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Geochemical and Taphonomic Analysis of Very Well-Preserved Late-Middle Cambrian Lingulid Brachiopods From Laurentia

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Geochemical and Taphonomic Analysis of Very Well-Preserved Late-Middle
Cambrian Lingulid Brachiopods From Laurentia

A Thesis submitted in partial satisfaction
of the requirements for the degree of

Master of Science

in

Geological Sciences

by

Matthew Richard Robles

June 2012

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To Sarah and Conner

I simply could not have accomplished this

without your love and support.

Thank you

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Introduction

Much recent research has highlighted intimate connections between the Earth's paleotemperature, atmospheric and oceanic composition, and its evolutionary history. Such work has spanned scales from major transitions in Earth's history (e.g. Scott et al., 2008; Johnston et al., 2012), to the exceptionally high resolution record of Neogene climate and atmospheric change for which driving processes can be dissected in detail (e.g. Huybers and Curry, 2006; Barker et al., 2011). It is now clear that, regardless of specific triggers for particular events, each of the major mass extinctions have involved significant changes in both global temperature and in the composition of the atmosphere (e.g. Finnegan et al., 2011; Schulte et al., 2010; Shen et al., 2011), and also that other geologically rapid changes in global temperature of profound effect have occurred sporadically throughout the Phanerozoic (Kemp et al., 2005). Such work is of pressing societal evidence in a time of human-induced climate change (Rosenzweig et al., 2008).

Knowledge of Paleozoic atmospheric/oceanic composition and temperature is less precisely constrained than that of more recent times, due mainly to the fact that older rocks are generally less well-preserved than younger ones. Occasionally, however, ancient rocks and their component constituents are preserved that have suffered relatively little alteration, and these can provide important windows into ancient environmental conditions. One region that has special importance with regard to inferring late Cambrian conditions is the upper

Mississippi Valley region of Laurentia. This is important not only as a representative of equatorial conditions in the late Cambrian (Scotese, 2001) but also for the fact that the rocks in this region appear never to have suffered burial-related heating to more than 50°C (Hyodo et al., 2011). Accordingly, these rocks have significant promise as some of the most faithful records of late Cambrian oceanic conditions.

This thesis concerns Cambrian phosphatic-valved brachiopods from late Cambrian rocks of the upper Mississippi Valley whose spectacular appearance, in addition to the geological setting, suggest minimal alteration. As such these fossils are potential indicators of Cambrian environmental conditions, and have explicitly been considered as such (see Cowan et al., 2005). Similar valves from these and other parts of Laurentia have been interpreted to indicate temporal trends in paleotemperatures (Elrick et al., 2011), and offer further potential for constraining markedly contrasting paleoclimatic interpretations for local and global paleotemperatures during the late Cambro-Ordovician interval. For example, whilst Trotter et al. (2008) suggested hot ambient seawater temperatures at this time, Runkel et al. (2010) presented evidence of icy conditions along a local paleoshoreline. Additionally, these specimens are appealing because of their occurrence near the onset of the Steptoean positive carbon isotope excursion (SPICE) event, a globally recognized and well-studied excursion (Saltzman et al., 1998).

Here I provide a detailed analysis of the geological setting, taphonomic history, and preservational quality of phosphatic brachiopod valves from three localities in the Eau Claire Formation from west-central Wisconsin. Having demonstrated that the preservation of the valves indicates minimal structural and chemical alternation, this work then seeks to examine the geochemical record within and between individual valves. The purpose of this is to assess whether marked intra-valve variability is detected that might suggest marked seasonal or otherwise fluctuations in ambient water temperatures in the context of the debate about regional temperature discussed above. Investigations have thus concentrated on 1) the stratigraphic and depositional setting of the rocks containing these fossils, 2) the biostratinomy of the valves, 3) the physical structure of the valves, and 4) their chemical composition. From these analyses I conclude that the preservational quality is sufficient to merit analysis of their paleotemperature by measuring the stable isotopes of oxygen ($\delta^{18}O_{PO_4}$) within the brachiopod phosphate valve. Analyses of these data suggest that late Cambrian $\delta^{18}O_{PO_4}$ values at the onset of the SPICE varied within <1‰ during the life span of an individual brachiopod and that these values correspond to calculated temperatures in the range of ~34°C – 40°C.

Paleotemperatures in the equatorial late Cambrian

Recent interest in the reconstruction of ancient atmospheric and oceanic conditions, driven partly by advances in analytical techniques, has prompted attempts to infer ancient seawater temperatures and chemistry. For the

Cambrian, the availability of exceptionally well-preserved rocks on the Laurentian continent has lead to a research focus on this paleocontinent.

During the middle to late Cambrian Laurentia straddled the equator (Scotese, 2001). This geographical position, along with the estimates of carbon dioxide levels suggesting greenhouse conditions (Berner, 1990), is generally thought to indicate relatively hot temperatures associated with this region during this period in Earth's history (Trotter et al., 2008). Estimates of late Cambrian to lower Ordovician seawater temperature, derived mostly from conodont oxygen isotopic data, suggest that ambient seawater temperatures during this time were about 42°C (Trotter et al., 2008). This is in marked contrast to the recent inference of seasonal ice along the late Cambrian shoreline, as evinced by meter scale ice cemented brecciated intraclasts (Runkel et al., 2010). This inference was based on observations made within the upper Mississippi Valley local to the sites from which the brachiopods studied herein were collected and in the same depositional suite, although likely some 4-7 million years younger. The contrast between these results indicates that first-order uncertainties remain about the nature of the late Cambrian equatorial climate, even within an area in which rocks of this age are exceptionally well preserved. Furthermore, the location of the upper Mississippi Valley as both the equatorial and most shoreward marine facies of the Cambrian transgression (Peters and Gaines, 2012) suggests that this region may have been prone to extremes related to restricted circulation from the open ocean (Holmden et al., 1998), and intense evaporative cooling that

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would have placed an upper limit on possible water temperatures (Norris et al., 2002).

The SPICE Event

The SPICE is a positive (~4-6‰) excursion $\delta^{13}C_{CARB}$ (Gill et al. 2011) with a relatively long duration ~ 4 my (Elrick et al., 2011), that took place during the interval in which the brachiopods studied herein were alive. Additionally, the timing of the SPICE is well constrained by trilobite biostratigraphy with the onset occurring at the Steptoean Stage (=*Pterocephaliid* biomere) and ending at the start of the Sunwaptan Stage (=*Ptychaspid* biomere) (Saltzman et al., 1998). Biomeres represent repeated episodes of evolutionary diversification in trilobites that are bounded by marked extinctions (Palmer, 1965), and their causes have been suggested to relate to major fluctuations in oceanic chemistry (Palmer 1979) or ocean floor temperature (Stitt, 1977). More recently the cause of the perturbation in heavy carbon was linked to increased burial of organic matter facilitated by high rates of weathering and erosion of continental material leading to ocean anoxia (Saltzman et al., 2004). Recently, new evidence has added to the growing knowledge of this event by reporting an equally dramatic, globally recognized, positive sulfur excursion ($\delta^{34}S_{CAS}$) that coincides with the timing of the SPICE event (Gill et al., 2011). The inclusion of this positive $\delta^{34}S$ excursion, along with molybdenum and degree of pyritization (DOP) data, indicates widespread euxinic conditions (i.e. anoxic and sulfidic bottom waters)(Gill et al., 2011). More recently, investigations into the oxygen isotopic composition of the

ocean during the late Cambrian are adding to the SPICE narrative. This inclusion of oxygen analyses to these data is offering possible insight to the climatic conditions (i.e. ocean temperatures) leading up to and during the SPICE event.

Brachiopod valve geochemistry as a paleoenvironmental proxy

Researchers investigating stable isotope compositions have long realized the utility of employing the mineralized remains of marine invertebrates both extant and fossil for paleoclimate reconstructions and, while many different types of organisms are suited for this type of research (e.g. brachiopods, conodonts, coral, bivalves, etc.), brachiopods feature prominently, particularly with regard to lower Paleozoic rocks in which they are relatively common (Buening, 2001). In addition, as brachiopods are sessile benthic organisms that grow by successive accretion of valve material, their shells provide a record of incremental growth through the life of an individual the chemistry of which may relate not only to oceanic composition, but may also serve as a proxy for oceanic paleotemperatures (Buening, 2001).

Many successful studies of stable isotope geochemistry in brachiopods (e.g. Brand, 1982; Rush and Chavetz, 1990; Shields et al., 2003; Auclair et al., 2003) use calcitic-valved members of the phylum, such as rhynchonellids and craniids (Buening 2001). However, the valves of Cambrian aged well-preserved calcitic-valved brachiopods are particularly uncommon and consequently, geochemical studies of calcitic brachiopod valves have rarely been applied to lowermost Paleozoic strata. Accordingly, various researchers (e.g. Azmy et al.,

1998; Rodland et al., 2003; Cowan et al. 2005; Elrick et al., 2010; Kocsis et al., 2012) interested in exploring lowermost Paleozoic paleotemperatures, have focused on to lingulid (i.e. phosphatic-valved) brachiopods.

Lingulid brachiopod valves contain alternating layers of carbonate-flouroapatite, $Ca_5(PO_4,CO_3)_3(CO_3,F,OH)$, and organic chitin (Williams and Cusak, 1997). The secretion of this valve material is thought to occur in isotopic equilibrium with the surrounding ocean water (Lécuyer et al., 1996). Thus, each successive lamination within an individual valve is expected to record the localized seawater composition at the time of valve growth (Williams and Cusak, 1997). In addition to the relative the abundance of lingulid brachiopods in lowermost Paleozoic rocks, the calcium phosphate valve chemistry is more resistant to diagenesis than are calcitic valves (Longinelli and Nuti, 1968; LaPorte et al., 2009).

Oxygen isotope paleothermometry

Analyzing stable isotopes of oxygen as a proxy for paleotemperatures has been widely employed (see Longinelli and Nuti, 1968; Lécuyer et al., 1996; Wenzel et al., 2000; Rodland et al., 2003, Jaffres et al., 2007; LaPorte et al., 2009). Such analyses generally investigate the difference in ratio of $^{18}O/^{16}O$ relative to a standard (e.g. the Vienna standard mean ocean water -VSMOW) reported as the $\delta^{18}O$ or per mil (‰) difference relative to that standard (Jaffres et al., 1997). This difference in heavy (^{18}O) to light (^{16}O) oxygen in seawater is controlled by several factors (see Wallmann, 2001) with the preferential

evaporation of ^{16}O oxygen relative to ^{18}O playing a roll (Wallmann, 2001). In times of glacial maxima ^{16}O, evaporated and transported to higher latitudes, becomes sequestered in high latitude ice thus enriching the oceans in the ^{18}O. Conversely, in a greenhouse world the ocean is more homogenous in its oxygen composition since little to no sequestering of ^{16}O occurs (see Wallmann, 2001). It follows then that during times of glacial maxima (i.e. colder temps) the ocean will be slightly enriched in ^{18}O resulting in relatively higher $\delta^{18}O$ values.

While the use of oxygen paleothemometry as a proxy for temperature is generally accepted for relatively modern analyses a consensus on its applicability to older material (i.e. lower Paleozoic material) has yet to be reached (Jaffres et al., 2007). This is due to mainly to uncertainty of the oxygen composition of the ocean, where questions still remain as to whether ocean oxygen composition has remained constant through time (see Holland, 2004) or has fluctuated over Earth's history (see Veizer et al., 1996). Since oxygen paleothermomtery values are determined based on the oxygen composition of the ocean, this discrepancy has significant implications (Jaffres et al., 2007).

Consensus on the utility of oxygen paleothermometry in phosphatic-valved brachiopods has been equally problematical (Rodland et al., 2003). Some of these difficulties relate to sample size and analytical precision in particular studies (LaPorte et al., 2009), as well as, diagenetic alteration of valve material (Buening, 2001). However, even with exceptional preservation, questions as to the reliability of the phospatic brachiopod valve remain (see Rodland et al.,

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2003). Rodland et al. (2003) performed a detailed analysis of oxygen isotopes paleothermometry utilizing brachiopod phosphate and showed both inter- and intravalve variation of $\delta^{18}O$ signal in both modern and fossil inarticulate brachiopods. These were concluded to be due to non-equilibrium secretion of valve material with ocean water and/or physiological vital effects (Rodland et al., 2003). These findings, however, disagree with those of Lécuyer et al. (1996) and Bassett et al. (2007) and highlight the need to investigate the utility of phosphatic-valved brachiopods for oxygen isotope paleothermometry. Recent improvements to both sample preparation procedures and analytical processing are enhancing the precision of the technique (LaPorte et al., 2009).

Brachiopods of late Cambrian Laurentia

Lingulid (phosphatic-valved) brachiopods, are common in Cambrian rocks throughout the world, and recently have become the focus of enhanced research attention. Good preservation of their phosphatic skeletons offers the possibility for detailed investigation of valve composition and structure (Williams & Cusack 1994, 1998) growth (Williams, 1977), biogeography (Roberts & Jell, 1990) and biostratigraphy (e.g. Popov et al., 2002), in addition to their value as paleoenvironmental indicators.

