concentrations of organic matter and magnesium, stating that beds with high magnesium weather to a lighter color, while beds with lower magnesium and more organic content undergo less change in color during weathering. We have not found any evidence of differences in magnesium content within dark-to-light grey layers, and Raman mapping of organics does not show an increased concentration of organic carbon content among dark grey and black laminae compared to light grey laminae.

Accessory minerals such as pyrite, quartz, and feldspars are most abundant in chert lenses and feldspathic layers. Rounded pyrite and feldspar grains observed in petrological and SEM micrographs indicate their detrital origin (Figs. 7H, S6C in supplementary material). The detritus materials are likely fluvial (Dalton et al., 2014) and aeolian (Miller, 1941) sediments transported by streams and wind, respectively. Ti-oxide phases include anatase and rutile, the former being the most abundant, and these minerals are scattered throughout the samples and are not limited to any specific layer(s). Fe-oxides are less common than Ti-oxides and occur sporadically throughout the samples. The deformed (warped) Fe- and Ti-oxides observed in this study (Fig. S6A in supplementary material) were likely altered in their original environment before final deposition and therefore are not indicative of the deposition settings of the study area. Fine-grained dolomite crystals, finely layered stromatolitic laminae, channel deposits with rip-up clasts, and detrital feldspars and quartz are microtextures frequently observed in tidal flat environments (Siedlecka, 1978; MacNaughton et al., 2019).

5.2. Dolomitization

Traces of precursory limestone of the Allentown Formation have not been identified (Dalton et al., 2014), so the baseline for comparison of dolomitized geochemistry and setting to that of the Cambrian marine setting is missing, which makes interpretations of diagenetic stages or recrystallization settings more difficult. There is no evidence for non-stoichiometric metastable magnesium carbonate minerals that are presumed to form during initial dolomitization stages, indicating that the formation has been entirely replaced by dolomite.

Petrographic features, luminescence, and microprobe analyses suggest multistage dolomitization. Dolomite petrography shows three texturally different crystal phases that are compositionally different to one another (Fig. 4). Determining the order of dolomite crystal formation is essential to reconstruct the paragenetic sequence (Fig. 13) and to reveal if chemical, thermal, or textural overprinting by later crystal generations exists. The following sections discuss the interpreted formation of each phase of dolomite.

5.2.1. Dolomitizing Fluids

The composition of dolomitizing fluids can be constrained by the relative abundance of major and trace elements in dolomite, including the Mg/Ca ratio, Fe, Mn, Zn, Sr, and Si concentrations (Morrow, 1982; Tucker and Wright, 1990; Gasparrini et al., 2006; Zhang et al., 2009; Guido et al., 2018). The Si concentrations detected within the dolomite are not well understood and are rarely reported in literature. Silica was not detected in these areas using Raman spectroscopy, suggesting that Si is not sourced from submicron fluid inclusions or mineral coatings. Si detected by EPMA could have originated from dissolved silica in the seawater during the dolomite's formation (Ramseyer et al., 2013; Dong et al., 2015). The lack of detectable Sr in any of the dolomite phases may be the result of dolomitization in seawater with low Sr content (Vahrenkamp and Swart, 1990), or recrystallization (Land, 1980). Cambrian dolomites formed from seawater can have Sr compositions of <300 ppm (Vahrenkamp and Swart, 1990; Jiang et al., 2019), which is below EPMA detection limits at 0.03 wt%. Therefore, undetectable Sr (<300 ppm) is in line with that expected of dolomites formed from fluids with typical seawater Sr/Ca ratios (Vahrenkamp and Swart, 1990). This, along with the detection of Si, suggests that the Allentown microspar and zoned dolomite phases may have precipitated from seawater (Fig. 4F). Alternatively, it is common in burial diagenesis that Sr and Na concentrations decrease while Fe and Mn increase (Wright and Tucker, 1990; Warren, 2000). However, this continuous increase in Fe and Mn observed across all dolomite phases when coupled with the presence of saddle dolomite and stylolites indicate an increasing burial origin. The saddle dolomite phase that is enriched in Mn and Fe was likely produced from burial fluids when externally sourced fluids rich in Fe and Mn mixed with dolomitizing fluids that circulated through the host rock in a water-buffered system (Budd, 1997).

