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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 $\Sigma$REE) show insignificant correlations with the $\delta^{18}$O and $\delta^{13}$C values, thus supporting the preservation of at least near-primary geochemical compositions. Among the three lots of shells, the mean $\delta^{18}$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 $\delta^{18}$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 $\delta^{13}$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 Sebree 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 *Heterorthina* 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 Sebree 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 dolograinstone. 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,
trepostome bryozoans, and gastropods at several horizons. This shale unit is approximately
coeval with the Kope Formation in the Cincinnati Arch areas, where *Cincinnetina* occurs in
abundance. The shale-dominated strata, together with its underlying black shales of the upper
Lindsay Formation, suggest an episode of relatively deep-water depositional environments, with
local and episodic anoxia.

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

3. Methodology

The investigated Upper Ordovician dalmanelloid brachiopods (~ 1 cm long; Fig. 2a) were
selected following the protocol described in Azmy et al. (1998). A preliminary exam with a hand
lens allowed the elimination of recrystallized shells. Complete shells were cut, through the umbo,
for thin sections and studied under polarizing microscope. Only samples having fibrous
secondary layer were considered for more screening. Also, thin sections were examined under a
cathodoluminoscope to evaluate the petrographic preservation. Cathodoluminescence (CL) was
performed by a ChromaCL detector (Gatan Inc., Pleasanton, CA, USA) attached to a Quanta 400
SEM (FEI, Hilsboro, OR, USA), which is equipped with an energy dispersive X-ray (EDS) microanalytical system (Bruker AXS, XFlash Detector 4010; Bruker Corporation, Billerica, MA, USA). The CL system is equipped with three detectors that correspond to red, green and blue colors, thus showing image colors that are very close to those of real luminescence emitted from the studied samples (e.g., Olanipekun and Azmy 2017). The images were obtained at 15 kV acceleration voltage and 13 nA beam current.

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

For C- and O-isotope analyses, ~ 200 µg of powder sample, microsampled from the fibrous secondary layer in the middle area of the shell to avoid the umbo zone (e.g., Takizawa et al. 2017), was reacted in an inert atmosphere with ultrapure concentrated (100%) orthophosphoric acid at 70°C in a Thermo–Finnigan GasBench II. The liberated CO₂ was automatically delivered 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‰ (2σ) for the analyses were determined by repeated measurements of NBS-19 (δ^{18}O = −2.20‰ and δ^{13}C = +1.95‰ vs. VPDB) and L-SVECS (δ^{18}O = −26.64‰ and δ^{13}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 (ThO^+/Th^+ <0.3%). The laser was operated with a repetition rate of 5 Hz, an energy density of 4 J/cm^2, 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 $\delta^{18}O$ counterparts (Fig. 3b). Also, the Fe contents (298 ± 245 ppm, Table 1) have insignificant correlation ($R^2 = 0.02$) with those of $\delta^{18}O$ (Fig. 3c) and similarly the total REE contents ($\Sigma$REE = 28.5 ± 28.8 ppm; $R^2 = 0.02$ Appendix 1; Table 1; Fig. 3d). The $\delta^{13}C$ 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 $\Sigma$REE with their $\delta^{13}C$ counterparts (Appendix 1).

Most of the $\delta^{18}O$ and $\delta^{13}C$ 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 cathodolumiscope (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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 δ^{18}O counterparts (Fig. 3c). The ∑REE concentrations have recently found to be enriched in carbonates with diagenesis (Azmy et al. 2011) but yet they exhibit very poor correlations with the δ^{18}O values (R^2 = 0.02; Fig. 3d), which supports the preservation of at least near-primary δ^{18}O signatures.

The impact of diagenesis on the alteration of the δ^{18}O composition of carbonates is expected to be much higher than that on the δ^{13}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 δ^{13}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 δ^{18}O of carbonates quickly at variable degrees depending on the water/rock interaction ratio. Thus, the alteration of the δ^{13}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 δ^{13}C signatures of the examined shells are also well preserved and at least near-primary.

Generally speaking, except for few samples, the δ^{18}O and δ^{13}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 δ¹⁸O 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
δ¹⁸O 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 δ¹⁸O 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., Etenson 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 δ¹⁸O 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 δ¹⁸O 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 δ¹⁸O 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 $\delta^{13}C$ 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 $\delta^{13}C$ 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 Stoney 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 $\delta^{18}O$ values show clearly the influence of the paleo-latitudinal effect on the examined shells. Those from the higher tropics (Lexington Formation) had higher $\delta^{18}O$ values compared to their counterparts from the mid-tropics (the Sheguindah Shale) or the sub-equatorial region (Stony Mountain Formation).

The relatively higher $\delta^{13}C$ 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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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) Sheguiandah 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 $\delta^{18}$O, (c) Fe with $\delta^{18}$O, and (d) $\sum$REE with $\delta^{18}$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 $\delta^{18}O_{\text{seawater}}$ for various $\delta^{18}O_{\text{shell}}$ values reconstructed from the equation $10^3 \ln \alpha_{\text{calcite-water}} = 2.7 \times 10^6 T^{-2} - 2.89$ (Friedman and O’Neil, 1977). The vertical bars indicate the ranges of $\delta^{18}O_{\text{seawater}}$ based on the ranges of measured $\delta^{18}O_{\text{shell}}$ 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.
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.
$R^2 = 0.02$
Fig

$\delta^{13}$ C (‰) VPDB vs $\delta^{18}$ O (‰) VPDB

- Series 1
- Series 3
- Series 2

$R^2 = 0.0021$
Table 1. Summary of geochemical results of the investigated brachiopod shells.

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* 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.

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Canadian Journal of Earth Sciences
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