With regard to the paleoenvironment of the Cambrian of Laurentia Cowan et al. (2005) recorded a positive excursion in $\delta^{13}C$ values recorded from phosphatic-valved brachiopods that mimicked the Steptoean positive carbon isotope excursion (SPICE) event as defined by other analyses (see Saltzman et

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al., 2004). It has been interpreted to record an episode of changing seawater chemistry related either to fluctuations in carbon burial and attendant seawater oxygenation (Gill et al., 2007) or to the degree of euxinia (Gill et al., 2011). Interestingly, the analyses of phosphatic brachiopod valves also from the upper Mississippi Valley showed a consistently ~ 6‰ lighter offset (Cowan et al 2005) than those obtained from contemporary $\delta^{13}C$ samples that were used to established the SPICE excursion (Saltzman et al., 1998, 2000, 2004). The nearshore environment in which continental runoff enriched with lighter carbon values diluted ocean waters relative to the heavier offshore values recorded was proposed to explain this (Cowan et al., 2005). These brachiopod specimens analyzed were sampled from outcrops in Wisconsin and Minnesota, and included whole, undifferentiated, brachiopod valves from the Eau Claire Formation (Cowan et al., 2005). These specimens provided $\delta13C$ values for the upper *Cedaria* zone at ~ -6‰ and values for the *Crepicephalus* zone at ~-7‰ (Cowan et al., 2005).

Elrick et al. (2010) analyzed the $\delta^{18}O$ of lingulid brachiopods from three localities, two in Utah and one a core sample from Iowa (Rhinehart A-1 Core). The rocks from these locations all represented Laurentian Cambrian shallow shelf environments. The authors showed a correlation between $\delta^{18}O$ values obtained and the carbon and sulphur isotopic values considered characteristic of the SPICE event (Gill et al., 2007, 2011) and suggest relatively elevated $\delta^{18}O$ values (implying relatively cooler temperatures) at the onset of the SPICE and

decreasing values (relatively warm temperatures) at the peak. Temperatures

calculated from the $\delta^{18}O$ values (12.5‰-16.5‰) generated from their analysis

indicate very warm temperatures (~45-62°C) prompting the authors to invoke

possible diagenetic alteration caused by microbial enzymatic activity within voids

of the brachiopod specimens shortly after death (Elrick et al., 2011). Curiously,

however, the authors contend that the pattern of decreasing and increasing $\delta^{18}O$

values correlate with the $\delta^{13}C$ values during the SPICE event (Elrick et al., 2011),

and does indicate that a change in temperature paralleled that seawater

chemistry. How this related to the diagenesis invoked was unresolved.

Accordingly, in both these studies the isotopic signals from the lingulid

brachiopods analyzed are either shown to be different (perhaps due to local

dilution) or are expected to be different (due to evident diagensis) from results

derived from elsewhere. Thus, while results indicate that the isotopic values

obtained from these ancient valves may provide meaningful paleoenvironmental

information diagensis may have had an important influence, which questions the

reliability of data derived from them for paleoenvironmental interpretation.

Here I address the question of how well-preserved the best of these

specimens actually are, and then investigate whether high-resolution (i.e.

annual/seasonal) temperature fluctuations in individual valves can be detected in

rocks deposited near the onset of the SPICE event at ~ 500 mya. Specifically,

given the fact that the rocks I have studied are part of the same depositional suite

and set of cyclically reoccurring lithofacies (see Runkel et al., 2007) as those

invoked to show marked temperature fluctuation including seasonal ice (Runkel et al 2010), I test the prediction that marked fluctuation in $\delta^{18}O$ values will be recorded in individual valves and that these will suggest marked seasonality of the local climate.

Geological Setting

The sedimentary rocks of the upper Mississippi Valley (UMV), consisting of both quartzose and feldspathic sandstones, along with shales and dolomite-rich beds in some horizons, make up the St. Croixan Series (Ostrom, 1978), also known as the Sauk sequence (Sloss, 1963) (Fig. 1). These deposits fringed an area of positive relief called the Wisconsin arch (Runkel et al., 2007) and on-lapped the Precambrian shield along a depression along which the Mississippi and St Croix rivers now flow and which marks the site of a depocenter known as the Keweenawan rift (Chase and Gilmer, 1973). The St. Croixan Series spans an interval between the late Marjuman Stage (latest middle Cambrian) (Runkel et al., 2007) at about 505 Ma (Ogg et al., 2008), and extends up to the base of the Skullrockian Stage (Palmer, 1998) at about 490 Ma (Ogg et al., 2008)

The St Croixan Series represents onshore environments, ranging from fluvial and eolian dispersed sands deposited along a barren landscape (Dott et al., 1986) to relatively shallow-marine facies (Runkel et al., 1994). Recent work by Runkel et al. (2007) offers a high-resolution sequence stratigraphic framework that identifies stratigraphic packages deposited along a very shallowly dipping shelf bathymetry with extremely slow subsidence along a very low angle shelf

gradient. Within these packages, multiple scales of transgression and regression are expressed, the larger of which had relatively long duration and wide spatial distribution (Runkel et al., 2007). The brachiopods analyzed in this study are all from the Eau Claire Formation, which is part of the basal St Croixan Series underlain by the Mt Simon Formation (Ostrom, 1978).

The Eau Claire Formation (ECF)

The Eau Claire Formation (ECF), as recognized from four locations throughout west-central Wisconsin (Fig. 2), is the first formation dominated by heterolithic lithology in the St Croixan Series, and its sediment deposition spanned portions of the *Cedaria* and *Crepicephalus* trilobite zones, dated to about 500 ma (Saltzman et al., 2004). It consists of moderately bioturbated heterolithic, very fine-grained, feldspathic and occasionally glauconitic sheet sandstones interbedded with green claystones. These are interbedded with trough cross-bedded channeled sandstones with erosional bases (Figs. 3 & 4).

The Eau Claire Formation sampled for brachiopods contains two major lithofacies, a heterolithic facies consisting of alternations of muds and sands on a scale of (~ 1–2 cm) (~ 5–10 cm) respectively. A dolomitic cement pervades the sandstone layers in some levels. Sedimentary features associated with the sand layers include parallel lamination, hummocky cross stratification, and wave ripple lamination. Primary current lineation occurs rarely on the bases of sand layers. Flat topped ripples with runzel marks on the planed ripple crests are recorded from one horizon at about 5.9 meters in Old Albertville Quarry (Fig. 4) and though

once considered diagnostic of exposure are presently more commonly interpreted as structures related to algal binding of sediment surface (Seilacher & Pflüger, 1994; Hagadorn & Bottjer, 1997). Primary current lineation and wave ripple crests suggest an approximately ESE-WNW transport direction. The beds show common mudcracks and are commonly bioturbated with ichnofabric indices (Droser and Bottjer 1986) ranging from 1– 4, and most commonly about 3. Phosphatically-valved brachiopods, hyolithids, and trilobites all occur concentrated at particular layers in both the mudstone and the sandstone components. This lithofacies is interpreted to represent shelfal conditions below fairwater wave base, with sands introduced episodically as the result of storm events.

The other lithofacies too is comprised of thick feldspathic, rarely glauconitic, very fine-grained sandstones up to 50 cm thick. These are made up of individual bedsets up to about 30 cm thick that may show parallel lamination, hummocky cross stratification, or trough cross-bedding, with individual foresets up to 20 cm high. Internally these bedsets may have angular bases. Brachiopods are commonly found in high concentration and in various degrees of fragmentation along bedding, and are particularly common along the trough cross-bedded foresets Occasional thin (<5 cm thick), trough cross-bedded quartz sandstones of medium grade (see 11.0 meter level in Fig. 3) also occur in these units.

The facies reported in the two sections studied in detail are comparable to those established in a recent study by Aswasereelert et al. (2008). The heterolithic facies corresponds with Aswasereelert et al's (2008) lithofacies A-C, which they interpreted to represent more distal environments, and the laminated sand lithofacies corresponds to their lithofacies D-E, which represent a more proximal setting. The laminated sandstone facies is relatively high energy, and portions of it (that containing the trough cross-beds) represent conditions above fair weather wave base.

The phosphatically-valved brachiopods *Dicellomus politus* (Hall, 1861) occur particularly commonly along a single bedding plane at 1.6 m and 6.8 m (see Fig. 3) within the green mudstone at Strum. The specimens from Colfax Quarry, *Lingulella ampla* (Owen, 1852) were collected from loose blocks at the side of the abandoned quarry, but the very fine-grained feldspathic sandstones show clear trough cross-bedding, so they clearly belong to the laminated sandstone lithofacies.

The beds of the Eau Claire Formation indicate a shallow marine depositional facies with a series of small-scale transgressive/regressive depositional cycles alternating between heterolithic units and the laminated sandstones, with the latter representing relative sea level fall (Hughes and Hesselbo, 1997). These units are interpreted by Runkel et al (2007) as a nearshore marine parasequence stack representing high stand system track (HSST) deposits that accumulated in a shallow shelf setting to depths of tens of

meters. The stratigraphic positions of the brachiopods studied in this analysis are constrained by the trilobite biozonation. The *D. politus* occurring on the mudstone surfaces from Strum are within the *Cedaria* Biozone of the upper Mississippi Valley, approximately 500 Ma old, and *L. ampla* from Colfax are from the Crepicephalus Biozone.

Brachiopods of the Eau Claire Formation

In life position modern (Thayer and Steele-Petrovic, 1975) and fossil lingueliform brachiopod valves (Pemberton and Kobluk, 1978; Yugan et al., 1993) lived orientated orthogonal to bedding occupying burrows from which they protrude via extension of their fleshy pedicle. Rarely these fossils are preserved in life position (*e.g.* Over, 1988), as such linguliform brachiopod valves of Eau Claire Formation, collected from four locations (as indicated in Fig. 2), are common in many beds but are concentrated with their valve axes parallel to particular bedding planes. These valves were typically found in convex up position. Rose diagram plots from two bedding surfaces collected from Colfax Quarry and Strum Quarry, show a lack of valve alignment (Fig. 5).

The valves of *L. ampla* from Colfax Quarry (Fig. 6A-D) are off-white to cream in color with concentric color bands ranging from light to medium brown. This color banding ranges in intensity and in size (50 μm–200 μm). All valves are disarticulated and collected from foreset laminae of trough cross-beds. Fracturing is minimal, and where it occurs is primarily constrained to the valve edges and to the umbo. Typical valve size ranges from 5-8 mm in length and 3-4 mm in width.

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The valves of *D. politus* (Strum Quarry) (Fig. 7A-D) are off-white/cream to light brown in color with concentric color bands ranging from light/medium to dark brown to orange and red. This color banding ranges in intensity and in size (40 μm to 200 μm). All valves are disarticulated and fractured, but fracture fragments are associated, suggesting that fracturing was compactional in origin. The valves range in size from 4-6 mm length and 3-4 mm width.

Valves of *Obolella sp?* (Billings, 1861) from Remington Quarry (Fig. 8A-B) are off-white to cream to brown in color with concentric color bands ranging from light to dark brown to orange. This color banding ranges in intensity and in size (30 μm to 300 μm). High gloss sheen is visible on the valve surface. All valves are disarticulated with minimal to no fracturing. Valves range in size from 3-4 mm length and 2-3 mm width.

The color banding in all valves from each location show no distinct pattern associated within or between individual valves. It is not certain whether this coloration reflects original valve coloration patterns or is a post-burial artifact, possibly from the uptake of iron into the valve as organic matter degrades and is replaced shortly death (Williams and Cusak, 1997).

The taphonomy of these beds clearly indicates that the brachiopod valves have been disturbed from life position, have become disarticulated in almost all cases, and have been transported, sometimes in a relatively high energy environment. Nothing about the geological setting of these brachiopods suggests extensive diagenetic alteration. Furthermore, the spectacular color banding,

whether original or not, suggests that preservation is among the best known in Cambrian brachiopods. The excellent quality of their appearance argues against prolonged reworking in a high energy setting, however it is clear from taphonomic studies of modern clam shells in time averaged assemblages that apparent shell quality can be a poor guide to when the animals were alive (Kowalewski and Flessa, 1996).

Modern linguliform brachiopods live on the order of 5-8 years (Lecuyer et al., 1996), and deposition of the Eau Claire Formation likely lasted approximately 75 – 150 k.y. (Runkel et al., 2007). Each bedding surface containing well-preserved brachiopods may thus represent valves that were deposited over time frames somewhere in the range of the range of 10^1 to 10^3 years, and thus does not represent either a cohort of individuals that settled from a single spat-fall, or a dynamic population of contemporaries. Rather individual surfaces likely contain individuals spanning multiple generations. All are apparently transported, and those in the trough cross-beds in the laminated sand facies were presumably living in quite proximal marine environments. Lithofacies occurrence patterns suggest that *D. politus* may have favored a slightly more distal setting that *L. ampla.*

The lingulid species used in this study include both specimens collected from exposed outcrops (as described above) and also additional specimens from some of the same localities on loan from the University of Wisconsin, Madison Geology Museum. The total number of species collected and studied include 40

specimens of *L. ampl*a from Colfax Quarry, WI; 100+ specimens of *D politus* from Strum Quarry, WI and *Obolella* sp? Remington Quarry, WI. All specimens were analyzed under a binocular scope for determination of shell quality and taxonomic affinity. These specimens were then imaged using Nikon D300 digital camera.

Analyses of the preservational quality of Eau Claire Formation brachiopod valves

A series of detailed investigations of the valve structure and chemistry were performed to evaluate diagenetic alteration. The analyses I performed are those routinely used when assessing the suitability of phosphate valves for sclerochronology (see Kohn & Cerling, 2002). These tests included thin section analysis of individual valves, cathodoluminescence (CL), X-ray diffraction (XRD) of powdered shell material, and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX). Subsequent to these oxygen isotope analysis was completed utilizing high temperature conversion elemental analyzer isotope ratio mass spectrometry (TC/EA-IRMS).