5.2.1.1. Microspar dolomite

Microspar dolomite (M) is a finely crystalline replacive dolomite with microspar-sized crystals (Folk, 1959). An average crystal size of 20 µm was estimated using confocal Raman microscopy. Microcrystalline textures in dolomite (<10 microns) are thought to be from fluids that are highly saturated with respect to dolomite (Sibley, 1991) and are common in early near-surface dolomitization (Moore, 1989; Sibley, 1991; Lukoczki et al., 2020; Ryan et al., 2020). This phase of dolomite exhibits nonplanar, irregular intercrystalline grain boundaries (Fig. S4 in supplementary material), which is common for crystal growth at temperatures greater than 50°C (Gregg and Sibley, 1984; Sibley and Gregg, 1987; Warren, 2000), however, this texture has also been observed in microspar formed in low temperature, subaerial environments in the presence of concentrated Mg ion solutions which enable rapid nucleation of crystals during dolomitization (Sibley and Gregg, 1987; Sijing et al., 2014). In either case, the limestone dolomitized early in the marginal marine setting that produced microspar dolomite, which is the dominant dolomite phase in the studied outcrop (Fig. S4 in supplementary material). The preservation of primary porosity (fenestral pores) and fine-scale stromatolitic laminae within microspar beds is evidence for early, near-surface dolomitization (Fig. 7). Therefore, the microspar dolomite is likely a result of rapid crystal growth under high fluid Mg/Ca ratios.

The CL spectral peaks at 389 nm and 650 nm (Fig. 4D) are due to intrinsic lattice defects in the CO_3^{2-} structure and the substitution of Mg^{2+} with Mn^{2+} into the carbonate lattice, respectively (Walker et al., 1989; Machel et al., 1991; Habermann et al., 1997; Richter et al., 2003).

Accordingly, the peak shift that is present at 389 nm (Fig. 4D) may be due to different types of crystallographic lattice defects, and if so, variations in crystallographic defects may account for the variations in CL colors of increasing wavelength from blue and grey, to gold (Fig. 4E).

5.2.1.2. Zoned dolomite

Zoned dolomite (Z) occurs as small rhombohedral shaped crystals that infill pore space within the microspar (M) dolomite (Fig. 5A), and larger cavity lining crystals that exhibit patchy rhombic cores in CL but not in plane polarized light (Fig. 5B). The rhombohedral cores are chemically distinct from the zonation bands that outline them. The cores exhibit the same blue, grey, and gold CL characteristics as the microspar and may represent penecontemporaneous formation with the microspar dolomite, from the same type of fluids (Fig. 5). Additionally, microspar and zoned dolomite contain trace amounts of Si (Fig. 4F) which also suggest the same formational fluids for both phases. The presence of patchy cores detected in CL, but not observable under plane polarized light (PPL), within some of the larger rhombic cores is not well understood. Kaczmarek and Sibley (2014) suggest this pattern may be derived from inhomogeneous fluids during crystal growth or recrystallization. Alternative explanations include multiple dolomite dissolution-precipitation phases (Sena et al., 2014), or inclusions (Budd, 1997). We do not see evidence for inhomogeneous fluids from EPMA line scans, and Raman did not detect any non-carbonate related peaks to explain inclusions, nor were inclusions observed within the crystals. Additionally, we do not have supporting evidence for dissolution-precipitation phases and therefore an interpretation based on direct evidence is not available at the moment.

The concentric pattern of zonation, that outlines the rhombic cores, is a result of primary crystal growth stages and relates to the fluctuating fluid chemistry during formation (Reeder, 1991; Budd, 1997). The crystal zones altered between Ca:Mg zones (light bands) and Fe:Mg zones (dark bands) indicating changes in Ca, Mg and Fe concentrations in dolomitizing fluids during the crystal growth (Figs. 5G, 6B). The dark bands are likely from Fe- and Mn-rich fluids that periodically entered the system during dolomitization.

