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Geochemistry of Late Ordovician dalmanelloid brachiopods from Laurentia: Testing the effects of paleolatitudinal gradient

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Abstract

Dalmanelloid brachiopod shells were collected from the Upper Ordovician Lexington Formation (lower Katian) of Kentucky, Sheguindah Shale (middle Katian) on the Manitoulin Island, Ontario, and the Stony Mountain Formation (upper Katian) in the Winnipeg area, Manitoba. They were investigated to test the hypothesis of paleo-latitudinal zonation of the shelly benthos. A multitechnique approach was applied to evaluate the petrographic and geochemical (isotopic and elemental) preservation of the secondary layer of shells. The preliminary conventional microscopy, cathodoluminescence (CL) and Scanning Electron Microscopy (SEM) confirmed the retention of primary shell ultrastructure (prismatic low-Mg calcite). The geochemical diagenesis proxies (e.g., Sr, Mn, Fe, and ΣREE) show insignificant correlations with the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, thus supporting the preservation of at least near-primary geochemical compositions. Among the three lots of shells, the mean $\delta^{18}\text{O}$ value is the highest in those from the Lexington Formation (-4.5 ± 0.3 ‰VPDB), lowest from the Stony Mountain (-6.8 ± 0.4 ‰VPDB), and intermediate from the Sheguindah shale (-6.0 ± 0.8 ‰VPDB). The relative gradient in $\delta^{18}\text{O}$ increase is in agreement with the paleo-latitudinal gradient, with Kentucky in subtropical, southern Ontario in mid-tropical, and southern Manitoba in subequatorial latitudes. The Lexington Formation shells also have the highest mean $\delta^{13}\text{C}$ value (0.8 ± 0.2 ‰VPDB) and relatively high P contents (170 ± 27 ppm), suggesting higher organic productivity, consistent with previous interpretation of frequent upwelling of nutrient-rich cool waters along the southeastern margin of Laurentia during the Katian. The Lexington shells also

have a lower mean Th/U (0.6 ± 0.6), which is consistent with blooming organic productivity that likely led to more consumption of oxygen in the water column.

Key words: Stable O and C isotopes, dalmanelloid brachiopods, Late Ordovician, Laurentia, paleolatitudinal gradient

1. Introduction

The abundance of planktonic and benthic foraminifers in the Cenozoic marine carbonates provided suitable material for the geochemical studies that reconstructed the environmental variations during that time interval (e.g., Lear et al. 2000). However, this is not the case for the Paleozoic where calcareous shells were relatively less abundant. Well-preserved fossil brachiopods, that were abundant in the Paleozoic seas, have been proven to retain reliable geochemical proxies for investigating the paleo-environmental conditions such as paleolatitude (climate), oceanography, and seawater composition (e.g. Veizer et al. 1999; Angiolini et al. 2007, 2009; Mii et al. 2013). Their primary/near-primary oxygen-isotope compositions provide an archive of the paleotemperature of ambient seawater in which they lived, which reflects the dominant climatic and depth conditions (e.g., Azmy et al. 1998, 2006). Most of calcitic brachiopods precipitate their shells as low-Mg calcite, a stable phase of CaCO_3 , in isotopic equilibrium with the seawater (e.g., Carpenter and Lohmann 1995; Veizer et al. 1999; Brand et al. 2003; Takizawa et al. 2017). The low-Mg calcite, relative to other CaCO_3 phases, resists diagenetic alteration and therefore, at times, retains the primary/near-primary elemental and isotopic geochemical signatures in equilibrium with the seawater.

The current study investigates Late Ordovician brachiopod shells from shallow shelf and epeiric-sea depositional environments, collected from three different basins across Laurentia that were located at paleolatitudes ranging from the subtropics to the equator. The main objectives of the current study are to:

- (1) evaluate the preservation of the investigated brachiopods,
- (2) study the influence of the paleolatitude on the isotopic compositions of those shells,
- and
- (3) explore the influence of paleoenvironment, if applicable, on the trace element compositions of brachiopods.

2. Material and geologic background

The dalmanelloid brachiopods used for this study are ideal because of their general abundance and cosmopolitan distribution across a wide range of paleoecological and paleogeographical settings. This makes it easy to compare geochemical signatures within shells of the same taxonomic group. They were collected from Upper Ordovician shallow-water sediments of three basins (Fig. 1) that were located at different paleolatitudes from the cool-water subtropics to the warm-water equator during the Late Ordovician (Cocks and Torsvik 2011; Jin et al. 2013; Jin and Harper 2016; Sproat and Jin 2017).

Heterorthina macfarlani Neuman, 1967 is from the Logana Member, Lexington Formation, of Chatfieldian (early Katian) age, collected from a roadcut section on Route 127 (Owenton Road) north of Frankfort, Kentucky (UTM Zone 16N, 0687945E, 4232384N).

The Lexington Formation consists of alternating weathering-resistant limestone and soft, poorly cemented micritic mudstone, accumulated in the Cincinnati Arch area, paleogeographically located on the southeastern margin of the Laurentia (ca. 20°S during the

Late Ordovician), with the Seabee Trough to the northwest and the Taconic Foreland Basin to the southeast (McLaughlin et al. 2008).

The paleogeographical distribution of *Heterothina* in North America was restricted largely to the high paleotropics in the southern hemisphere. Globally, *Heterothina* occurred most commonly in the cold-water environment of temperate peri-Gondwana from late Middle Ordovician to Late Ordovician. This led Jin and Harper (2015) to regard the genus as a cool-water brachiopod genus.

In the Cincinnati Arch area, the Sandbian-Katian boundary is thought to be within the basal part of the Curdsville Member of the Lexington Formation, marking a change from tropical warm-water carbonate to cool-water, mixed carbonate-siliciclastic deposition (Holland and Patzkowsky 1996; Pope and Read 1997; McLaughlin et al. 2008). The episodic occurrences of *Heterothina* in the muddy facies of Logana Member (lower Lexington Limestone) was interpreted by Jin and Harper (2015) as opportunistic invasions following cool-water upwelling from the Seabee Trough or the Appalachian Basin. The Logana Member was the thickest package of micritic mudstone and calcareous shale in the Lexington Formation deposited during a sea-level highstand (McLaughlin et al. 2008).

The commonly squashed shells of *Cincinnetina* sp. are from the Sheguindah Shale (Copper 1978) exposed at the Highway 6 roadside section at Strawberry Creek (UTM 17T, 429668E, 5087487N), Manitoulin Island, Ontario. These strata were considered equivalent to the Blue Mountain Formation (mid-Katian age) by Brunton et al. (2009). The Sheguindah Shale is greyish brown to green, intercalated with thin- to medium-bedded dolowackestone to dolograstone. Most of the Sheguindah shaly strata are non-fossiliferous (as are the black shales of the underlying Lindsay Formation), but *Cincinnetina* occurs with abundant delicate,

102 trepostome bryozoans, and gastropods at several horizons. This shale unit is approximately
103 coeval with the Kope Formation in the Cincinnati Arch areas, where *Cincinnetina* occurs in
104 abundance. The shale-dominated strata, together with its underlying black shales of the upper
105 Lindsay Formation, suggest an episode of relatively deep-water depositional environments, with
106 local and episodic anoxia.