TC/EA-IRMS

Individual specimens of *L. ampla* and *D. politus* were drilled using a 300 μm bit attached to a Brasseler USA Dental Rotary Instrument DLT 50k series 2. Specimens were handheld and viewed under a Lecia binocular microscope while drilling. Drilling was directed along individual growth line "sets" (with the drill bit width encompassing the width some 3-5 individual growth lines) that mirrored

successive stages of the progressive distal growth of the valve margin. Drilling

progressed from the commissure (anteriorly) toward the umbo (posteriorly) in a

series of arcuate stripes (Fig. 9). Due to the smaller size of *D. politus* drilling

along growth line sets was unattainable and thus whole valve sampling was used

in order to obtain adequate powder samples. Approximately 750 μm of powdered

shell material was removed per growth line set (or region) and analyzed for

oxygen isotope composition. For this analysis a slightly modified method of silver

phosphate (Ag_3PO_4) extraction from Venneman et al. (2002) and Bassett et al.

(2007) was employed. A slight deviation from these published methods was

applied in the drying of the samples. Rather than placing samples in an oven at

40^oC, the specimens were dried in opened micro-tubes in a standard flow fume

hood for 12 days. Micro-tubes were covered with sanitized tissue to prevent

contamination from foreign objects. This alteration to the method allowed for

slower evaporation of the ammonia solution and thus resulted in the precipitation

of larger Ag_3PO_4 crystals that retained their more vibrant yellow coloration.

Preservation of Valve Structure

Specimens of *L. ampla* from Colfax, and *D. politus* from Strum were

thin sectioned for analysis of internal shell structure by impregnating rocks

samples containing the valves in clear epoxy and then cutting along the axis of

valve symmetry so as to achieve a proximal to distal profile of shell growth.

These specimens were then viewed under binocular microscope and imaged

using a Leica binocular scope with a camera and imaged utilizing Leica Acquire software.

Pronounced growth and color banding was visible on the surfaces of all valves. These features vary in frequency within each valve and occur at varying widths (from 30 μm – 300 μm) along the shell growth; no distinct pattern of either banding is recognized within individual valves or between valves from the same location. In thin section internal growth laminae are observed (Fig. 10A). Valve imaged is ~2.5 mm in length, ~ 70 μm thick from the commissure to mid valve and increases to ~140 μm thick at this point to umbo. These laminae occur as sets of alternating bands of light and dark material that vary in size from 3-6 μm up to 30-50 μm and are oblique to the valve surface. These growth sets are interpreted to be the display the succession of primary and secondary layer, which is characterized by alternating apatite (light) and organic (dark) layers at similar scales (Williams et al., 1994). Within these growth sets there appears to be a rhythmic alternation of the darker material at about <1μm (Fig. 10B). Under-plating these oblique laminae are tightly packed laminae at ~40 μm that are parallel to the valve surface. Within this layer individual laminae are ~3-4 μm thick. These laminae pinch out at ~500 μm from the valve edge. These observations indicate that valve structures, such as individual growth laminae are preserved distinctly, with no evidence of internal recrystalization of shell material.

Specimens of both *L. ampla* and *D. politus* were picked from bedding planes and fractured along both along the plane of symmetry and perpendicular

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to this plane. Three specimen fractures from each were then analyzed utilizing a LEO 982 Digital Field Emission scanning electron microscope with Bunker AXS Microanalysis Gmbh (X Flash Detector) and an EDS (Energy Dispersive X-Ray Microanalysis) attachment for elemental mapping. Additional specimens of *L. ampla* and *D. politus* were fractured along their plane of symmetry and perpendicular to this plane. These fragments were carbon coated and analyzed utilizing an XL30-FEG scanning electron microscope.

In *D. politus* fragments displayed distinct valve layering with "compact laminae" made up of a dense mass of mineral (Cl)(~2 μm thick) sandwiching less dense layer (~5μm)(Fig 11). These valve structures are visible in each *D. politus* fragment imaged.

Lingulella ampla produced similar valve structures. In fragment LA1 definitive micro-laminae structures such as alternating sets consisting of primary layer, compact laminae (2 μm wide) and baculate laminae (~5-10μm wide)(Fig. 12A-B and13A-B) this primary layer is recognized as the dense upper-most layer of each laminae and is in sharp contrast to the less dense compact and baculate laminae below (Williams et al., 1994). The baculate laminae layers are comprised of small (~1 μm along the C axis) needle-like crystal prisms (Fig. 14A-B). In general the axes of the crystalline rods that make up the baculate laminae are orthogonal to the compact laminae. Additionally, tightly packed rhombohedral polygonal structures occurring on the upper portion of individual compact laminae of *L. ampla* are approximately 5 microns across (Fig. 15A-B).

The structures described above are recognized as main structural components of other extant (see Popov & Holmer, 2003) and modern phosphatic-valved brachiopods (Williams et al., 1998a, 2003, 2008). Comparison of structures from my analysis, such as primary layer, compact and baculate laminae, and surface imprints occur at scales in consistent with these published results. Among these the most striking features are the preserved rhombohedral surface imprints occurring on the surfaces of compact laminae. Imprints such as these are recognized from modern and extant *discinid* lingulid brachiopods and are interpreted as the impressions of cell polygons during juvenile shell growth (see Williams et al., 1998; Williams, 2003) and suggest pristine structural preservation of the valve.

From these analyses I can confidently conclude that the valves analyzed herein are pristinely preserved and that there is no evidence of secondary inclusions or cement present. Given that there is no indication of any significant micro-structural alteration to these valves any alteration would have to have occurred at a chemical level without significantly changing the structural components of the phosphate valve.

Evaluation of Valve Chemistry

Valve fragments of *L. ampla* (from Colfax Quarry) and *D. politus* (from Strum Quarry) were picked off slabs and cleaned with a stainless steel surgical pick. These were then powdered using a mortar and pestle and slide mounted for X-ray diffraction (XRD) analysis using a Shimadzu Lab-X, XRD6000, X-Ray

Diffractometer. The bulk valve composition for both samples confirmed a calcium-fluorapatite [$Ca_5(PO_4)_3F$] valve composition. No other mineral phases were detected. This determination confirms that the prismatic crystals observed in the SEM analysis are apatitic, and this is a common habit for this mineral (Battey, 1981).

In order to examine valve chemistry in more detail, and particularly to see whether substantial ion substitution might have occurred within the apatitic lattice, five thin sectioned valves from the Eau Claire Formation and one modern brachiopod valve were analyzed for luminescence using a Reliotron Cold-Cathode Luminescence (CL) Imaging System operating at ~ 8 Kv. This procedure is often used in assessing the diagenetic alteration of minerals (Joachimski et al., 2009). Typically, non-altered biogenic phosphates will not luminess during CL analysis (Joachimski et al., 2009). Specimens in this study each display some degree of luminescence, which varied among individual valves a consistent bright orange color to a consistent dull yellow (Fig. 16A-D). No notable variation of color occurred within individual valves except at the termination of growth laminae, confirming the in tact preservation of shell structure. The luminescence of the mineralized valves may be attributable to post-burial uptake of rare earth and trace elements and does not indicate substantive diagenetic alteration (Joachimski et al., 2009). Localized differences in REE or trace elements may relate to minor differences in pore water composition. This was observed in further analysis utilizing EDAX for elemental

analysis confirmed phosphate valve composition with trace elements (i.e. O, Fe, Mg, Ca) occurring in appreciable amounts (Fig. 17A-B). Additional chemical analysis employing inductively coupled plasma mass spectrometry (ICP-MS) confirmed these and additional trace elements including, Mn, and U.

The confirmation of valve structures and valve chemistry consistent with modern brachiopods is evidence for the exceptional preservation of these specimens. Thus, these analyses provide confidence in assessing the isotopic composition of these 500 my-old brachiopod specimens for paleoclimate reconstructions.

Oxygen Isotopes ($\delta^{18}O_{PO4}$) from 500 my-old Brachiopods

Overall, the results from the analysis of the oxygen isotope content ($\delta^{18}O_{PO4}$) of individual growth line sets from single valves of *Lingulella ampla* indicate relatively little variation along the axis of growth and also that these values are relatively constant between valves (Table 2). There are, however, some significant differences in mean temperature within values, even though the variations are quite small. This variation from the mean in the $\delta^{18}O_{PO4}$ measured along the axis of growth of five individual valves of *L. ampla*, is <0.653‰; <0.700‰; <0.547‰; <0.872‰; and <0.359‰ (+/- 0.21‰) and the associative change in temperature ($\Delta°C$) with these values along the axes of growth suggest temperature fluctuations not exceeding +/-2.8°C, +/-3.0°C, +/-2.3°C, +/-2.0°C, +/-1.6°C respectively (see Table 2). Figure 18 displays this variation as plotted

along the axis of growth and highlights the consistency of variation within an individual valve regardless of mean value differences between valves.

Mean $\delta^{18}O_{PO_4}$ values from individual valves of *L. ampla* range between 17.5‰ –16.1‰ which suggest average seawater temperatures of 39.1ºC – 44.8ºC. Additionally, analysis of three whole valves of *D. politus*, inferred to inhabit more distal environments, also provided a variance in $\delta^{18}O_{PO_4}$ with values ranging from 16.9‰ – 15.4‰; temperatures associated with these values are 41.4ºC- 47.8ºC.

All temperature values are determined utilizing the fractionation equation from Pucéat et al. (2010): $T^{\circ}C = 118.7 - 4.22(\delta^{18}O_{PO_4} - \delta^{18}O_W)$ and assuming a $\delta^{18}O_{sw}$ of 1.4‰ for an ice free world (Lhomme et al., 2005).

Discussion

The most striking result obtained is the suggestion of seawater temperatures in excess of 35˚C. Although the geographic setting of an equatorial, shallow shelf with possibly restricted access to the open ocean would be a likely environment for very warm oceans and is broadly consistent with some previous estimates (Trotter et al., 2008), the physics of evaporative cooling suggests that raising sea temperatures to the levels suggested (ie >35˚C) is implausible. Physical constraints both related to water vapor/cloud forcing (Ramanathan & Collins, 1991) and in the sensitivity of organisms, specifically metazoans, to temperature extremes (Pörtner, 2001) place an upper limit on sea surface temperatures (SST's). In the case of the former (i.e. water vapor effects) an

increase in SST's will result in increased evaporation and the formation of cloud cover, thus reducing the radiative heating of the planet driving temperatures down (Ramanathan & Collins, 1991). Hence an alternative explanation for these values must be explored.

Diagenetic alteration of the valve chemistry is commonly the cause of anomalously light oxygen values, but the extremely high fidelity of the physical and chemical preservation documented herein suggests that this does not appear to have been the case in this example. It is thus necessary to look for an alternative explanation that pertained during the lives of these animals and resulted in the unusually light values.

The most plausible explanation is that the water composition of the seawater in which these organisms lived differed from that of standard mean ocean water (SMOW) values that are used in when applying the Pucéat et al. (2010) equation to estimate temperature. Substituting an $\delta^{18}O_{ecns}$ (equatorial Cambrian near-shore seawater) value for SMOW of approximately -2.5‰ based both on modern latitudinal variations in $\delta^{18}O$ (Pearson et al., 2001) and the inference of light isotopic runoff enrichment (^{13}C) from continental weathering (see Cowan et al., 2005), temperature calculations using the fractionation equation from Pucéat et al. (2010) indicate an average of ~38°C. This value is more plausible given ocean thermodynamics, and will be tested via comparison of the results of the clumped isotope method that is being applied to specimens from the same localities by colleagues in CalTech.

Aside from absolute temperature, the data provide some indication of the range of variation in temperatures experienced during valve accretion during the lifespans of individual brachiopods. Such lifetimes are estimated, on the basis of the growth rates of modern lingulid brachiopods, to be approximately 5-8 years (see Lecuyer et al., 1996). Within individual values temperature fluctuations between $1.5^{\circ}C - 3^{\circ}C$ have been observed, and though the magnitude of these is quite small, differences are significant in some cases (see Fig. 18). This suggests that mean sweater temperatures did vary during the lives of these animals. Resolving the causes for such variations is hindered by the fact that each individual sample likely included several growth laminae, with likely as many as 3-5 laminae per sample. What can be said with confidence is that the fluctuations in temperature witnessed suggest differences in temperature of only a couple of degrees. If marked variations in temperatures occurred during the time that valve material was being accreted this was not detectable at the resolution of the analysis that was performed.

Conclusion

Diagnostic tests performed on these seemingly very well-preserved ~500my brachiopods showed no indication that the valves had undergone any significant diagenetic alteration that might have distorted their oxygen isotopic ratios from those emplaced during the lives of these animals. The fact that the samples passed each of the diagnostic tests for precluding diagenesis is

congruent with what is known of their specific geologic occurrence and of the regional diagenetic and metamorphic history of the region.

Conclusions from these analysis thus include: 1) Brachiopods from the upper Mississippi Valley Eau Claire Formation have remained in practically pristine condition both in structure and in chemical composition, permitting insight into both valve structure and chemistry, 2) The application of micro drilling, along with Ag_3PO_4 oxygen isotope extraction, as a method for small-scale analysis along the axis of growth of individual brachiopod valves offers promise in that the observed variation in $\delta^{18}O$ along the axis of growth for several specimens indicated that through the life of an individual variation in temperature possibly related to seasonal temperature fluctuation is recorded at the level of analytical precision applied, 3) Isotope analyses from these valves indicate relatively little variation along the axis of growth of an individual brachiopod. Assuming that the oxygen isotope proxy as currently configured is accurately recording paleotemperature two possible explanations for this pattern remain. Either local seawater temperatures remained relatively constant during and between the lifetimes of the values both from individual bedding plane assemblages and in the time-scales represented between these beds, or variations were at such a fine scale that my analyses were unable to detect them. If the latter is the case it is surprising that different valves within and between assemblages should show such constancy of value and therefore I incline toward the former explanation. Accordingly, the data suggests that the late Cambrian environment of the upper

Mississippi Valley during the deposition of the Eau Claire Formation experienced equitable and rather constant seawater temperatures, likely in the range of ~35-39˚C.