5.2.1.3. Saddle dolomite

Ongoing, deeper burial produced late stage chemical compaction from overburden pressure resulting in stylolites and localized dissolution seams that are concentrated in the lagoonal facies and occur throughout the outcrop (Figs. 2B, O). The second stage of microfracturing produced fractures that later infilled with saddle dolomite (Fig. S5 in supplementary material). The dull luminescence of saddle dolomite (S), Fe-rich chemistry, and saddle shape are all features of late stage, high temperature dolomite formation (Machel, 1987; Radke and Mathis, 1980; Warren, 2000). Although there is no direct evidence for primary precipitation, the lack of floating particles of other minerals within the crystals, and the lack of irregular and sutured crystal boundaries, indicate that this is not a replacement phase (Radke and Mathis, 1980), but rather a primary precipitate during burial diagenesis. Possible penecontemporaneous formation of saddle dolomite and stylolites may be inferred from one crosscutting feature observed at the outcrop, where an overlying stylolite seemed collapsed into a large vug and is surrounded by the infilling saddle dolomite (Fig. 2Q). The saddle dolomite was likely formed in a water-buffered, isotopically open, system where Fe and Mn fluids were incorporated into the dolomite along with the Mg/Ca dolomitizing fluids (Budd, 1997). This final stage of burial diagenesis thermally overprinted the entire formation as revealed from organic carbon Raman D and G bands and previous CAI thermometry temperatures of the microspar dolomite (Table 4).

Based on petrographic features, CL, and EPMA, the three dolomite mineral phases are multi-generational and formed over three stages (Fig. 13). The first, second, and third generations of dolomite are microspar, zoned, and saddle, respectively.

5.2.2. Carbonate $\delta^{18}O$ and $\delta^{13}C$ composition

The low $\delta^{18}O_{dolo}$ values (-18.23‰ to -6.05‰ VPDB) reflect the deep burial diagenetic setting where the saddle dolomite formed (Haas et al., 2017; Al-Aasm and Crowe, 2018), in an isotopically open system and at higher temperatures than those of microspar and zoned dolomite formation (Fig. 9). A comparison of $\delta^{18}O_{dolo}$ values from the micro-drilled saddle and microspar dolomites shows that these values cannot be differentiated from bulk carbonate $\delta^{18}O_{dolo}$ values as they fall within the range of error bars (Fig. 9). The overlap of $\delta^{18}O_{dolo}$ values in dolomite phases (Fig. 9) might be explained by the formation of dolomite in an isotopically open system, or the resetting of isotopes during burial diagenesis or recrystallization under high temperatures (Land, 1980; Malone et al., 1994; Warren, 2000; Swart, 2015). Because burial diagenesis and recrystallization can result in the same signatures (Kaczmarek and Sibley, 2014), the Allentown dolomite, if recrystallized, would be significantly recrystallized with respect to depleted $\delta^{18}O$, and insignificantly recrystallized with respect to all other evaluated parameters (Machel, 1997). However, due to burial evidence (e.g., stylolites) the depleted $\delta^{18}O$ signature is likely more appropriately attributed to a burial diagenetic setting.

Variations in the origin of sedimentary materials and diagenesis should be taken into account when interpreting the $\delta^{13}C_{dolo}$ and $\delta^{13}C_{org}$ (Swart, 2015). The low $\delta^{13}C_{dolo}$ values (e.g., -6‰

VPDB) can indicate thoroughly altered isotopic compositions, as a result of diagenesis in an open system with high fluid:rock ratios (Lohmann, 1988; Sharp, 2007). This interpretation corresponds well with findings of the saddle dolomite in the Allentown samples. In order for saddle dolomite to form, the Fe and Mn-rich fluids needed to mix with the dolomitizing (Mg/Ca) fluids, which requires a high fluid:rock ratio most likely found in an open system (Brand and Veizer, 1980; Budd, 1997). This interpretation fits well with the Allentown $\delta^{13}C_{dolo}$ values (Fig. 9) and petrographic data. Alternatively, the low $\delta^{13}C_{dolo}$ values may derive from diagenetic alteration of oxidized organics in the system (Irwin et al., 1977; Lohmann, 1988; Schidlowski, 1988; Swart, 2015). The relatively low TOC (Table S1 in supplementary material) in the Allentown samples suggests that the organic signature is not likely the main, or single, influence on $\delta^{13}C_{dolo}$ values.