107 The shells of *Diceromyonia storeya* (Okulitch, 1943) were collected from the Gunn
108 Member of the Stony Mountain Formation (upper Katian), southern Manitoba (Winnipeg area)
109 where the Gunn Member is the basal unit of the Stony Mountain Penitentiary (50°04'56"N,
110 97°12'42"W) and rich in *Diceromyonia* brachiopod shells (cf. Jin and Zhan 2001). During the
111 Late Ordovician, southern Manitoba was located in the northeastern part of the roughly circular,
112 intracratonic Williston Basin. The member consists of reddish-weathering, argillaceous
113 wackestones and packstones, with abundant brachiopods and corals. Many shaly beds in the
114 member weather recessively. Bioturbation and relatively well-preserved burrows (e.g.
115 *Chondrites*) are common in the Gunn Members. The lithology and fauna, therefore, indicates a
116 relatively deep-water (near storm wave base), open-marine environment.

117 3. Methodology

118 The investigated Upper Ordovician dalmanelloid brachiopods (~ 1 cm long; Fig. 2a) were
119 selected following the protocol described in Azmy et al. (1998). A preliminary exam with a hand
120 lens allowed the elimination of recrystallized shells. Complete shells were cut, through the umbo,
121 for thin sections and studied under polarizing microscope. Only samples having fibrous
122 secondary layer were considered for more screening. Also, thin sections were examined under a
123 cathodoluminoscope to evaluate the petrographic preservation. Cathodoluminescence (CL) was
124 performed by a ChromaCL detector (Gatan Inc., Pleasanton, CA, USA) attached to a Quanta 400

125 SEM (FEI, Hillsboro, OR, USA), which is equipped with an energy dispersive X-ray (EDS)
126 microanalytical system (Bruker AXS, XFlash Detector 4010; Bruker Corporation, Billerica, MA,
127 USA). The CL system is equipped with three detectors that correspond to red, green and blue
128 colors, thus showing image colors that are very close to those of real luminescence emitted from
129 the studied samples (e.g., Olanipekun and Azmy 2017). The images were obtained at 15 kV
130 acceleration voltage and 13 nA beam current.

131 The mirror-image slabs of samples with preserved secondary layer were cleaned with de-
132 ionized water and dried before microsampling under a binocular microscopes. The primary layer
133 was carefully and gently removed (shaved) using a slow microdrill under binocular microscope
134 until the fibrous secondary layer was exposed. It was difficult to cut a thin section from the
135 smaller (<1 cm) and thin delicate shells and individual valves but it was possible to remove the
136 primary layer and/or the altered topmost part of the secondary layer by a microdrill to expose the
137 secondary layer and confirm the preservation of its fibrous structure under microscope before
138 microsampling. Small specks of the secondary layer were extracted under a binocular
139 microscope and examined under the Scanning Electron Microscope (SEM) to evaluate the
140 preservation of the shell ultrastructure (e.g., Azmy et al. 1998, 2006; Veizer et al. 1999). The
141 preliminary evaluation of shells led to the selection of 59 samples, with high petrographic
142 preservation, for geochemical analyses (Appendix 1).

143 For C- and O-isotope analyses, ~ 200 µg of powder sample, microsampled from the fibrous
144 secondary layer in the middle area of the shell to avoid the umbo zone (e.g., Takizawa et al.
145 2017), was reacted in an inert atmosphere with ultrapure concentrated (100%) orthophosphoric
146 acid at 70° C in a Thermo–Finnigan GasBench II. The liberated CO₂ was automatically delivered
147 to a ThermoFinnigan DELTA V plus isotope ratio mass spectrometer in a stream of helium,

where the gas was ionized and measured for isotope ratios. Uncertainties of better than 0.1 ‰ (2 σ) for the analyses were determined by repeated measurements of NBS-19 ($\delta^{18}\text{O} = -2.20$ ‰ and $\delta^{13}\text{C} = +1.95$ ‰ vs. VPDB) and L-SVECS ($\delta^{18}\text{O} = -26.64$ ‰ and $\delta^{13}\text{C} = -46.48$ ‰ vs. VPDB).

For elemental analyses, the chemical composition of the fibrous secondary layer was directly measured by using a LA-ICPMS because of the small size of shells and the thickness of the targeted layer of the shell. The measurements were performed with a GeoLas 193nm ArF excimer laser (Coherent, Göttingen, Germany) coupled with an Element XR (Thermo Fisher Scientific, Bremen, Germany). The ICP-MS was daily tuned for high sensitivity and low oxide formation rate ($\text{ThO}^+/\text{Th}^+ < 0.3\%$). The laser was operated with a repetition rate of 5 Hz, an energy density of 4 J/cm², a crater size of 80 μm , and a carrier gas flow of 1 L/min of He. Fifty pre-ablation pulses were applied prior to each analyses to remove the primary layer of the shell and/or clean the topmost part of the secondary layer, the background was recorded for 30 s and ablation was performed for 50 s. The NIST SRM 610 was used for standardization and MACS-1 as a quality control standard. Data evaluation was done with SILLS (Guillong et al. 2008) and the relative uncertainties of the measurements are better than 5% of the reported concentrations. Calcium (^{42}Ca) was used as a reference ion and calcium concentration was assumed to be 40%.

4. Results

Petrographic examinations indicate the investigated shells had fibrous secondary layers that were not exposed to significant alteration (Fig. 2b–c) and exhibit dull luminescence (Fig. 2d). The SEM images show highly preserved calcite prisms with insignificant dissolution features (Fig. 2c, e).

The geochemical characteristics of the investigated shells are tabulated in Appendix 1 and their statistics are summarized in Table 1. The investigated shells have mean Mg contents of 3191 ± 935 ppm and the Stony Mountain Formation shells have the lowest Mg contents (2177 ± 277 ppm) compared with their counterparts from the Sheguindah Shale and Lexington Formation (3922 ± 722 ppm and 3140 ± 480 ppm, respectively). The Sr contents of the entire population vary between 448 and 1666 ppm (1189 ± 364 ppm), whereas their Mn counterparts vary between 31 and 386 ppm (135 ± 86 ppm) and they exhibit insignificant correlation ($R^2 = 0.04$; Fig. 3a). The Mn/Sr ratios vary between 0.02 and 0.37 (0.13 ± 0.10) exhibit insignificant correlation ($R^2 = 0.005$) with their $\delta^{18}\text{O}$ counterparts (Fig. 3b). Also, the Fe contents (298 ± 245 ppm, Table 1) have insignificant correlation ($R^2 = 0.02$) with those of $\delta^{18}\text{O}$ (Fig. 3c) and similarly the total REE contents ($\sum\text{REE} = 28.5 \pm 28.8$ ppm; $R^2 = 0.02$ Appendix 1; Table 1; Fig. 3d). The $\delta^{13}\text{C}$ values vary between -1.6 and +1.1 ‰VPDB (0.0 ± 0.8 ‰VPDB; Table 1). Similar general poor correlations ($R^2 < 0.1$) have been found for the Sr, Mn, Fe, Al, and $\sum\text{REE}$ with their $\delta^{13}\text{C}$ counterparts (Appendix 1).

Most of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values fall within the range suggested for the best-preserved brachiopod shells of the Late Ordovician (Fig. 4) immediately before the latest Ordovician (Hirnantian) glaciation (Veizer et al. 1999).