Figures and Tables

Figure 1 – Stratigraphic column showing the various rock units of the lower Paleozoic Upper Mississippi Valley; S. Dakota/Nebraska, Iowa, Minnesota, and Wisconsin (modified from Runkel et al. 2007)

	Sequence	Sub Sequence	Stage	System
Wisconsin				
Ironton Member			Steptoean	Upper Cambrian
Galesville Member	Sauk Sequence	Sauk II		
Eau Claire Formation			Marjuman	
Mount Simon Formation				

Legend:
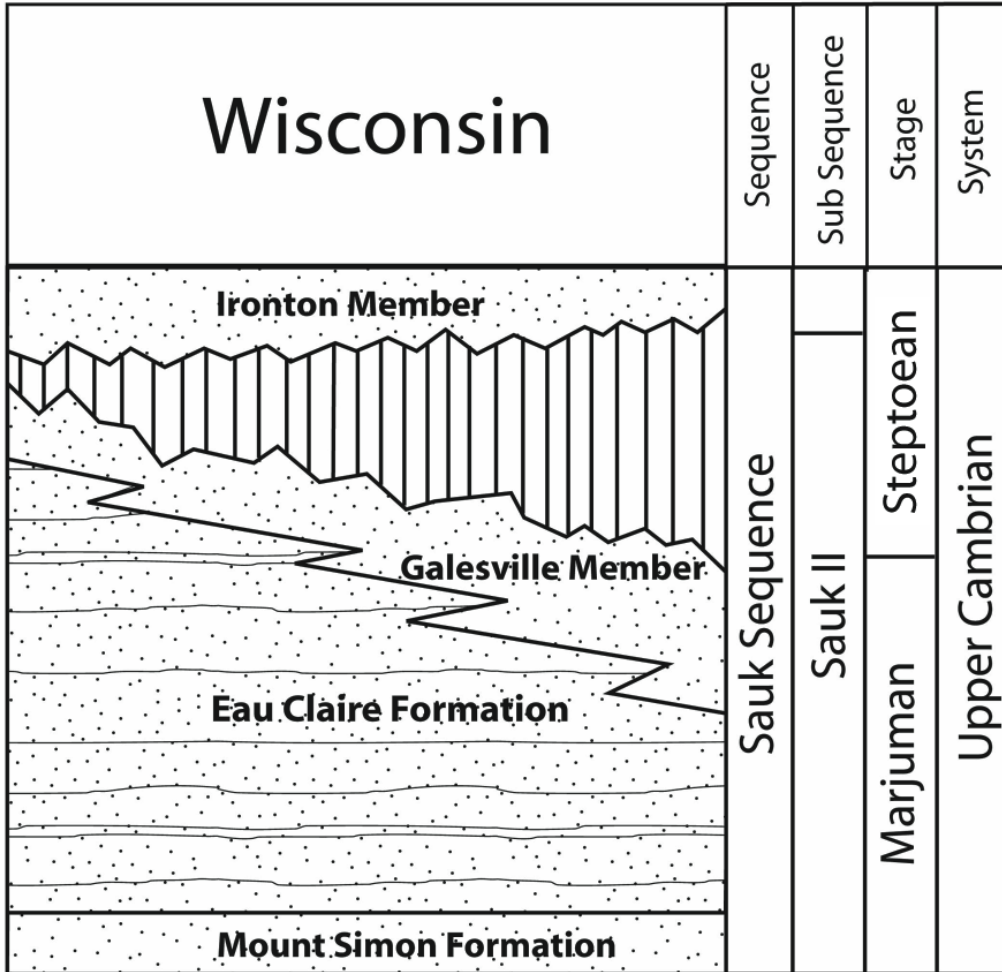
Medium to Coarse Grained Sandstone

Fine Grained Sandstone, Siltstone, Shale

No Record

—— Contact

Figure 2 – Map of Wisconsin showing collection locations. A) Colfax Quarry - 45° N 0'33.55" W 91°44'13.29" B) Old Albertville Quarry - 44°55'53.61"N 91°35'58.57"W C) Remington Quarry - 44°47'42.27"N 91°33'26.93"W D) Strum Quarry - 44°33'33.65"N 91°23'23.47"W
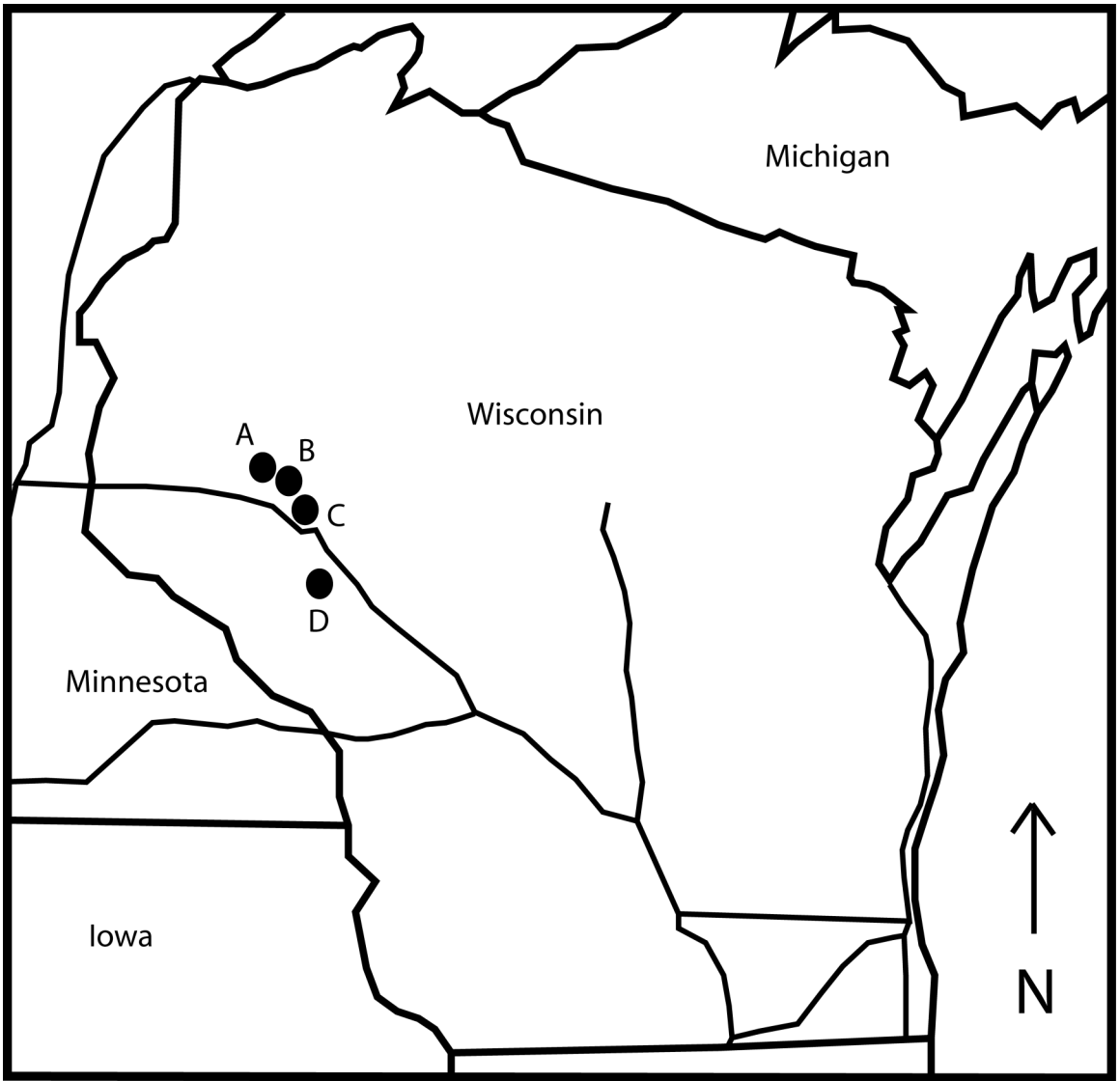
Figure 3 – Stratigraphic Log of Eau Claire Formation at Strum Quarry, WI. Ichnofabric
Indices from Droser and Bottjer (1986)

STRUM QUARRY LOG

Legend:
- Sand
- Clay
- Cross-beds
- Laminated beds
- Glauconite
- 240° Paleocurrent direction
- 1-4 Ichnofabric index
- ▲ Inarticulate Brachiopods
- O *Menomonia*
- □ *Cedaria*
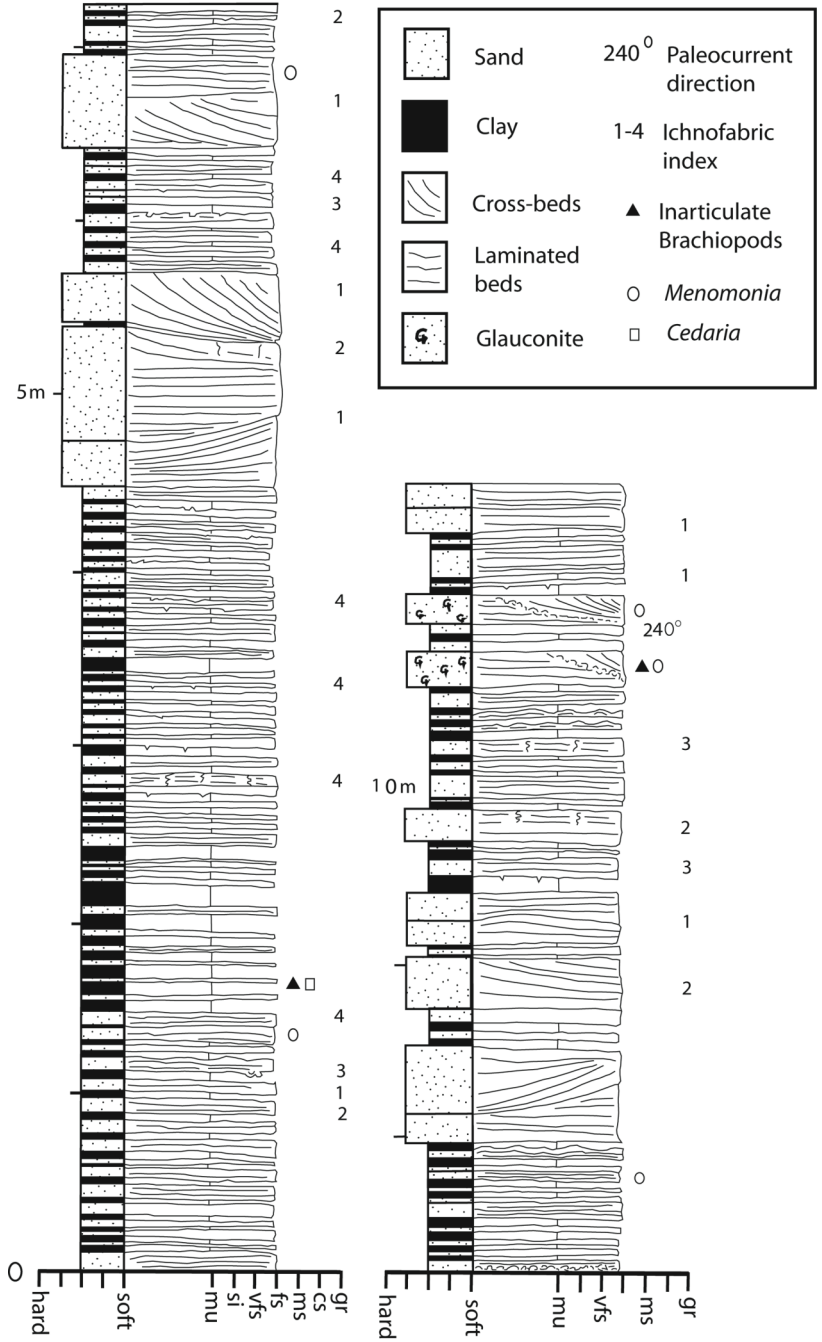
Figure 4 - Stratigraphic Log from Old Albertville Quarry, WI. Ichnofabric Indices from Droser and Bottjer (1986)