Coupling of $\delta^{18}O_{dolo}$ and $\delta^{13}C_{dolo}$ isotopes suggests contemporaneous alteration from the same source(s) for both $\delta^{18}O_{dolo}$ and $\delta^{13}C_{dolo}$ isotopes and all samples (Des Marais et al., 1992; Jiang et al., 2012) (Fig. 10B). The decoupled trends of $\delta^{13}C_{org}$ with $\delta^{18}O_{dolo}$ and $\delta^{13}C_{dolo}$ may be related to diagenetic alteration in a system that was not rock buffered and does not retain the original $\delta^{13}C_{dolo}$ values (Grotzinger et al., 2011; Jiang et al., 2012; Oehlert and Swart, 2014). The decoupling trend may occur due to variations in $\delta^{13}C_{org}$ values that may reflect mixed organic sources and diagenesis (Swart, 2015). Alternatively, the decoupled $\delta^{13}C_{org}$ and $\delta^{13}C_{dolo}$ values may imply relatively unaltered values that reflect values of the shallow water organic matter. In this scenario, a lack of correlation between the two values may occur due to the wide range of $\delta^{13}C$ from organic matter and a relatively narrow range in $\delta^{13}C$ from inorganic matter (Oehlert et al., 2012; Swart, 2015).

Jiang et al. (2012) reported decoupled $\delta^{13}C_{org}$ and $\delta^{13}C_{dolo}$ in Cambrian carbonates with low TOC (<0.1 wt%) and interpreted this as a result of diagenetic alteration of organic carbon, amplification of detrital organic carbon isotope signature in organic-poor carbonates, or both processes simultaneously. In an oxidizing setting, primary marine-derived organic carbon will degrade faster than terrestrial organics, and a low TOC (<0.2 wt%) with negative $\delta^{13}C_{org}$ can result (Oehlert and Swart, 2014). Evidence for various organic matter sources is supported by Raman data where D and G bands cluster based on the type of carbonate deposit (stromatolite, thrombolite, and oolitic) in tidal flat to shoal facies. Additionally, Lamb et al. (2006) showed that the provenance of organic matter sources varies within the peritidal sequence of a coastal environment. Organic sources may vary from near-shore tidal flats hosting a mix of marine and terrestrial tides and river derived organics, to ooid shoals dominated by in situ marine derived organic sources from isolated waters (Lamb et al., 2006). Based on the Allentown's depleted isotope measurements, low TOC, high temperature and burial settings (saddle dolomite, stylolites), the Allentown isotopic values are likely the result of diagenetic alteration of organic carbon and a detrital organic carbon isotope signature (Jiang et al., 2012).

5.3. Characterization of organic carbon

Organic carbon is characterized based on TOC, $\delta^{13}C_{org}$, Confocal Raman microscopy, and D and G peak analyses in order to determine spatial relationships between organic matter and minerals, alteration and thermal maturity of the organic carbon.

5.3.1. TOC and $\delta^{13}C_{org}$

The samples with higher TOC concentrations (0.484 to 0.286 wt%) have lighter $\delta^{13}C_{org}$ compositions (-28.25 to -27.45‰ relative to VPDB), while samples with lower TOC (0.025 to

0.120 wt%) show heavier $\delta^{13}C_{org}$ compositions (-27.44 to -25.73‰ relative to VPDB**)** (Fig. 10A). Such a decrease in TOC coupled with heavier $\delta^{13}C_{org}$ values may be indicative of post-depositional thermal degradation (McKirdy and Powell, 1974; Strauss and Beukes, 1996; Eigenbrode and Freeman, 2006; Jiang et al., 2012). The overall TOC values for transect A are relatively similar and the TOC values of transect B are varying, but the $\delta^{13}C_{org}$ values are similar (Fig. 10). This TOC diversity and $\delta^{13}C_{org}$ similarity suggests that thermal degradation is not a dominate factor in characterization of the organics.

Oolitic dolosiltite sample B9 has the highest TOC at 0.48 wt%; this sample contains rip-up clasts, which are characteristic for tidal channel deposits formed during storms. High TOC concentrations are also present in oolitic dolarenite samples B10, B11, and oolitic dolosiltite sample B13, all of which include evidence of high energy, storm events (rip-up clasts and edgewise conglomerates), which had capacity to deliver additional organic input within these layers.