5. Discussion

The modern brachiopod shell generally consists of three layers: an outer organic periostracum, a middle few-microns thick granular calcitic primary layer, and an inner secondary layer composed of fibrous low-Mg calcite. In some families (e.g., pentamerids), a tertiary (innermost) layer of prismatic calcite may occur (McKinnon 1974). It has been well established that the fibrous layer, and the tertiary prismatic too, are precipitated in isotopic equilibrium with

the ambient seawater (e.g., Lowenstam 1961; Carpenter and Lohmann 1995; Brand et al. 2003). The low-Mg calcite of the fibrous layer is the most stable phase of CaCO_3 that may resist alteration during burial history (Veizer et al. 1999) although it is not entirely immune from diagenesis. This makes the fossil brachiopod shells among the ideal materials for the reconstruction of the paleoenvironmental (climatic and oceanographic) conditions that dominated during the Earth's history (e.g., Veizer et al. 1999; Takizawa et al. 2017). Therefore, the evaluation of petrographic and geochemical preservation of the fibrous secondary layer is essential for the construction of the paleoenvironmental conditions.

Shell preservation

The examined material of the current study was selected from the well-preserved non-luminescent fibrous secondary layer of dalmanellids (Fig. 2b), where the primary layer and altered material were removed either mechanically (shaved by microdrill under a binocular microscope to expose the fibrous secondary layer) for isotope analyses or by pre-ablation (using the laser beam of the LA-ICPMS) for trace element analyses. Although it is almost impossible that ancient carbonates, particularly those from the Paleozoic, remain entirely unaffected by diagenetic fluids through their burial history, the degree of alteration is at times restricted and thus leaving the carbonates with minimum/insignificant recrystallization. The good petrographic preservation of the fibrous secondary layer of selected brachiopod shells was confirmed by the preliminary examination of thin sections under conventional polarizing microscope (Fig. 2b) and the dull to no luminescence under cold cathodoluminescence (Fig. 2c) as well as the SEM images of clean low-Mg calcite fibers (prisms) showing insignificant dissolution features or precipitation of diagenetic cements between prisms (e.g., Casella et al. 2018; Fig. 2c, e). Luminescence in carbonates is mainly activated by high concentrations of Mn but quenched by high Fe contents

(Machel and Burton 1991). Although dull CL may reflect relative preservation of primary geochemical signatures and bright CL is exhibited by altered phase (Fig. 2c-d), diagenetic carbonates (e.g., late burial cements) might still exhibit no luminescence due to high Fe contents (Rush and Chafetz 1990). Therefore, cathodoluminescence is suggested to be used with caution and has to be complemented by additional screening tests (Brand et al. 2011). However, the good preservation of the ultrastructure of the low-Mg fibrous calcite would argue against the enrichment of Fe, which may require an aggressive dissolution-precipitation process at high water/interaction ratios usually associated with aggrading neomorphism and loss of primary sedimentary fabric (Banner and Hanson 1990).

It is well established that diagenesis of carbonates is associated with changes in the primary geochemical composition such as depletion in the Sr and $\delta^{18}\text{O}$ signatures and enrichment in others such as Mn, and Fe (Veizer 1983; Veizer et al. 1999). The mean Sr and Mn values of the shells from the Lexington Formation (1310 ± 526 ppm and 176 ± 151 ppm, respectively) and Sheguindah Shale (1434 ± 106 ppm and 127 ± 64 ppm, respectively; Table 1) are comparable but their counterparts from the Stony Mountain Formation are slightly lower (740 ± 245 ppm and 116 ± 30 ppm, respectively; Table 1). Thus, the lower Mn contents of the Stony Mountain Formation may still argue against significant alteration. Also, all of the investigated fossil shells have Sr contents that fall within the range documented for their modern counterparts (Brand et al. 2003) and similarly their Mn counterparts except for a few samples (Fig. 3a). This suggests insignificant influence of diagenesis particularly when the general correlation of the Mn/Sr values with their $\delta^{18}\text{O}$ counterparts is very poor ($R^2 = 0.007$; Fig 3b) and the SEM images of those shells show high preservation of shell ultrastructure (Fig. 2d).

In addition, the shells from the Stony Mountain Formation have the lowest Fe contents (174 ± 74 ppm; Table 1) and Fe values from all shells exhibit very poor correlation with their $\delta^{18}\text{O}$ counterparts (Fig. 3c). The ΣREE concentrations have recently found to be enriched in carbonates with diagenesis (Azmy et al. 2011) but yet they exhibit very poor correlations with the $\delta^{18}\text{O}$ values ($R^2 = 0.02$; Fig. 3d), which supports the preservation of at least near-primary $\delta^{18}\text{O}$ signatures.

The impact of diagenesis on the alteration of the $\delta^{18}\text{O}$ composition of carbonates is expected to be much higher than that on the $\delta^{13}\text{C}$ because the diagenetic fluid, in many cases, does not have enough CO_2 to reset the C-isotope composition of the calcite, which leads to the preservation of at least near-primary $\delta^{13}\text{C}$ signatures of carbonates (e.g., Veizer et al. 1999; Azmy 2018). On the contrary, the diagenetic fluids are basically water and their O-isotope composition resets the $\delta^{18}\text{O}$ of carbonates quickly at variable degrees depending on the water/rock interaction ratio. Thus, the alteration of the $\delta^{13}\text{C}$ composition of brachiopod fossil shells requires high water/rock interaction ratios and results in significant recrystallization and loss of the fibrous fabric of the secondary layer, which is inconsistent with preservation of the ultrastructure (fibrous calcite prisms) shown by the SEM images (Fig. 2c, e). Thus, the $\delta^{13}\text{C}$ signatures of the examined shells are also well preserved and at least near-primary.

Generally speaking, except for few samples, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the investigated shells (Fig. 4) fall within the average composition documented for the Late Ordovician well-preserved fossil brachiopod shells (Veizer et al. 1999), which is consistent with insignificant alteration.

In summary, the petrographic characteristics of the fibrous secondary layer of the investigated fossil shells and their geochemical composition support minimum influence of

diagenetic alteration and preservation of at least near-primary isotopic and elemental geochemical compositions.

Paleolatitudinal effect

The O-isotope composition of calcite is controlled by the temperature of its parent fluid (e.g., Faure and Mensing 2005) and has been utilized in biogenic calcite as a proxy of paleoclimate and temperature of seawater (e.g., Veizer et al. 1999; Brand et al. 2015; Jones et al. 2015; Vihtakari et al. 2016; Takizawa et al. 2017). Most of the brachiopod genera are believed to have no vital effect on their $\delta^{18}\text{O}$ composition particularly when samples are selected from the middle part of the shell (Auclair et al. 2003; Takizawa et al. 2017) and no vital control has been documented for fossil shells from the Paleozoic (e.g., Veizer et al. 1999).