Old Albertville Quarry Log

Legend:
- sand
- mud
- glauconite
- ▲ Lingulid Brachiopods
- ☐ *Cedaria*
- ○ *Menomonia*
- ■ *Crepicephalus*
- 1-4 Ichnofabric index
- 240° Paleocurrent direction
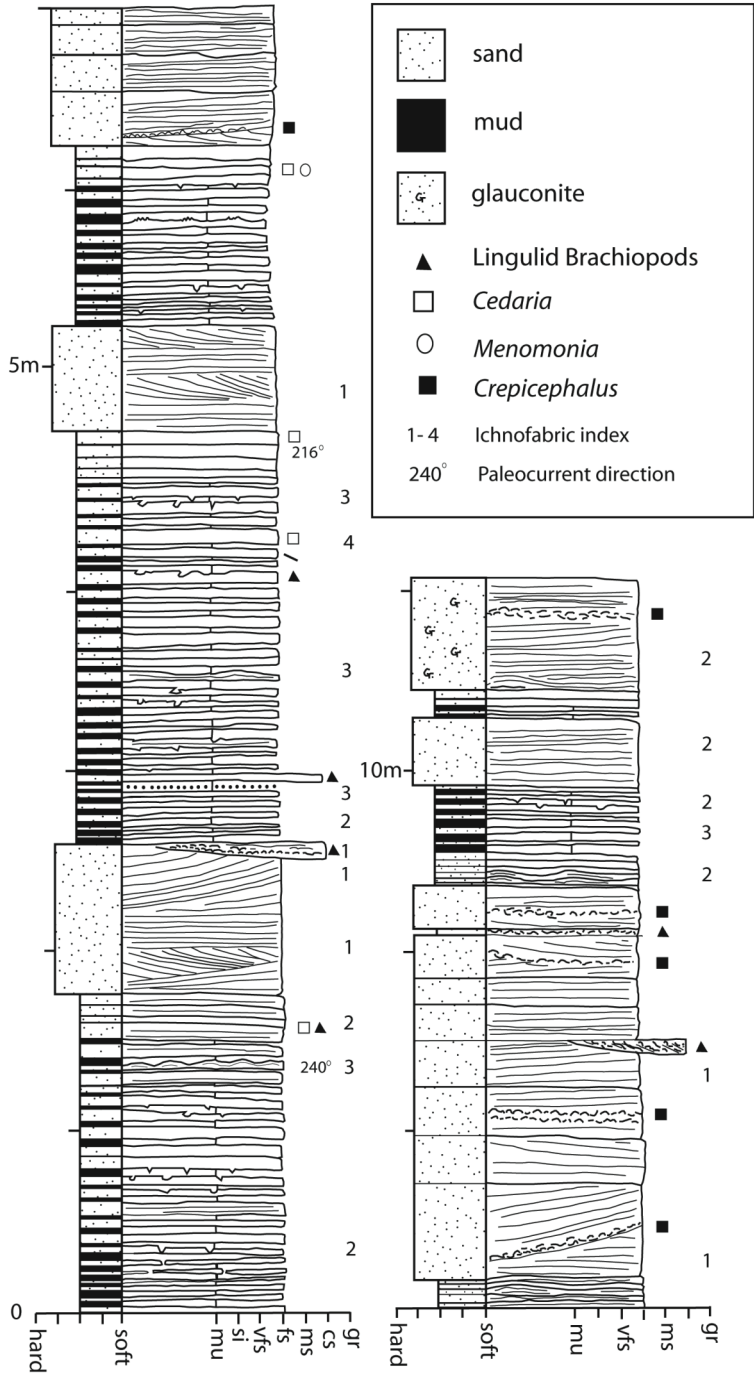
Figure 5 – Rose diagram showing valve orientation on bedding plane assemblages A) *Lingulella ampla* - Colfax Quarry (Specimen #UWGM1030), Colfax, WI and B) *Dicellomus politus* - Strum Quarry, Strum, WI
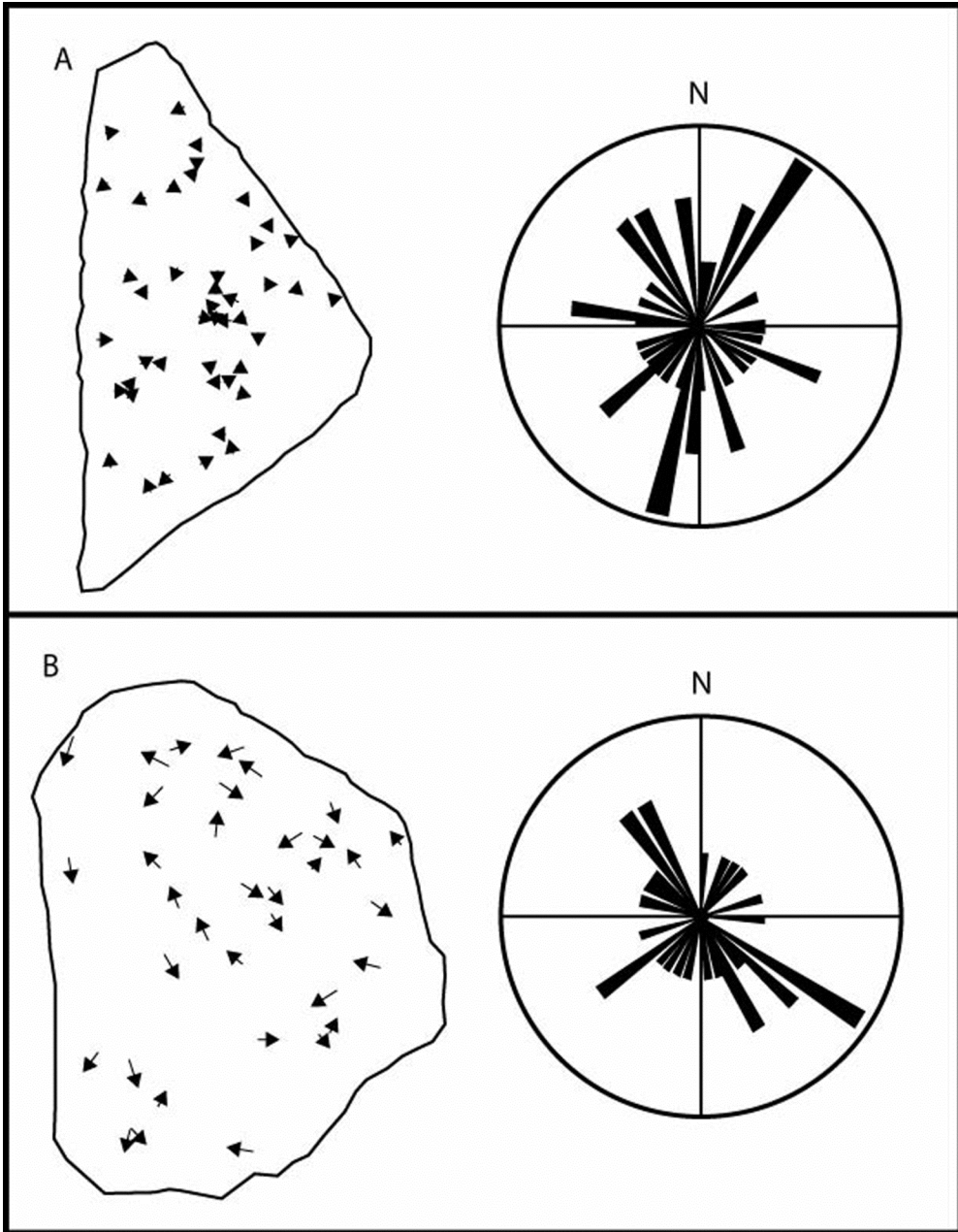
Figure 6 –*Lingulella ampla* (Colfax Quarry, WI) Specimen #UWGMXXXX-XXXX. Valves off-white to cream in color with concentric color bands ranging from light to medium brown. Valves are disarticulated with minimal fracturing to valve edges and umbo. Valves range from 5-8 mm L x 3-4 mm W (scale bar is 2mm)
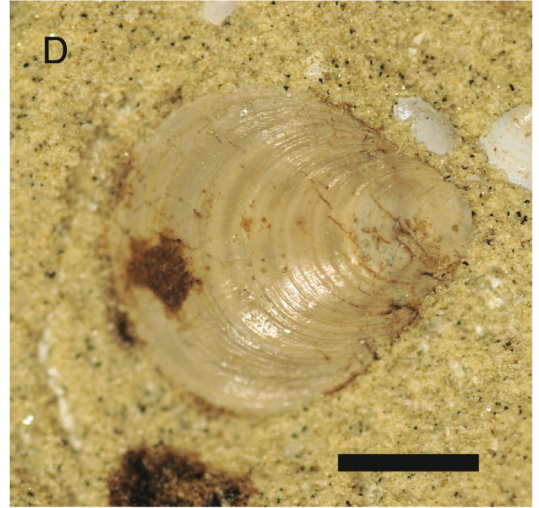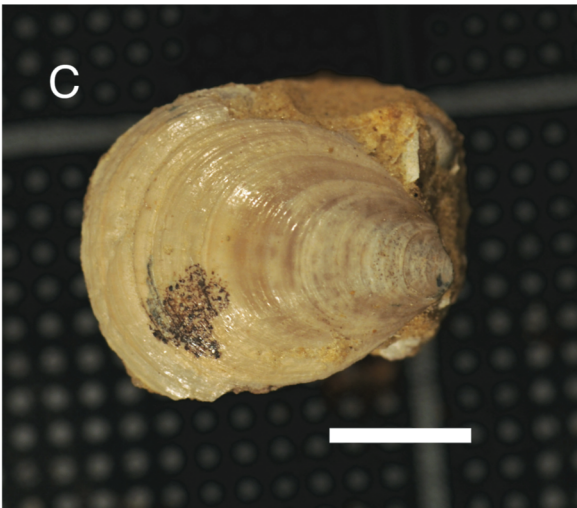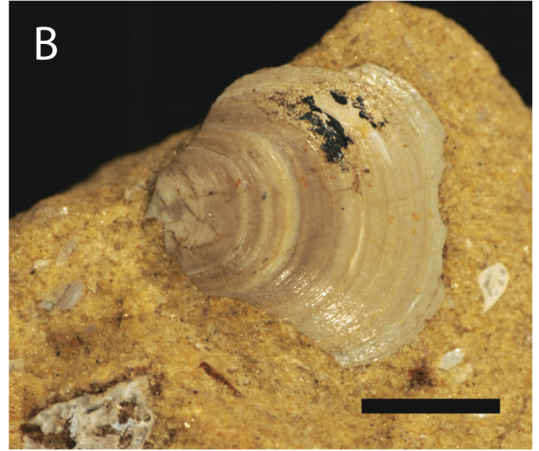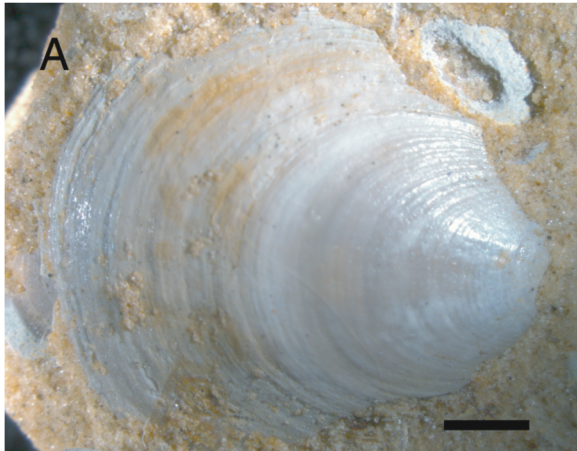
Figure 7 –*Dicellomus politus* (Strum Quarry, WI) Specimen #UWGMXXXX-XXXX.
Valves off-white to cream in color with concentric color bands ranging from light to dark
brown to orange. Valves are disarticulated with varying degrees of fracturing to valve
edges, umbo, and medial crest. Valves range from 4-6 mm L x 3-4 mm W scale bar is
2mm
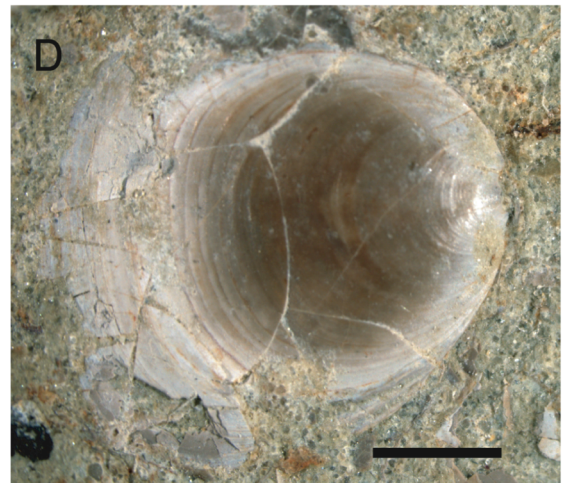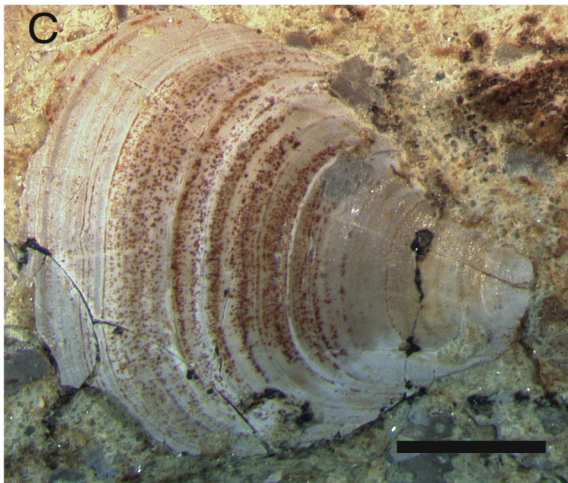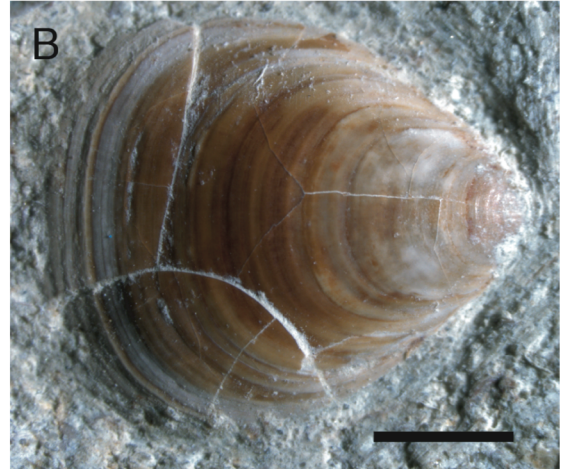
Figure 8 - *Obolella sp?* (Remington Quarry, WI) Specimen #UWGMXXXX-XXXX. Valves off-white to cream to brown in color with concentric color bands ranging from light to dark brown to orange. Valves are disarticulated with varying minimal to no fracturing to valve edges, umbo or medial crest. Valves range from 3-4 mm L x 2-3 mm W scale bar is 2mm
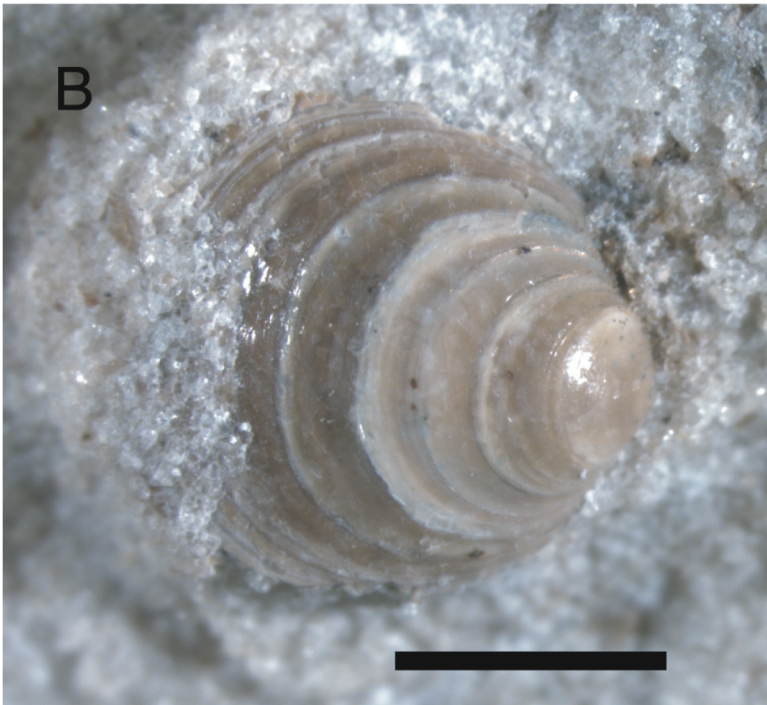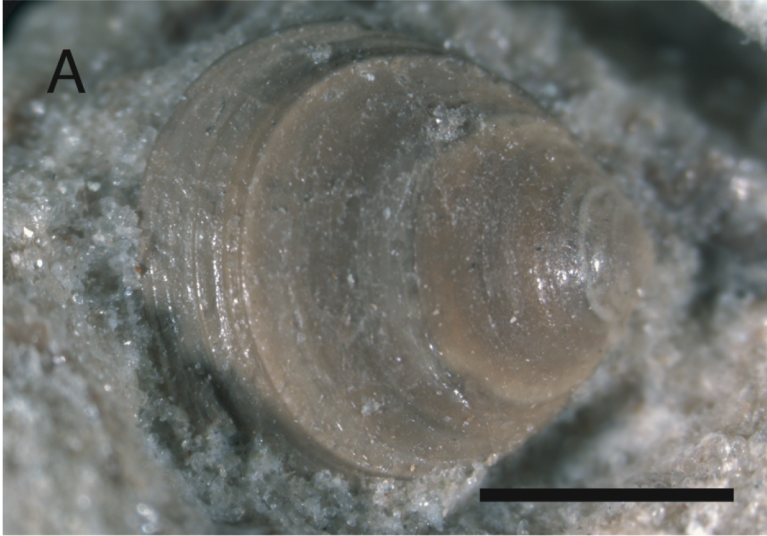
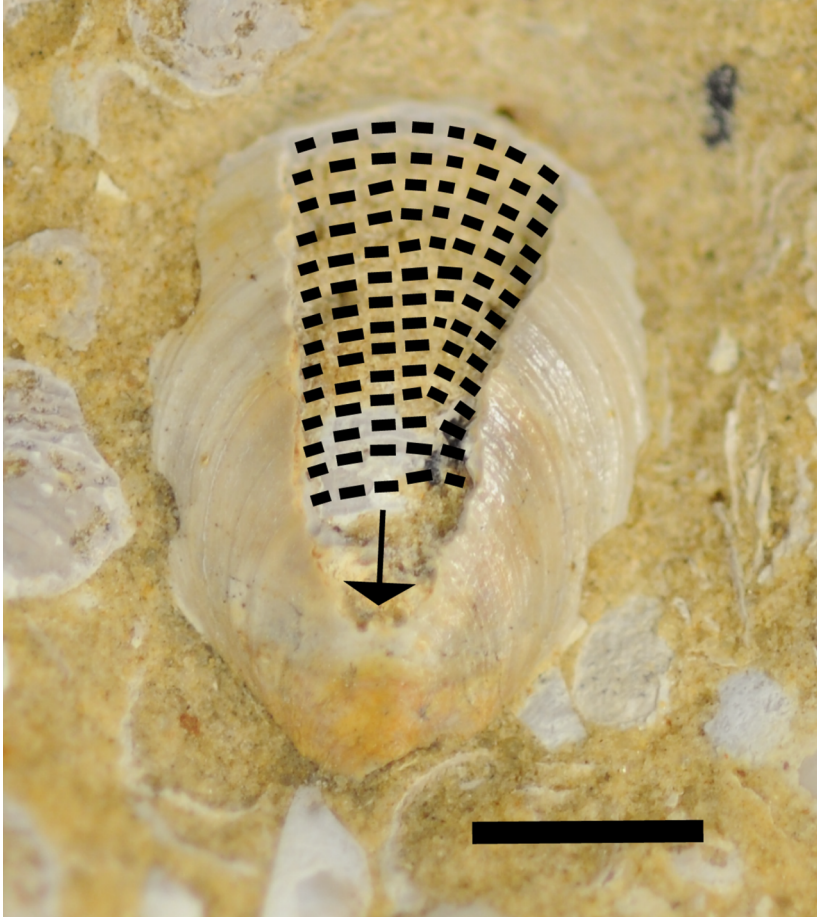Figure 9 –Drilled specimen (*L. ampla*), Specimen #UWGMXXXX-XXXX, with annotations to show arcuate micro-drill path with 30 μm drill bit.