The input of terrestrial organic matter washed in during storms in supra- to inter-tidal areas could had been incorporated in the sediments and stromatolitic laminae and in the thrombolites during deposition and contributed to the mixed pool signatures as seen in Raman (Fig. 11B) and $\delta^{13}C_{org}$ (Table S1 in supplementary material) data.

The measured values of $\delta^{13}C_{org}$ range from -25.73‰ to -28.25‰ relative to VPDB (Fig. 10B), which is broadly consistent with organic input from decaying organic matter or microbial metabolism (Irwin et al., 1977; Schidlowski, 1988; Lamb et al., 2006). The lighter values of oolitic samples (B transect) from the subtidal area likely reflect marine organics, while the heavier values of stromatolites and thrombolites likely include a mixture of terrestrial and marine organics (Torgersen and Chivas, 1985; Middelburg et al., 1997; Megens et al., 2002) (Fig. 10A, Table S1 in supplementary material).

5.3.2. Characterization of organic carbon based on confocal Raman spectroscopy

The spatial relation of the organic carbon to multi-generational dolomite is significant for determining if the carbon was already in place before dolomitization, and therefore syngenetic with the Cambrian stromatolites. Confocal Raman microscopy reveals that D and G bands of organic carbon are only present in the first generation of microspar dolomite and situated at or near grain boundaries (Fig. 11).

5.3.2.1. Raman thermometry

Oxygen isotope ratios are commonly used as a geothermometer to estimate the thermal history of carbonate minerals (Friedman and O’Neil, 1977; Land, 1983). However, the measured oxygen isotope values in this study reflect the late burial fluids from an open system that replaced the Cambrian isotopic seawater values and rendered them unusable (Land, 1980; Sharp, 2007).

The color alteration index (CAI) of conodont fossils is another method used as a geothermometer for sedimentary rocks (Epstein et al., 1977; Marshall et al., 2001). Conodont fossils found in Warren and Sussex counties of New Jersey Allentown outcrops have CAI (Epstein et al., 1977; Helsen et al., 1995) values of five indicating temperatures of at least 300°C and burial depths of at least 10 km (Harris et al., 1995). Burial depths around 10 km would correspond to burial pressure of at least 300 MPa (Tilley, 1924). Based on our outcrop observations and microtextural evidence, this outcrop had not been exposed to unidirectional stress that would align or elongate grains, but the pressure was likely lithostatic and uniform pressure derived from the burial process.

Calculated temperatures from Raman data yield a range 260 - 322°C (±30°C) for the Allentown organic carbon (Table 4). This type of organic carbon alteration is also reflected in the overall D and G band spectral characteristics, which exhibit D3 and D4 bands, and commonly have D and G bands that are equal in intensity (Table 3, Tables S3a, S3b in supplementary material). These newly calculated temperatures based on Raman data corroborate previously estimated temperatures based on conodont fossil CAI values.

Within the newly derived temperatures, two distinct groups of organic carbon differentiate (Table 4) stromatolite (A16) and oolitic samples (A7, B11, B12a) exhibit higher temperatures that average 314°C (±30°C) compared to thrombolite (A5) samples that average 271°C (±30°C). The D1 band positions, and associated temperatures are statistically different ($p<0.05$) between these rock types (Figs. S1b, S2 in supplementary material). Variations in D1 band characteristics between facies may be related to different types of initial organic matter (e.g., marine vs terrestrial), because the temperatures do not correlate with strata depth. For example, thrombolites record the lowest temperatures, while the stromatolites, which are coeval to or younger than thrombolites (Figs. 1C, 3), have higher average temperatures. The clear interpretation of these temperature differences is not attainable at the moment; however, based on the fact that they are separated as different facies, we may assume that different types of initial organic material contained in different facies may had altered differently despite the same diagenetic setting (Wopenka and Pasteris, 1993).