Unlike modern brachiopods that are most common in relatively deep and/or cool marine waters (e.g., Brand et al. 2003; Brand et al. 2015; Zaky et al. 2016), the Paleozoic brachiopods were more abundant and diverse in tropical to subtropical marine shelf environments (e.g., Clarkson 1993; Veizer et al. 1999). The brachiopod shells used in this study lived in shallow-water shelf or epeiric-sea settings during the Late Ordovician (e.g., Cocks and Torsvik 2012; McLaughlin et al. 2008; Jin and Harper 2015; Sproat and Jin 2017). The paleogeographic reconstructions (Cocks and Scotese 1991; Cocks and Torsvik 2011; Jin et al. 2013) suggest that the Lexington Formation accumulated in the higher paleotropics, whereas the Stoney Mountain Formation close to the equator, and the Sheguidah Shale in the mid-tropics (Fig. 1). The mean $\delta^{18}\text{O}$ value of the studied shells from the Lexington Formation (-4.5 ± 0.3 ‰ VPDB) is the highest, from the Stony Mountain Formation the lowest (-6.8 ± 0.4 ‰ VPDB), and from the Sheguindah Shale slightly higher than that of the Stony Mountain shells (-6.0 ± 0.8 ‰ VPDB). Thus, the variations in their mean $\delta^{18}\text{O}$ values are consistent with previous paleontological and

paleogeographic reconstructions (e.g., Cocks and Torsvik 2011; Jin and Harper 2015). A cool-water depositional environment, for example, has been suggested in several previous studies on the Lexington Formation based on sedimentological, paleontological, and paleogeographic data (e.g., Ettenson 2010; Servais et al. 2014; Jin and Harper 2016). The sub-equatorial setting of the Stony Mountain Formation in southern Manitoba (northeastern margin of the Williston Basin) has been discussed in detail based on paleogeographic, sedimentological, and paleontological data (e.g., Cocks and Torsvik 2011; Jin et al. 2013).

The tropical shelf water have generally homogenous temperatures and a well-mixed water column (e.g., Hays and Grossman 1991), except for a few hurricane-free equatorial areas with strong cold water upwelling, such as in the Eastern Equatorial Pacific Cold Tongue (for a recent summary see Jin et al. 2018). With the generally high degree of pristine preservation of the examined shells, it is possible to estimate the temperature of the ambient seawater. Early Paleozoic brachiopods, particularly those from the Late Ordovician and Silurian, have been known to dwell in warm shallow shelf environments and many were found associated with reefs, which are known to be stenothermal and stenohaline (e.g., Copper and Brunton 1991). Assuming that the investigated brachiopods, particularly those from the Sheguindah Shale and Stony Mountain Formation with the relatively lower mean $\delta^{18}\text{O}$ values (Table 1), lived in warm shallow water similar to our present day environment at temperature approximately between 18° and 30° C and considering the $\delta^{18}\text{O}$ mean values of the investigated shells between -4.5 ‰PVDB (relatively higher paleolatitude and cooler water) and -6.8 ‰VPDB (lower paleolatitude and warmer water), the expected seawater $\delta^{18}\text{O}$ composition will be approximately -3 ‰VSMOW (Fig. 5; Friedman and O'Neil 1977). This is consistent with the estimates documented in earlier studies for the Ordovician (e.g., Shields et al. 2003) and Silurian seawaters (-3.5 to -2.5 ‰

VSMOW; Azmy et al. 1998), particularly for the Late Ordovician towards the terminal glaciation, as well as with the evolution of the isotopic composition of seawater throughout the geologic history (Veizer et al. 1999).

Paleoenvironment

Variations in seawater nutrient levels control the organic productivity and are generally associated with changes in trace element concentrations in sediments due to inputs of terrestrial material and/or changes in redox conditions (e.g., Wignall and Twitchett 1996; Kimura et al. 2005; Arnaboldi and Meyers 2007; Śliwiński et al. 2010; Dickson et al. 2012). Therefore, the changes in $\delta^{13}\text{C}$ of shell calcite are expected to reflect relative changes in organic productivity and paleoredox conditions. The Lexington Formation shells of the higher paleolatitude (relatively colder) has the highest mean $\delta^{13}\text{C}$ values (0.8 ± 0.2 ‰VPDB; Table 1) compared with those of the Sheguindah Shale and Stony Mountain counterparts of the lower paleolatitudes (-0.4 ± 0.6 ‰VPDB and -0.9 ± 0.5 ‰VPDB, respectively; Table 1). This may suggest higher organic productivity in the relatively colder paleolatitudes due to higher nutrients in the water, which is consistent with the scenario of upwelling currents suggested by an earlier study (Jin and Harper 2016). Riverine inputs might have contributed to the effect too.

Phosphorous has been utilized as a proxy for bioproductivity (e.g., Morel et al. 2004; Śliwiński et al. 2010). The Lexington Formation shells from the higher paleolatitudes (relatively colder seawater) have mean P content (170 ± 27 ppm, Table 1) higher than that of the Stony Mountain Formation shells (79 ± 58 ppm) from the lower paleolatitudes (warmer equatorial seawater) and comparable to that of the Sheguindah Shale (173 ± 57 ppm) from intermediate paleolatitudes. The high P contents of the relatively higher paleolatitudes favours the earlier suggested upwelling scenario (Jin and Harper 2016).

Levels of oxygen in the water column control the solubility of redox sensitive elements in seawater and accordingly their degree of enrichment in marine sediments (e.g., Wignall and Twitchett 1996; Kimura et al. 2005; Arnaboldi et al. 2007). In oxidizing environments, uranium ions maintain the higher oxidation state (U^{+6}) and form uranyl carbonate, which is soluble in water. On the other hand, in reducing conditions, they retain the lower oxidation state (U^{+4}) and form the insoluble uranous fluoride, which is trapped into marine carbonates (Wignall and Twitchett 1996). Unlike U, Th is not affected by redox conditions in the water column and occurs permanently in the insoluble Th^{+4} state. Accordingly, the Th/U ratio increases in sediments with increasing oxidizing conditions and has been therefore used as a proxy for environmental redox conditions. The lower mean Th/U ratio of the Lexington Formation shells (0.6, Table 1) compared with those from the other formations (3.8 and 5.2 for the Sheguindah Shale and Stony Mountain Formation, respectively; Table 1) favours relatively lower oxygen possibly caused by the higher organic productivity, due to high inputs of nutrients coming with cool upwelling currents, which would have led to episodic eutrophication (e.g., Arnaboldi and Meyer 2007).

6. Conclusions

A multi-technique approach is applied in this study to evaluate the petrographic and geochemical preservation of the Upper Ordovician dalmanelloid brachiopod shells that were selected for the current investigation. The petrographic and geochemical screening suggest a high degree of retention of the fibrous ultrastructure of the targeted secondary layer of the shell and preservation of at least near-primary geochemical signatures particularly those of the carbon and oxygen isotopes.

The $\delta^{18}\text{O}$ values shows clearly the influence of the paleo-latitudinal effect on the examined shells. Those from the higher tropics (Lexington Formation) had higher $\delta^{18}\text{O}$ values compared to their counterparts from the mid-tropics (the Sheguindah Shale) or the sub-equatorial region (Stony Mountain Formation).

The relatively higher $\delta^{13}\text{C}$ values in the Lexington Formation shells are interpreted to reflect higher organic productivity, which is supported by the relatively higher P contents. The geochemical evidence of increased primary productivity is consistent with a possible cold-water upwelling scenario suggested in previous work.

The relatively lower Th/U values of the Lexington Formation shells suggest slightly lower oxygen content in the water, which may have been caused by a higher consumption of oxygen as a result of the blooming productivity.

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References

- Azmy, K. 2018, Carbon-isotope of the uppermost Cambrian in eastern Laurentia: implications for global correlation. *Geological Magazine* (*in press*). doi: 10.1017/S001675681800002X.
- Azmy, K., Brand, U., Sylvester, P., Gleeson, S., Logan, A., and Bitner, M.A. 2011. Biogenic low-Mg calcite (brachiopods): proxy of seawater-REE composition, natural processes and diagenetic alteration. *Chemical Geology*, **280**: 180–190.
- Azmy, K., Veizer, J., and Bassett, M.G., and Copper, P. 1998. Oxygen and carbon isotopic composition of Silurian brachiopods: Implications for coeval seawater and glaciations. *Geological Society of America Bulletin*, **110**: 1499–1512.