Figure 10 – A) Stitched image of thin-sectioned specimen showing preserved growth laminae (scale bar ~ 200 μm) Specimen #UWGMXXXX. B) Enlarged view of medial section (scale bar ~ 100 μm)
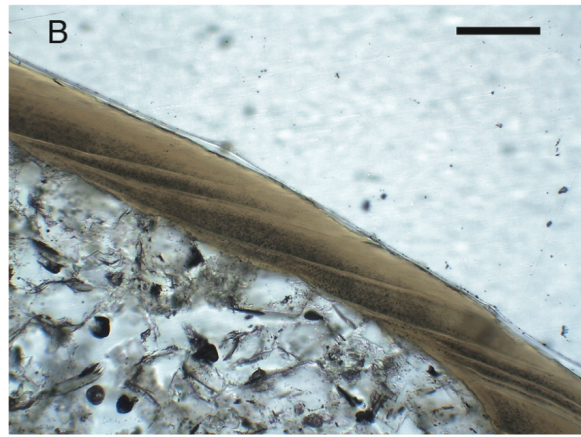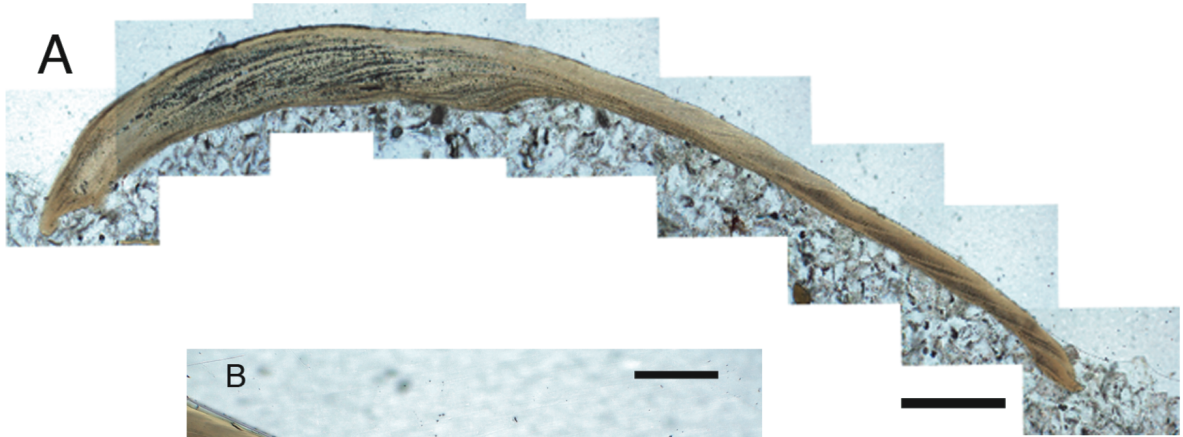
Fig 11 – *D. politus* SEM Image DB1-4 2 images A) (scale bar = 20 μm). B) (Scale Bar = 50 μm) [specimen destroyed]
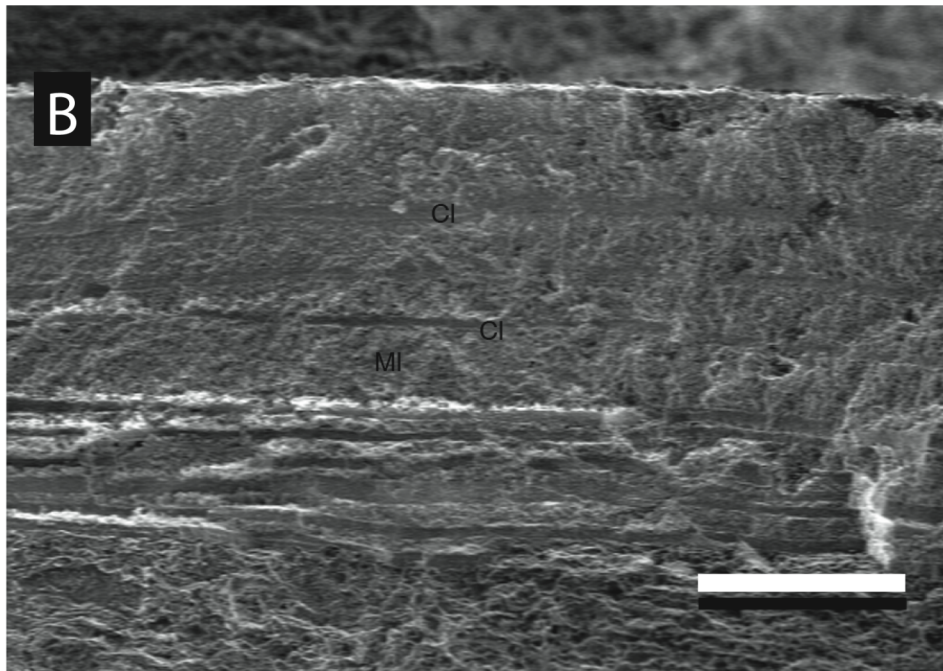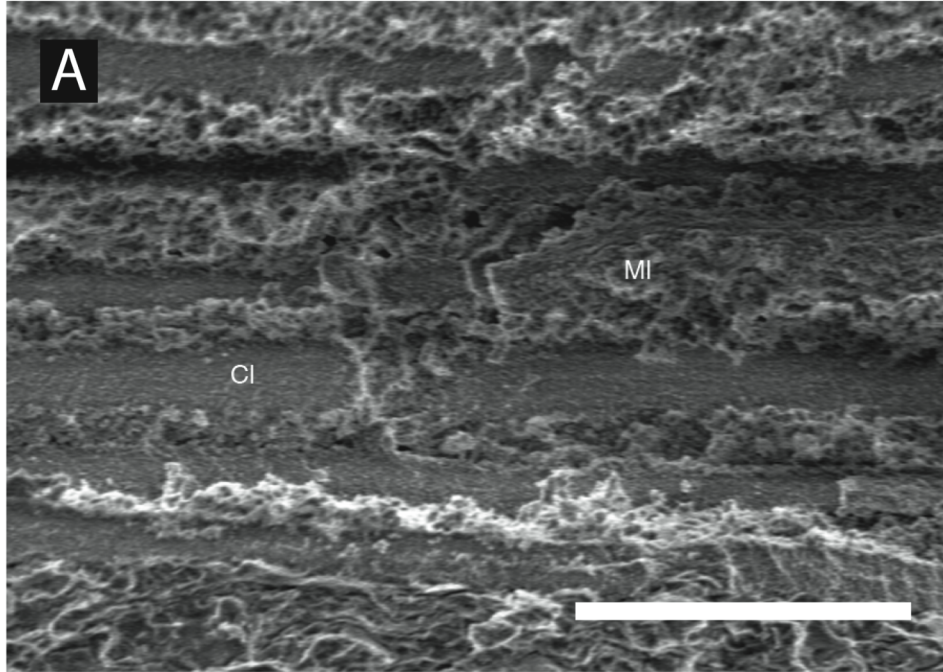
Figure 12 – SEM Images of *L. ampla.* A) cross-sectioned valve fractured along the axis of growth showing preservation of primary layer (PL) and baculate laminae (BL) (scale bar = 100μm). B) valve surface (VS) with underlying PL and alternating baculate laminae (BL) and compact laminae (CL) (scale bar = 50μm) Specimen mount #UWGMXXXX.
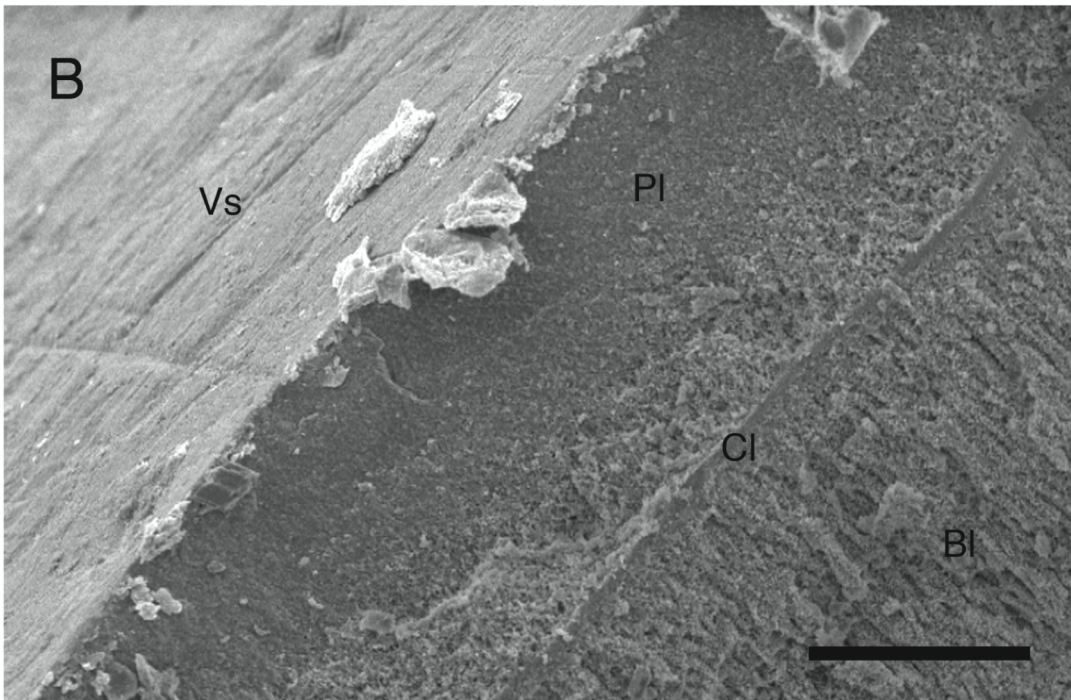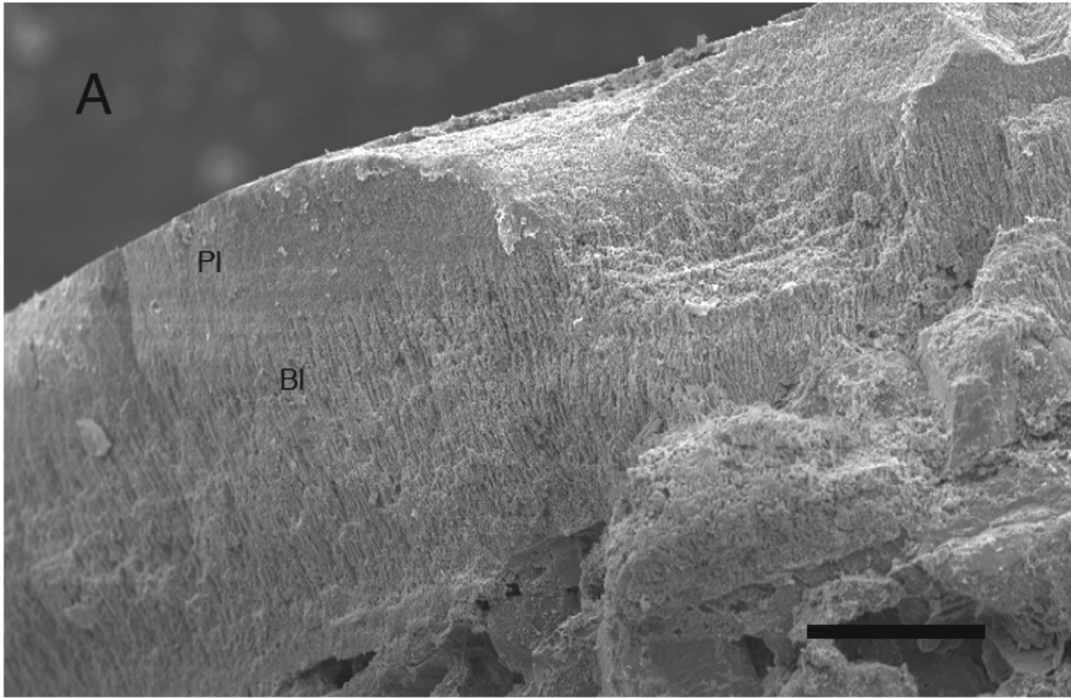
Figure 13 - SEM Images of *L. ampla.* A) cross-sectioned valve fractured along the axis of growth showing alternating baculate laminae (BL) and compact laminae (CL) (scale bar = 20μm). B) increased magnification showing apatite crystals of BL and CL (scale bar = 5μm) Specimen mount #UWGMXXXX.
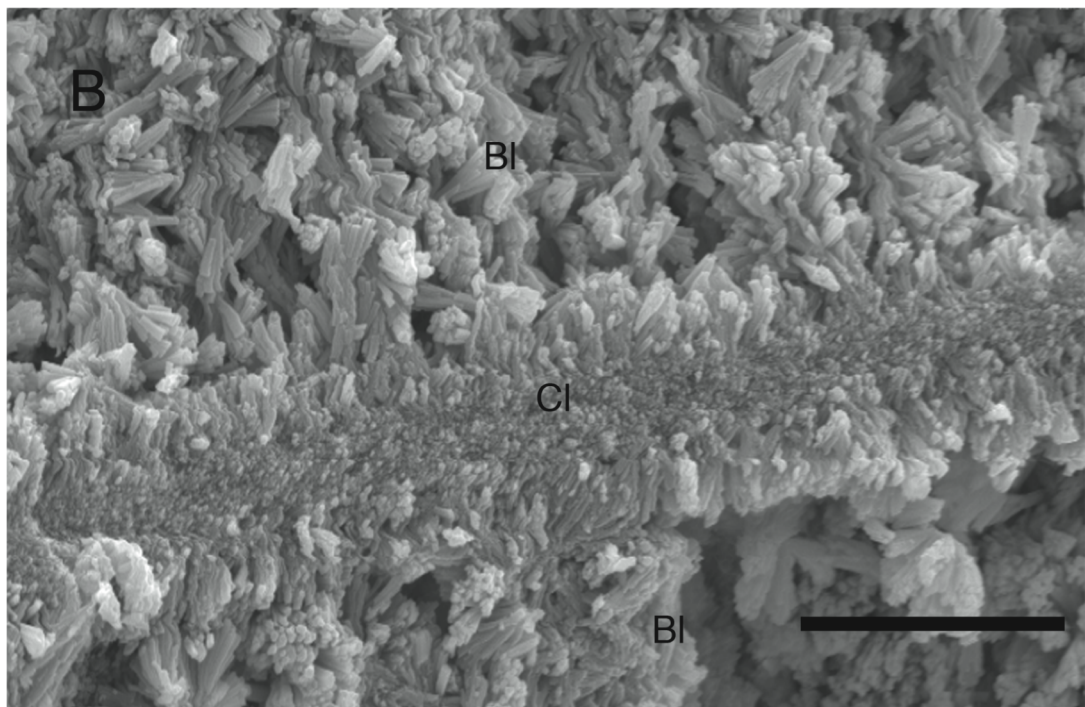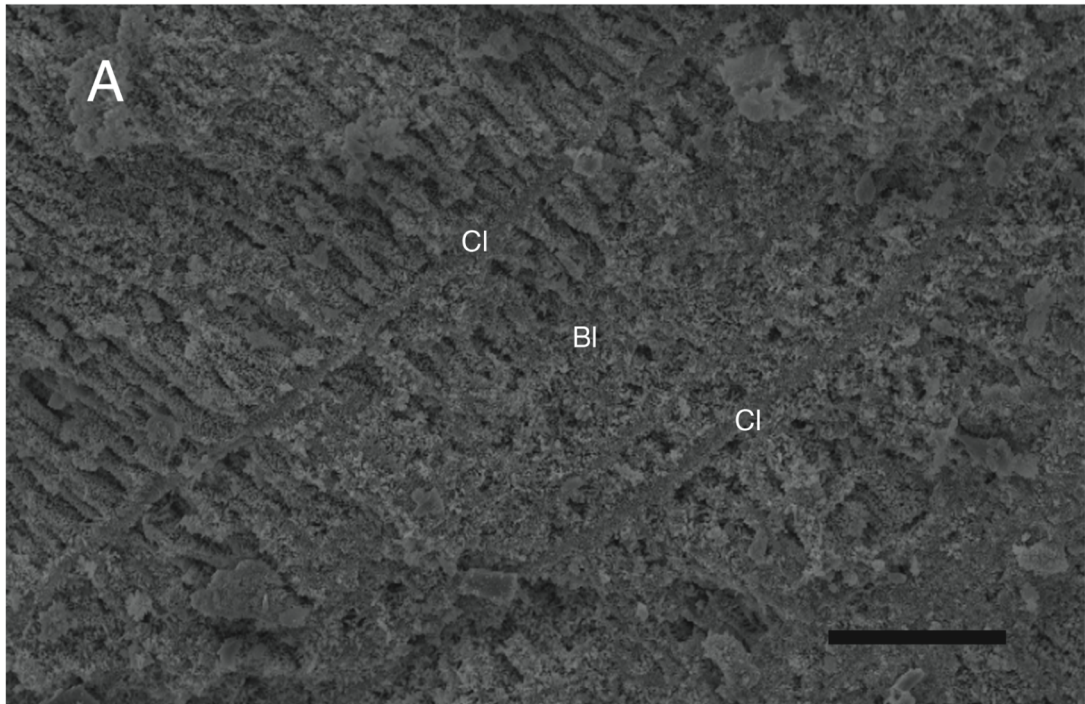