Other factors that may influence micron-scale variation of organic carbon include differential shear deformation (Bustin et al., 1995), artifacts from sample polishing (Beyssac et al., 2003), and mineral templating effects (van Zuilen et al., 2012). In this study, there is no evidence of shear stress or strain (i.e., grains are randomly oriented) and Raman spectra was taken beneath the sample surface to avoid polishing effects on carbon material. Additionally, dolomitization was pervasive and uniformly affected the organic carbon that is limited to the first generation of dolomite (microspar). The organic carbon in this study is not coating the grains as seen in mineral templating due to matrix effects in quartz matrix samples (e.g., van Zuilen et al., 2012) but rather situated between dolomite grain boundaries which is expected for organic material in carbonate rocks when trapped between grains during sediment lithification and mineral growth. The Raman heterogeneity observed in individual mapped areas of these samples (Fig. 11B-C) is therefore not caused by any known factors related to secondary geologic processes (i.e., diagenesis or metamorphism) and is likely due to primary biological variation related to variations from the original organic starting material (Foucher et al., 2015; Qu et al., 2015).

5.4. Organic carbon origins

Based on the spatial distribution and exclusive occurrence of organic material in the replacive microspar dolomite, it is very possible that the organic carbon was trapped in the samples during original limestone lithification, and thus was already in place during dolomitization (Fig. 11A, Figs. S8aC-E in supplementary material). This early dolomitization likely occurred from seawater supersaturated in Mg ions, that rapidly produced stoichiometric dolomite, a thermodynamically stable phase (Carpenter, 1980; Nordeng and Sibley, 1994; Mueller et al., 2019), which resisted further alteration during burial diagenesis and preserved the

Cambrian organics. The placement of organic carbon suggests it is indigenous and syngenetic to the primary fabric of the host rock. The Raman cluster maps show the peak variations overlap spatially within the same mapped area (Fig. 11B, Figs. S8aC-E in in supplementary material), suggesting all three varieties of organics were in place at the same time, matching the alteration temperature of the host rock.

Claims of biogenicity for organic carbon that is not associated with cellular morphological evidence should be approached with caution. The finding of organic carbon with an isotopic composition that may be indicative of microbial metabolism is not an explicit line of evidence for biogenicity (Braiser et al., 2004; De Gregorio and Sharp, 2006). Organic molecules can form from abiotic, autochthonous chemical reactions such as Fischer-Tropsch type processes in hydrothermal environments and decarbonation during metamorphism (McCollom and Seewald, 2006; Galvez et al., 2013; Bernard and Papineau, 2014). Although this null hypothesis cannot be fully rejected, there is no evidence of such hydrothermal processes in the outcropping area.

Evidence supporting a biogenic origin for Allentown organic carbon includes: (1) organic carbon is exclusive to the primary fabric (microspar dolomite) of the host rock which indicates a syngenetic origin, (2) the geological context is a marginal-marine setting that is a favorable habitat to marine organisms and overall rich in biological organic material, and one of the obvious sources of organics are numerous microbial stromatolite macrostructures observed at the outcrop, and (3) geochemical signals of $\delta^{13}C_{org}$ values are consistent with decaying organic matter or microbial metabolism (Irwin et al., 1977; Schidlowski, 1988; Lamb et al., 2006). Although the detection of disordered carbon by Raman spectroscopy is not alone indicative of biogenicity (Pasteris and Wopenka, 2003), the combined petrographic, sedimentary, and geochemical evidence from Allentown organic carbon supports a biogenic origin.

The degree of crystallinity in carbonaceous matter is affected by the type of organic matter and host rock composition during heating (Wopenka and Pasteris, 1993), therefore the D and G peak differences may be due to different types of organic starting material that altered, or decomposed, differently despite the same alteration setting (Lamb et al., 2006). The peak shifts in D and G band positions within the same mapped area (e.g., Fig. 11C) is indicative of three differently altered organic carbon molecules, which suggests different source pools of indigenous and syngenetic organic material. Lamb et al. (2006) reported organic matter in Holocene lagoonal and tidal flat sediments is mostly derived from suspended particulate organic matter such as plant detritus and phytoplankton from river and marine sources, respectively. This variation in tidal flat organics may potentially explain how three phases of organic carbon are found in the stromatolite and thrombolite samples (A16 and A5, respectively), while oolitic (A7, B11 and B12a) samples only have one carbon phase present (Fig. 11E, S8a in supplementary material). Since no nitrogen was detected by IRMS, characterization of organic sources based on C/N ratios (e.g., Lamb et al., 2006) is not possible. Instead, using the $\delta^{13}C_{org}$ values alone show an overlap of marine and freshwater organic carbon (Lamb et al., 2006).