- 377 Azmy, K., Veizer, J., Jin, J., Copper, P., and Brand, U. 2006. Paleobathymetry of a Silurian shelf
378 based on brachiopod assemblages: an oxygen isotope test. Canadian Journal of Earth
379 Sciences, **43(3)**: 281–293.
- 380 Angiolini, L., Darbyshire, D.P.F., Stephenson, M.H., Leng, M.J., Brewer, T.S., Berra, F., and
381 Jadoul, F. 2007. Lower Permian brachiopods from Oman: their potential as climatic
382 proxies. Earth and Environmental Science Transactions of the Royal Society of Edinburgh, **98**
383 **(3-4)**: 327–344.
- 384 Angiolini, L., Jadoul, F., Leng, M.J., Stephenson, M. H., Rushton, J., Chenery, S., Crippa, G.
385 2009. How cold were the Early Permian glacial tropics? Testing sea-surface temperature using
386 the oxygen isotope composition of rigorously screened brachiopod shells. Journal of the
387 Geological Society, **166 (5)**: 933–945.
- 388 Arnaboldi, M., and Meyers, P.A. 2007. Trace element indicators of increased primary production
389 and decreased water-column ventilation during deposition of latest Pliocene sapropels at five
390 locations across the Mediterranean Sea. Palaeogeography, Palaeoclimatology, Palaeoecology,
391 **249**: 425–443.
- 392 Auclair, A.C., Joachimski, M.M., and Lécuyer, C. 2003 Deciphering kinetic, metabolic and
393 environmental controls on stable isotope fractionations between seawater and the shell of
394 *Terebratalia transversa* (Brachiopoda). Chemical Geology, **202**: 59–78.
- 395 Banner, J.L., and Hanson, G.N. 1990. Calculation of simultaneous isotopic and trace element
396 variations during water-rock interaction with applications to carbonate diagenesis. Geochimica et
397 Cosmochimica Acta, **54 (11)**: 3123–3137.
- 398 Brand, U., Azmy, K., Bitner, M.A., Logan, A., Zushin, M., Ruggiero, E., and Colin, P.L. 2015.
399 Carbon isotope composition in modern brachiopod calcite: a case for equilibrium with seawater?
400 Chem Geol., **411**: 81–96.
- 401 Brand, U., Logan, A., Bitner, M.A., Griesshaber, E., Azmy, K., and Buhl, D. 2011. What is the
402 ideal proxy of Paleozoic seawater? The Association of Australasian Palaeontologists, Memoir,
403 **41**: 9–24.
- 404 Brand, U., Logan, A., Hiller, N., and Richardson, J. 2003. Geochemistry of modern brachiopods:
405 applications and implications for oceanography and paleoceanography. Chemical Geology, **198**:
406 305– 334.
- 407 Brunton, F.R., Turner, E., and Armstrong, D., 2008. A guide to the Paleozoic geology and fossils
408 of Manitoulin Island and northern Bruce Peninsula, Ontario, Canada. Canadian Paleontology
409 Conference, Field Trip Guidebook, no. 14, 77 p.
- 410 Carpenter, S.J., and Lohmann, K.C. 1995. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of modern brachiopods.
411 Geochimica et Cosmochimica Acta, **59**: 3749–3764.
- 412 Casella, L.A., Griesshaber, E., Simonet Roda, M., Ziegler, A., Mavromatis, V., Henkel, D.,
413 Laudien, J., Häussermann, V., Neuser, R.D., Angiolini, L., Dietzel, M., Eisenhauer, A.,
414 Immenhauser, A., Brand, U., and Schmahl, W.W. 2018. Micro- and nanostructures reflect the

- 415 degree of diagenetic alteration in modern and fossil brachiopod shell calcite: A multi-analytical
416 screening approach (CL, FE-SEM, AFM, EBSD). *Palaeogeography, Palaeoclimatology,*
417 *Palaeoecology*, **502**: 13–30.
- 418 Clarkson, E.N.K. 1993. *Invertebrate paleontology and evolution*. Chapman and Hall, London.
- 419 Cocks, L.R.M., and Scotese, C.R. 1991. The global biogeography of the Silurian Period.
420 *Palaeontology, Special Papers*, no. 44, 109–122.
- 421 Cocks, L.R.M., and Torsvik, T.H. 2011. The Palaeozoic geography of Laurentia and western
422 Laurussia: A stable craton with mobile margins. *Earth-Science Reviews*, **106**: 1–51.
- 423 Copper, P. 1978. Paleoenvironments and paleocommunities in the Ordovician-Silurian sequence
424 of Manitoulin Island. *Michigan Basin Geological Society, Special Papers*, no. 3, p. 47–61.
- 425 Dickson, A.J., Cohen, A.S., and Coe, A.L. 2011. Seawater oxygenation during the Paleocene-
426 Eocene Thermal Maximum. *Geology*, **40** (7): 639–642.
- 427 Ettensohn, F.R. 2010. Origin of Late Ordovician (mid-Mohawkian) temperate–water conditions
428 on southeastern Laurentia: glacial or tectonic? *GSA Special Papers*, no. 466, pp. 163–175.
- 429 Faure, G., and Mensing, T.M. 2005. *Isotopes: Principles and Applications*. Third edition. John
430 Wiley and Sons, Inc., Hoboken, New Jersey, pp 464.
- 431 Friedman, I., and O'Neil, J.R. 1977. Data of geochemistry: Compilation of stable isotope
432 fractionation factors of geochemical interest (Vol. 440). US Government Printing Office.
- 433 Guillong, M., Meier, D.L., Allan, M.M., Heinrich, C.A., and Yardley, B.W.D. 2008. Appendix
434 A6; SILLS; a MATLAB-based program for the reduction of laser ablation ICP-MS data of
435 homogeneous materials and inclusions, 40. Short Course Series Mineralogical Association of
436 Canada, pp. 328–333.
- 437 Holland, S.M., and Patzkowsky, M.E. 2008. Cincinnati (Masvillian–Richmondian) strata and
438 fossils in southern Ohio. *Cincinnati Museum Center Scientific contributions*, **2**: 260–279.
- 439 Hays, P.D., and Grossman, E.L. 1991. Oxygen isotopes in meteoric calcite cements as indicators
440 of continental paleoclimate. *Geology*, **19**: 441–444.
- 441 Jin, J., and Harper, D.A.T. 2015. Occurrences of the cool-water dalmanelloid brachiopod
442 *Heterorthis* in the Upper Ordovician of North America. *Papers in Palaeontology*, **1**(3): 237–
443 253.
- 444 Jin, J., Harper, D.A.T., Cocks, L.R.M., McCausland, P.J.A., Rasmussen, C.M.Ø., and Sheehan,
445 P.M. 2013. Precisely locating the Ordovician equator in Laurentia. *Geology*, **41**: 107–110.
- 446 Jin, J., Zhan, R.B., and Wu, R.C. 2018. Equatorial cold-water tongue in the Late Ordovician.
447 *Geology*, **46**: 759–762.