Figure 14 – A) SEM Images of *L. ampla*. A) acicular rods of the baculate laminae (scale bar = 2 μm), B) acicular rods as seen in baculate laminae (scale bar = 10 μm) Specimen mount #UWGMXXXX.
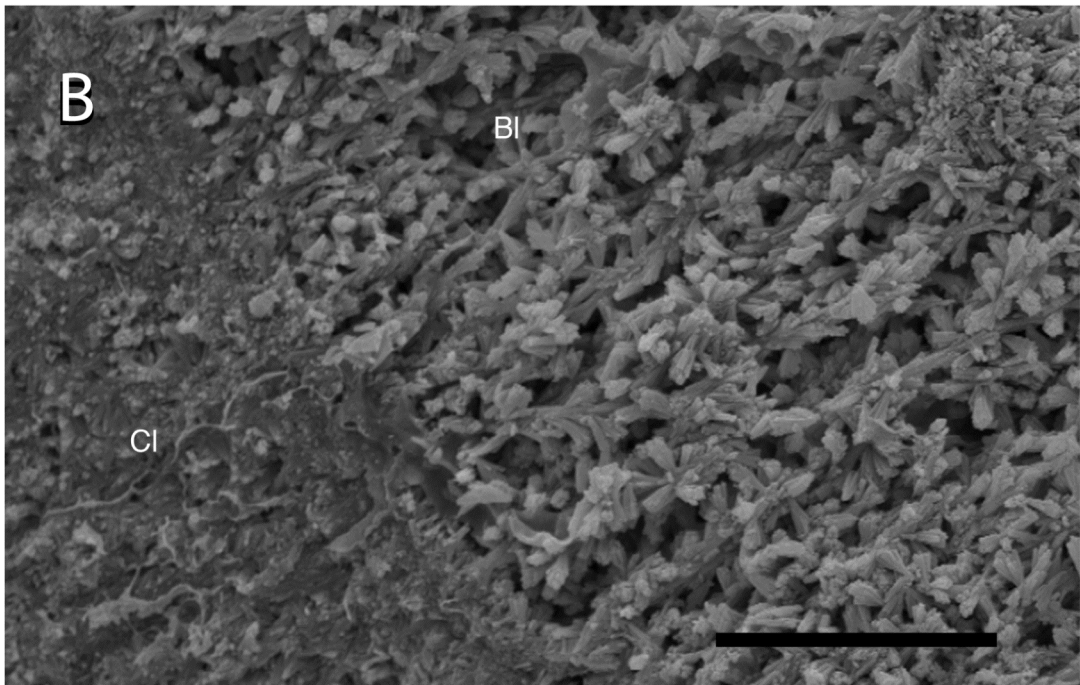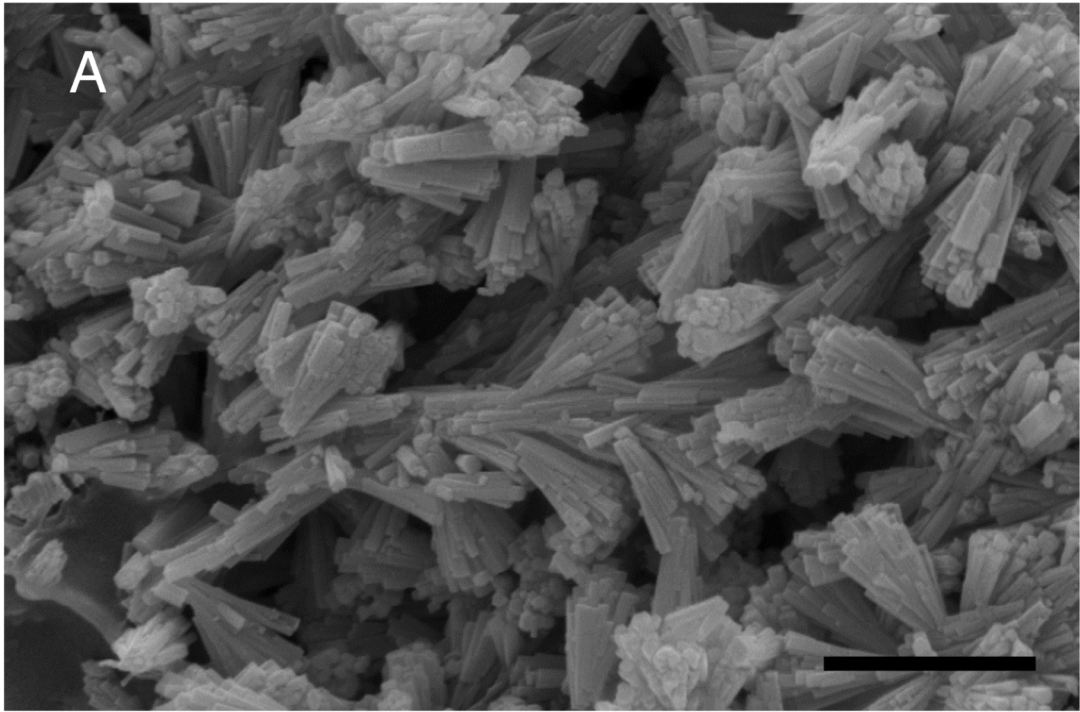
Figure 15 – A) Direct view of polygonal surface feature (SI) (scale bar = 20μm). B) Oblique view of polygonal surface imprints (SI) on laminae surfaces (scale bar = 20μm). [specimen destroyed]
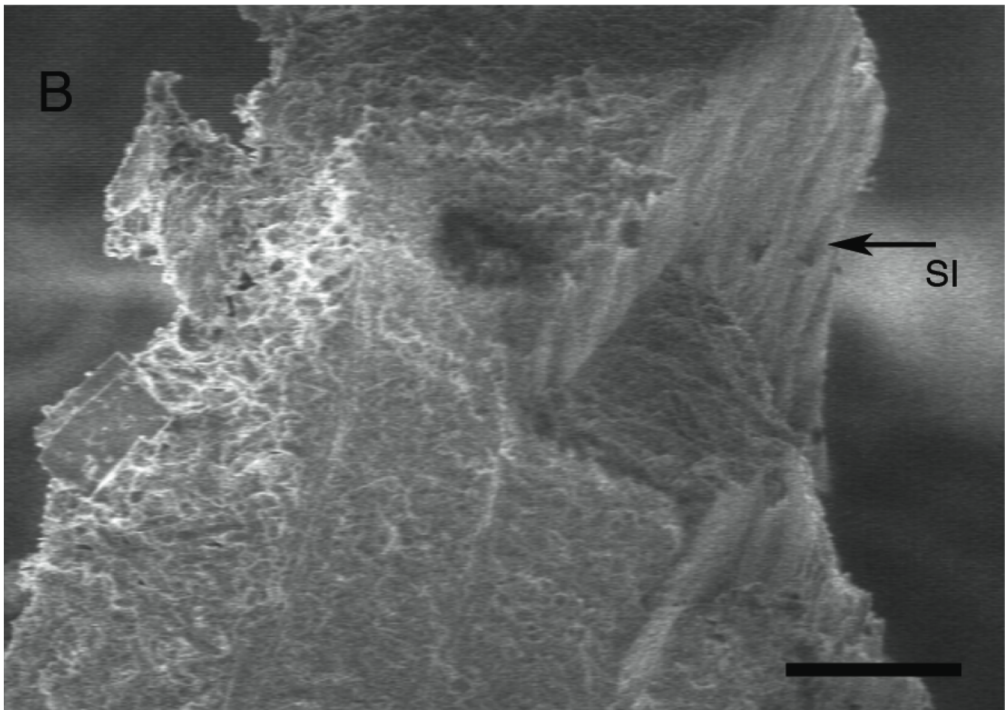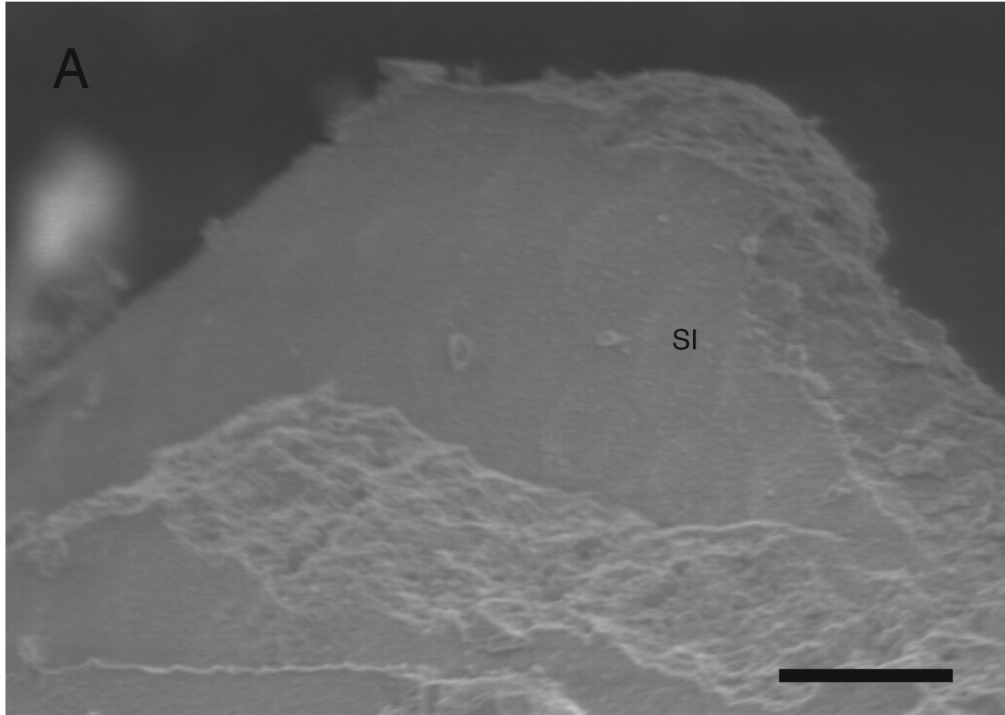
Figure 16 – Cathodoluminescence Images A) *Obolella* sp.?, Specimen #UWGMXXXX-XXXX, with weak, light orange luminescence from Remington Quarry, WI. B) *L. ampla* with weak light brown luminescence from Colfax Quarry, WI. C) *D. politus* with weak orange luminescence from Strum Quarry, WI D) *Glottidia* sp? (modern lingulid brachiopod) from the Gulf of Mexico displaying weak green luminescence.
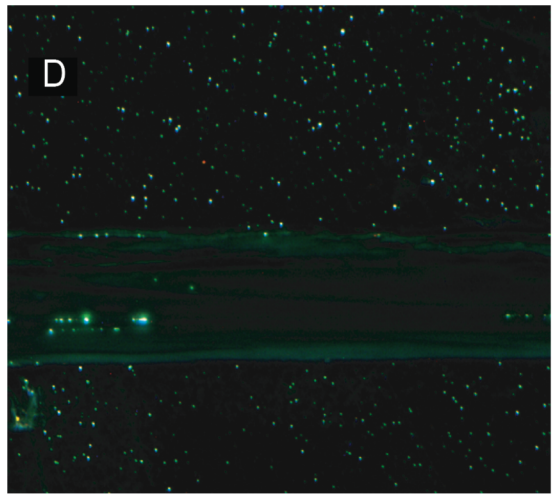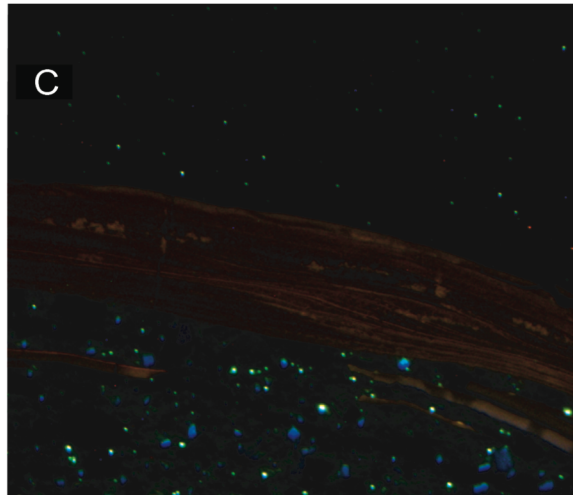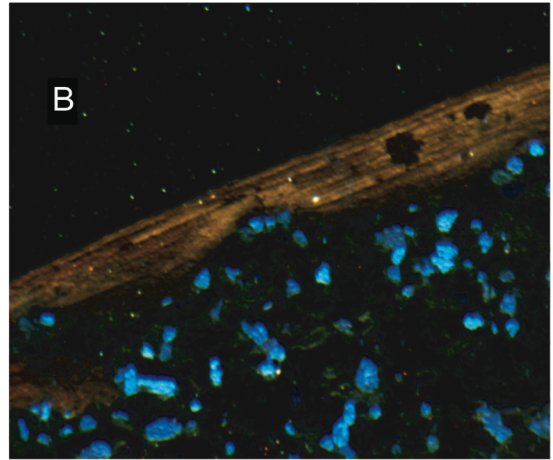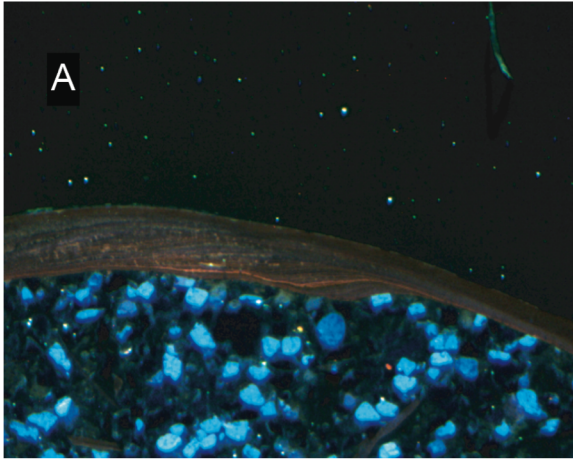
Figure 17 – EDX analysis of 2 individual valve fragments. A) *Lingulella ampla* fragment from mid valve along axis of growth - O (orange), P (red), - Fe (yellow) relates to valve laminae. B) Dicellomus politus fragment from mid valve along axis of growth - O (orange), P (red), - Mg (yellow) relates to valve laminae [specimens destroyed