6. CONCLUSIONS

Traditionally, secondary, stoichiometric, and ordered dolomite has been hypothesized to occur at either high temperatures or from multiple stages of recrystallization (Machel, 1978; Kupecz et al., 1993; Gregg et al., 2015) that would likely erase evidence of original texture, chemistry, and biology (Gregg and Sibley, 1984; Grotzinger and Knoll, 1999; Schopf, 1999; Warren, 2000). The results presented here indicate that stoichiometric and ordered dolomite can form within early dolomitization settings, undergo increasing temperature and burial diagenesis, and still retain syngenetic organic carbon. In summary:

- Outcrop scale observations (mudcracks, collapse breccia, rip-up clasts and edgewise conglomerates) and petrological microtextures characteristics (finely-laminated stromatolites, fenestral porosity, rip-up clasts, finely crystalline microspar dolomite) reveal that the Allentown depositional setting was a tidal flat along the Cambrian coastline where original calcium carbonate mineral precursors dolomitized early in a marginal marine setting.
- Bulk dolomite varies in cationic ordering from poorly to well ordered, and the stoichiometry varies from low Ca-excess to stoichiometric to low Mg-excess. Individual phases of dolomite are stoichiometric (microspar and zoned) and Ca-enriched (saddle).
- Geochemical characteristics recorded by each phase of dolomite suggest two dolomitization processes dominated: early dolomitization in the marginal marine setting and late dolomitization from deep burial diagenesis.
- Microspar and zoned dolomite phases formed by dolomitization in high Mg/Ca fluids, resulting in finely crystalline replacive dolomite crystals, and the preservation of primary depositional features such as fenestral porosity. Saddle dolomite formed by burial dolomitization as revealed by coarse void-filling crystals, dull luminescence, Fe and Mn enrichment, and low $\delta^{18}O_{dolo}$ values.
- Burial diagenesis likely thermally overprinted the microspar and zoned dolomite, as revealed by Raman thermometry.

- Raman D and G bands indicate greenschist-like thermal maturity of organic carbon within the formation which is in agreement with conodont fossil CAI geothermometry previously reported for the Allentown dolostone.
- Organic carbon is found at or near grain boundaries, exclusively within the first generation of microspar dolomite. This suggests the organics were in place when the grains of dolomite formed, indicating indigenous and syngenetic origins of the organic carbon within the Cambrian stromatolites.
- Identification by Raman spectroscopy of various pools of organic carbon was found in stromatolite, thrombolite, and oolitic deposits indicating that indigenous and syngenetic organic matter can be identified in many dolomitized facies.

This work shows that biosignature (e.g., organic carbon) preservation in carbonate environments extends beyond obvious microbial structures (e.g. stromatolites and thrombolites) and may also be preserved in shallow water environments that were rich in microbial life (e.g., coastal, marginal marine environments). This type of research is especially important when searching for life on other planets because microbial fossil preservation on Earth is rare, and different geologic environments and evolutionary histories on other planetary bodies will likely result in different signatures for life. Terrestrial analogs such as this study will allow for better interpretations of potential biosignatures in Martian carbonates, which may have undergone varying levels of alteration. Based on the data presented in this paper, the textural and mineralogical evidence that may be indicative of life and biosignature preservation in carbonate environments is not limited to silicified carbonates or obvious microbial structures (stromatolites), but extends to dolomitized carbonates and general shallow water settings, where fine-grained carbonate minerals indicate primary environments that are capable of preserving indigenous and syngenetic organic carbon. The Mars Perseverance rover has the ability to target fine-grained carbonate rock, such as the microspar dolomite in this study, for Raman analysis, and if carbon is detected, these may serve as high potential biosignatures to be cached for future sample return mission(s).

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DATA AVAILABILITY

Supplementary data related to this article can be found at http://dx.doi.org/10.17632/k57gbw78d9.4, hosted at Mendeley Data (Murphy et al., subm).

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