- 448 Jones, J.P., Carricart-Ganivet, J.P., Prieto, R.I., Enríquez, S., Ackerson, M., and Gabitov, R.I.
449 2015. Microstructural variation in oxygen isotopes and elemental calcium ratios in the coral
450 skeleton of *Orbicella annularis*. *Chemical Geology*, **419**: 192–199.
- 451 Kimura, H., Azmy, K., Yamamuro, M., Zhi–Wen, J., and Cizdziel, J.V. 2005. Integrated
452 stratigraphy of the Upper Proterozoic succession in Yunnan of South China: re-evaluation of
453 global correlation and carbon cycle. *Precambrian Research*, **138**: 1–36.
- 454 Lear, C.H., Elderfield, H., and Wilson, P.A. 2000. Cenozoic deep-sea temperatures and global
455 ice volumes from Mg/Ca in benthic foraminiferal calcite. *Science*, **287(5451)**: 269–272.
- 456 Lowenstam, H.A. 1961. Mineralogy, $^{18}\text{O}/^{13}\text{C}$ ratios, and strontium and magnesium contents of
457 recent and fossil brachiopods and their bearing on the history of oceans. *Journal of Geology*, **69**:
458 241–260.
- 459 Machel, H.G., and Burton, E.A. 1991. Factors governing cathodoluminescence in calcite and
460 dolomite, and their implications for studies of carbonate diagenesis. In: *Luminescence microscopy*
461 *and spectroscopy, qualitative and quantitative applications*, SEPM Short Course 25, 37–57.
- 462 McKinnon, D.I. 1974. The shell structure of spiriferid Brachiopoda. *Bulletin of British Museum*,
463 **25**: 187–261.
- 464 McLaughlin, P.L., Brett, C.E., McLaughlin, S.L.T., and Holland, S.M. 2008. Upper Ordovician
465 (Chatfieldian–Edenian) strata from central Kentucky to southern Ohio: Facies gradients, event
466 beds and depositional sequences. *Cincinnati Museum Center Scientific Contributions* 2, 8–42.
- 467 Mii, H.S., Shi, G.R., Cheng, C.J., and Chen, Y.Y. 2012. Permian Gondwanaland
468 paleoenvironment inferred from carbon and oxygen isotope records of brachiopod fossils from
469 Sydney Basin, southeast Australia. *Chemical Geology*, **291**: 87–103.
- 470 Morel, F.M.M., Milligan, A.J., and Saito, M.A. 2004. Marine bioinorganic chemistry: the role of
471 trace metals in the oceanic cycles of major nutrients. In *The Oceans and Marine Geochemistry*,
472 *Treatise on geochemistry. Edited by H. Elderfield, H.D. Holland, and K.K. Turekian*, volume 6.
473 Elsevier, Amsterdam, Heidelberg, pp. 113–143.
- 474 Olanipekun, B.J., and Azmy, K. 2017. In situ characterization of dolomite crystals: Evaluation of
475 dolomitization process and its effect on zoning. *Sedimentology*, **64**: 1708–1730.
- 476 Pope, M.C., and Read, J.F. 1997. High-frequency cyclicity of the Lexington Limestone (Middle
477 Ordovician), a cool-water carbonate clastic ramp in an active foreland basin. *SEPM Special*
478 *Publication* 56, 411–429.
- 479 Rush, P.F., and Chafetz, H.S. 1990. Fabric retentive, non-luminescent brachiopods as indicators
480 of original $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions: a test. *Journal of Sedimentary Petrology*, **60**: 968–981.
- 481 Śliwiński, M.G., Whalen, M.T., and Day, J. 2010. Trace element variations in the Middle
482 Frasnian punctata zone (Late Devonian) in the western Canada sedimentary Basin—changes in

- oceanic bioproductivity and paleoredox spurred by a pulse of terrestrial afforestation? *Geologica Belgica*, **4**: 459–482.
- Sproat, C.D., and Jin, J. 2017. Paleobiogeography of the early Late Ordovician “Trentonian” (latest Sandbian to middle Katian) brachiopod fauna during a major marine transgression and colonization of the epicontinental seas in Laurentia. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **487**: 105–117.
- Takizawa, M., Takayanagi, H., Yamamoto, K., Abe, O., Sasaki, K., and Iryu, Y. 2017. Paleooceanographic conditions at approximately 20 and 70 ka recorded in *Kikaithyris hanzawai* (Brachiopoda) shells. *Geochimica et Cosmochimica Acta*, **215**: 189–213.
- Veizer, J., Ala, D., Azmy, K., Bruckschen, P., Bruhn, F., Buhl, D., Carden, G., Diener, A., Ebner, S., Goddard, Y., Jasper, T., Korte, C., Pawellek, F., Podlaha, O., and Strauss, H. 1999. $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ evolution of Phanerozoic seawater. *Chemical Geology*, **161**: 59–88.
- Vihtakari, M., Renaud, P.E., Clarke, L.J., Whitehouse, M.J., Hop, H., Carroll, M.L., and Ambrose Jr, W.G. 2016. Decoding the oxygen isotope signal for seasonal growth patterns in Arctic bivalves. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **446**: 263–283.
- Wignall, P.B., and Twitchett, R.J. 1996. Oceanic anoxia and the end Permian mass extinction. *Science*, **272**: 1155–1158.
- Zaky, A., Azmy, K., Brand, U., and Svavarsson, J. 2016. Rare earth elements in the deep-water articulated brachiopods: evaluation of seawater masses. *Chemical Geology*, **435**: 22–34.

Figures and Tables

Fig. 1. Map of Late Ordovician of Laurentia (modified from Cocks and Torsvik 2011) showing the locations of the (1) Stony Mountain Formation, Winnipeg area, southern Manitoba, (2) Sheguindah Shale, Highway 6, Manitoulin Island, and (3) Lexington Limestone, Kentucky.

Fig. 2. Photomicrographs of the secondary layer of investigated shells showing, (a) a whole shell (Sample LN12), (b) well-preserved fibrous structure under plane polarized light (Sample RV10), (c) SEM image of a thin section of well-preserved fibrous secondary layer with the internal sediments (Sample LX4), (d) CL image of (c) where preserved shell is dull to non-CL but internal sediments (altered phase) has bright red CL, and (e) SEM image of a speck of a secondary layer of a shell showing excellent preservation. Arrows point at clean crystal boundaries (no dissolution features or cement between fibres) of calcite prisms (Sample RV9) and clean prism fracture. Detail in text and Appendix 1.

Fig. 3. Scatter diagram of correlation of (a) Mn with Sr, (b) Mn/Sr with $\delta^{18}\text{O}$, (c) Fe with $\delta^{18}\text{O}$, and (d) ΣREE with $\delta^{18}\text{O}$. The square in (a) marks the range of composition of modern brachiopod shells from low, mid and high latitudes (Brand et al., 2003).

Fig. 4. Oxygen- vs. carbon-isotope values for the analyzed brachiopod shells. The square marks the range of mean values of best preserved brachiopod shells of Upper Ordovician immediately below the Ordovician terminal glaciation (Veizer et al., 1999). Legend as in Figure 3.

Fig. 5. Plot of Temperature vs $\delta^{18}\text{O}_{\text{seawater}}$ for various $\delta^{18}\text{O}_{\text{shell}}$ values reconstructed from the equation $10^3 \ln \alpha_{\text{calcite-water}} = 2.7 * 10^6 T^{-2} - 2.89$ (Friedman and O'Neil, 1977). The vertical bars indicate the ranges of $\delta^{18}\text{O}_{\text{seawater}}$ based on the ranges of measured $\delta^{18}\text{O}_{\text{shell}}$ values and temperatures of modern tropical seawater.

Table 1. Summary of statistics of geochemical results of the investigated brachiopod shells.

Appendix 1. Elemental and isotopic geochemical compositions of the investigated shells. Stable isotope values are expressed in ‰ VPDB and concentrations of elements in ppm.

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Fig. 2. Photomicrographs of the secondary layer of investigated shells showing, (a) a whole shell (Sample LN12), (b) well-preserved fibrous structure under plane polarized light (Sample RV10), (c) SEM image of a thin section of well-preserved fibrous secondary layer with the internal sediments (Sample LX4), (d) CL image of (c) where preserved shell is dull to non-CL but internal sediments (altered phase) has bright red CL, and (e) SEM image of a speck of a secondary layer of a shell showing excellent preservation. Arrows point at clean crystal boundaries (no dissolution features or cement between fibres) of calcite prisms (Sample RV9) and clean prism fracture. Detail in text and Appendix 1.

3a

3b

3d

Fig

Fig

Table 1. Summary of statistics of geochemical results of the investigated brachiopod shells.

Formation		$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Mg	Sr	Mn	Fe	P	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U	Th/U	ΣREE
All samples	<i>n</i>	59	59	29	29	29	27	28	29	29	29	29	29	29	28	29	29	29	29	29	29	29	29	29	29	29
	mean	-5.5	0.0	3191	1189	135	298	145	5.731	11.666	1.433	5.519	1.098	0.250	0.987	0.136	0.767	0.140	0.369	0.050	0.346	0.051	0.119	0.034	3.5	28.5
	stdev	1.1	0.8	935	364	86	245	66	5.884	11.778	1.434	5.657	1.156	0.277	1.014	0.143	0.783	0.135	0.346	0.045	0.316	0.048	0.130	0.024	2.6	28.8
	max	-4.0	1.1	5643	1666	386	883	236	27.127	52.823	6.361	24.694	5.100	1.141	4.379	0.635	3.467	0.607	1.579	0.198	1.241	0.188	0.506	0.097	8.4	129.5
	min	-7.7	-1.6	1848	448	31	31	19	0.204	0.325	0.033	0.110	0.026	0.005	0.060	0.005	0.030	0.006	0.024	0.007	0.035	0.005	0.002	0.002	0.1	0.8
Lexington	<i>n</i>	26	26	7	7	7	7	7	7	7	7	7	7	7	6	7	7	7	7	7	7	7	7	7	7	7
	mean	-4.5	0.8	3140	1310	176	155	170	1.634	2.435	0.238	0.803	0.149	0.022	0.195	0.030	0.226	0.057	0.208	0.040	0.363	0.064	0.007	0.026	0.6	6.4
	stdev	0.3	0.2	480	256	151	247	27	1.495	2.229	0.221	0.749	0.138	0.018	0.130	0.027	0.213	0.055	0.210	0.040	0.371	0.066	0.007	0.028	0.6	6.0
	max	-4.0	1.1	3711	1632	386	711	194	4.194	6.464	0.656	2.234	0.411	0.053	0.413	0.079	0.609	0.157	0.597	0.116	1.066	0.188	0.018	0.071	1.8	17.2
	min	-4.9	0.4	2320	1003	31	31	113	0.204	0.325	0.033	0.110	0.026	0.005	0.060	0.005	0.030	0.006	0.024	0.007	0.035	0.006	0.002	0.002	0.1	0.8
Sheguindah Shale	<i>n</i>	23	23	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13
	mean	-6.0	-0.4	3922	1434	127	441	173	9.097	19.329	2.370	9.252	1.843	0.445	1.592	0.224	1.227	0.215	0.538	0.069	0.436	0.060	0.113	0.033	3.8	46.7
	stdev	0.8	0.6	722	106	64	230	57	7.372	13.887	1.673	6.567	1.362	0.312	1.211	0.173	0.962	0.167	0.434	0.056	0.359	0.049	0.062	0.025	1.5	34.5
	max	-4.5	0.7	5643	1666	261	883	236	27.127	52.823	6.361	24.694	5.100	1.141	4.379	0.635	3.467	0.607	1.579	0.198	1.241	0.167	0.255	0.097	6.8	129.5
	min	-7.7	-1.6	3004	1295	63	133	19	1.930	5.193	0.634	2.466	0.491	0.106	0.444	0.061	0.299	0.054	0.131	0.015	0.084	0.011	0.013	0.008	1.7	11.9
Stony Mountain	<i>n</i>	10	10	9	9	9	7	8	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9
	mean	-6.8	-0.9	2177	740	116	174	79	4.055	7.775	1.009	3.794	0.759	0.148	0.640	0.091	0.523	0.095	0.250	0.032	0.202	0.027	0.215	0.042	5.2	19.4
	stdev	0.4	0.5	277	245	30	74	58	1.310	2.343	0.292	1.202	0.251	0.055	0.244	0.039	0.243	0.047	0.133	0.019	0.130	0.018	0.178	0.021	2.9	6.2
	max	-5.7	0.2	2751	1191	165	287	218	6.086	11.204	1.461	5.746	1.193	0.239	1.006	0.148	0.950	0.183	0.511	0.070	0.490	0.068	0.506	0.071	8.4	28.6
	min	-7.2	-1.5	1848	448	77	87	36	2.680	4.812	0.636	2.516	0.503	0.092	0.369	0.043	0.202	0.031	0.078	0.009	0.049	0.005	0.030	0.013	0.6	12.5

* The δ values are expressed in ‰VPDB and concentrations of elements in ppm.

Appendix 1. Elemental and isotopic geochemical compositions of the investigated shells. Stable isotope values are expressed in ‰ VPDB and concentrations of elements in ppm.

Sample id#	Formation	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Mg	Sr	Mn	Fe	P	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U	Th/U	ΣREE
LN1	Sheguindah Shale	-5.9	0.0	4873	1457	261	634	234	4.562	8.793	1.084	4.314	0.813	0.211	0.807	0.130	0.818	0.169	0.510	0.069	0.473	0.069	0.132	0.060	2.2	23
LN2	Sheguindah Shale	-6.2	-0.7	3909	1348	80	222	134	12.995	27.905	3.468	13.620	2.724	0.648	2.400	0.332	1.767	0.299	0.713	0.090	0.543	0.071	0.138	0.043	3.2	68
LN3	Sheguindah Shale	-6.8	-0.9	3092	1553	82	731	168	5.863	13.091	1.590	6.096	1.135	0.281	0.913	0.127	0.713	0.133	0.282	0.040	0.245	0.037	0.154	0.043	3.6	31
LN4	Sheguindah Shale	-7.7	-1.6																							
LN5	Sheguindah Shale	-6.1	-0.7	3719	1438	97	320	162	12.728	26.893	3.349	13.270	2.629	0.623	2.380	0.322	1.748	0.286	0.641	0.077	0.527	0.070	0.102	0.022	4.7	66
LN6	Sheguindah Shale	-6.7	-1.5	3372	1666	113	133	216	3.089	7.219	0.924	3.625	0.726	0.181	0.577	0.086	0.458	0.080	0.185	0.025	0.157	0.022	0.097	0.015	6.3	17
LN7	Sheguindah Shale	-4.5	0.7	3648	1551	79	359	171	11.707	25.966	3.339	13.136	2.660	0.643	2.280	0.312	1.573	0.261	0.601	0.074	0.450	0.062	0.117	0.027	4.3	63
LN8	Sheguindah Shale	-5.8	-0.8	4310	1414	228	883	213	27.127	52.823	6.361	24.694	5.100	1.141	4.379	0.635	3.467	0.607	1.579	0.198	1.241	0.167	0.255	0.097	2.6	130
LN9	Sheguindah Shale	-5.9	-0.3	3581	1357	118	328	214	7.348	16.730	2.071	8.152	1.567	0.402	1.318	0.170	0.959	0.168	0.428	0.057	0.331	0.046	0.061	0.013	4.8	40
LN10	Sheguindah Shale	-7.2	-0.6	3716	1302	187	717	181	18.640	35.600	4.197	16.548	3.342	0.843	3.067	0.437	2.583	0.463	1.213	0.161	1.068	0.151	0.164	0.045	3.6	88
LN11	Sheguindah Shale	-6.2	-0.8	4266	1444	66	476	156	3.114	9.427	1.098	4.102	0.825	0.193	0.612	0.082	0.395	0.069	0.170	0.019	0.111	0.016	0.046	0.015	3.0	20
LN12	Sheguindah Shale	-5.1	0.0	3848	1408	63	209	236	3.442	8.977	1.162	4.220	0.790	0.187	0.565	0.074	0.364	0.060	0.154	0.017	0.099	0.013	0.060	0.019	3.1	20
LN13	Sheguindah Shale	-5.5	-0.9	5643	1295	165	376	19	1.930	5.193	0.634	2.466	0.491	0.106	0.444	0.061	0.299	0.054	0.131	0.015	0.084	0.011	0.013	0.008	1.7	12
LVN2	Sheguindah Shale	-4.9	0.5																							
LVN3	Sheguindah Shale	-5.7	0.0	3004	1414	112	350	144	5.714	12.663	1.539	6.031	1.154	0.325	0.957	0.145	0.804	0.149	0.390	0.051	0.335	0.045	0.126	0.019	6.8	30
LVN4	Sheguindah Shale	-5.0	0.1																							
LVN5	Sheguindah Shale	-5.4	0.2																							
LVN5	Sheguindah Shale	-7.2	-1.1																							
LVN6	Sheguindah Shale	-6.2	-0.4																							
LVN7	Sheguindah Shale	-6.5	-0.6																							
LVN8	Sheguindah Shale	-5.8	-0.3																							
LVN9	Sheguindah Shale	-6.5	-0.4																							
LVN10	Sheguindah Shale	-5.5	-0.1																							
LX1B	Lexington	-4.8	0.7	3558	1193	252	92	171	2.392	3.632	0.348	1.196	0.226	0.034	0.244	0.048	0.355	0.091	0.325	0.061	0.545	0.096	0.015	0.071	0.2	10
LX2	Lexington	-4.8	0.6	2736	1632	69	711	187	0.656	1.038	0.096	0.334	0.068	0.008	0.102	0.010	0.083	0.019	0.059	0.014	0.110	0.019	0.004	0.012	0.3	3
LX3	Lexington	-4.9	0.9	3166	1446	86	122	168	0.872	1.308	0.137	0.444	0.076	0.013	0.119	0.019	0.125	0.032	0.112	0.022	0.209	0.035	0.002	0.004	0.5	4
LX4a	Lexington	-4.3	0.6	3350	1261	55	48	194	0.401	0.674	0.075	0.268	0.047	0.008	0.060	0.008	0.056	0.012	0.044	0.008	0.074	0.012	0.018	0.010	1.8	2
LX4b	Lexington	-4.0	0.8																							
LX5	Lexington	-4.5	0.8																							
LX6	Lexington	-4.4	1.1																							
LX7	Lexington			2320	1601	31	31	169	0.204	0.325	0.033	0.110	0.026	0.005		0.005	0.030	0.006	0.024	0.007	0.035	0.006	0.002	0.002	0.9	1
LX8	Lexington	-4.8	1.0																							
LX9	Lexington	-4.2	0.7	3138	1003	352	31	186	2.722	3.607	0.319	1.033	0.192	0.030	0.232	0.040	0.324	0.081	0.293	0.052	0.503	0.090	0.005	0.023	0.2	10
LX10	Lexington	-4.7	1.0	3711	1034	386	48	113	4.194	6.464	0.656	2.234	0.411	0.053	0.413	0.079	0.609	0.157	0.597	0.116	1.066	0.188	0.006	0.059	0.1	17
LXV1	Lexington	-4.2	0.5																							
LXV1c	Lexington	-4.1	0.8																							
LXV2	Lexington	-4.9	0.4																							
LXV3	Lexington	-4.5	0.8																							
LXV4	Lexington	-4.2	1.1																							
LXV5	Lexington	-4.2	0.5																							
LXV6	Lexington	-4.4	0.6																							
LXV7	Lexington	-4.6	0.7																							
LXV7a	Lexington	-4.5	0.8																							
LXV7b	Lexington	-4.9	0.7																							
LXV8	Lexington	-4.3	0.8																							
LXV10	Lexington	-4.3	1.0																							
LXV11	Lexington	-4.8	0.9																							
LXV12	Lexington	-4.8	0.7																							
LXV13	Lexington	-4.7	0.7																							
LXV14	Lexington	-4.4	0.8																							
RV1	Stony Mountain	-6.8	-0.8	2034	802	122	150		2.880	5.103	0.683	2.665	0.546	0.115	0.543	0.072	0.466	0.087	0.209	0.025	0.155	0.021	0.030	0.046	0.6	14
RV2	Stony Mountain	-7.0	-0.9	2162	1046	77	87	77	2.680	4.812	0.636	2.516	0.503	0.104	0.442	0.062	0.350	0.062	0.160	0.020	0.130	0.017	0.057	0.025	2.2	12
RV3	Stony Mountain	-6.6	-0.4	1944	730	152	175	36	4.956	9.435	1.226	4.557	0.936	0.180	0.813	0.122	0.705	0.131	0.347	0.046	0.257	0.035	0.241	0.029	8.4	24
RV4	Stony Mountain	-7.1	-1.1	2751	448	120	287	44	2.895	6.597	0.832	2.746	0.574	0.092	0.394	0.056	0.316	0.055	0.156	0.018	0.108	0.015	0.488	0.061	8.0	15
RV5	Stony Mountain	-7.1	-1.5	1848	542	165		49	6.086	11.204	1.374	5.309	1.022	0.216	0.927	0.148	0.950	0.183	0.511	0.070	0.490	0.068	0.506	0.071	7.1	29

RV6	Stony Mountain	-6.8	-1.0																							
RV7	Stony Mountain	-7.0	-0.8	2474	582	77	262	63	3.214	7.036	0.953	3.167	0.606	0.099	0.369	0.043	0.202	0.031	0.078	0.009	0.049	0.005	0.103	0.013	7.9	16
RV8	Stony Mountain	-7.0	-1.4	2138	566	121	111	61	5.903	11.117	1.461	5.746	1.193	0.239	1.006	0.142	0.766	0.135	0.355	0.043	0.292	0.037	0.099	0.018	5.4	28
RV9	Stony Mountain	-5.7	0.2	2081	1191	93		85	4.027	7.330	0.879	3.245	0.579	0.112	0.480	0.072	0.389	0.076	0.187	0.023	0.159	0.022	0.275	0.056	4.9	18
RV10	Stony Mountain	-7.2	-1.1	2159	753	118	145	218	3.852	7.339	1.034	4.194	0.871	0.172	0.785	0.103	0.558	0.101	0.246	0.029	0.178	0.025	0.137	0.058	2.4	19

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