A

SE P Al Si Ca K Fe O

BKHP80C 8F
MAG: 200 x HV: 10.0 kV WD: 13.0 mm
200 μm

B

SE P Al Si Ca O Na Mg

BKHP80C 100
MAG: 200 x HV: 5.0 kV WD: 14.0 mm
200 μm

64
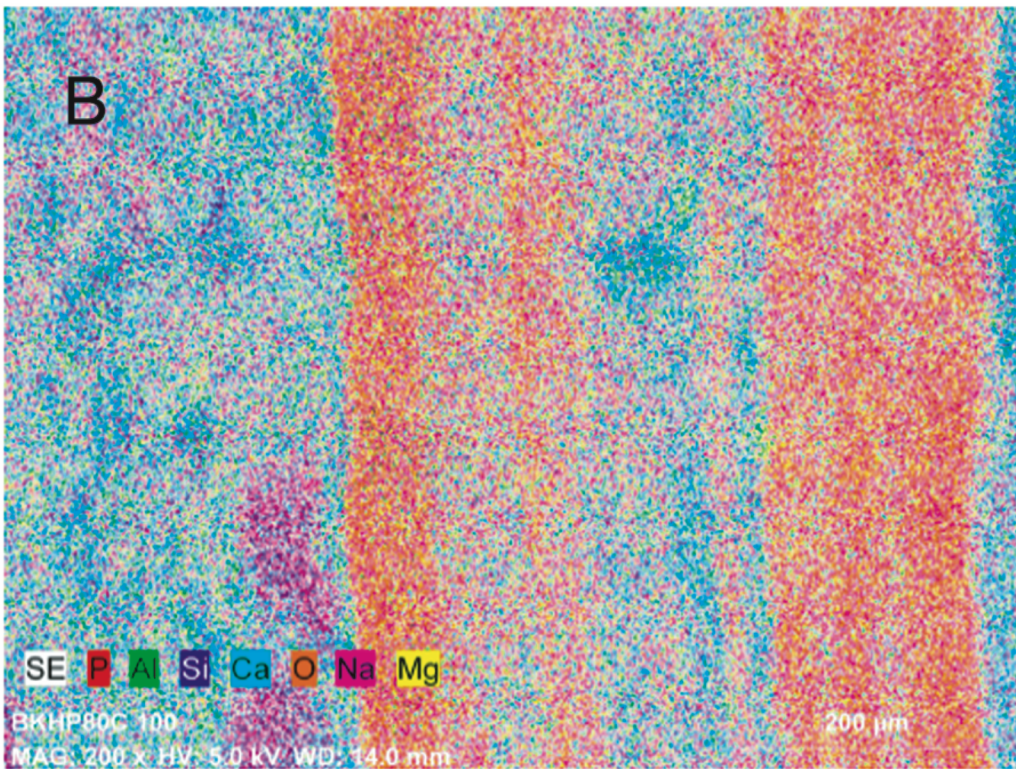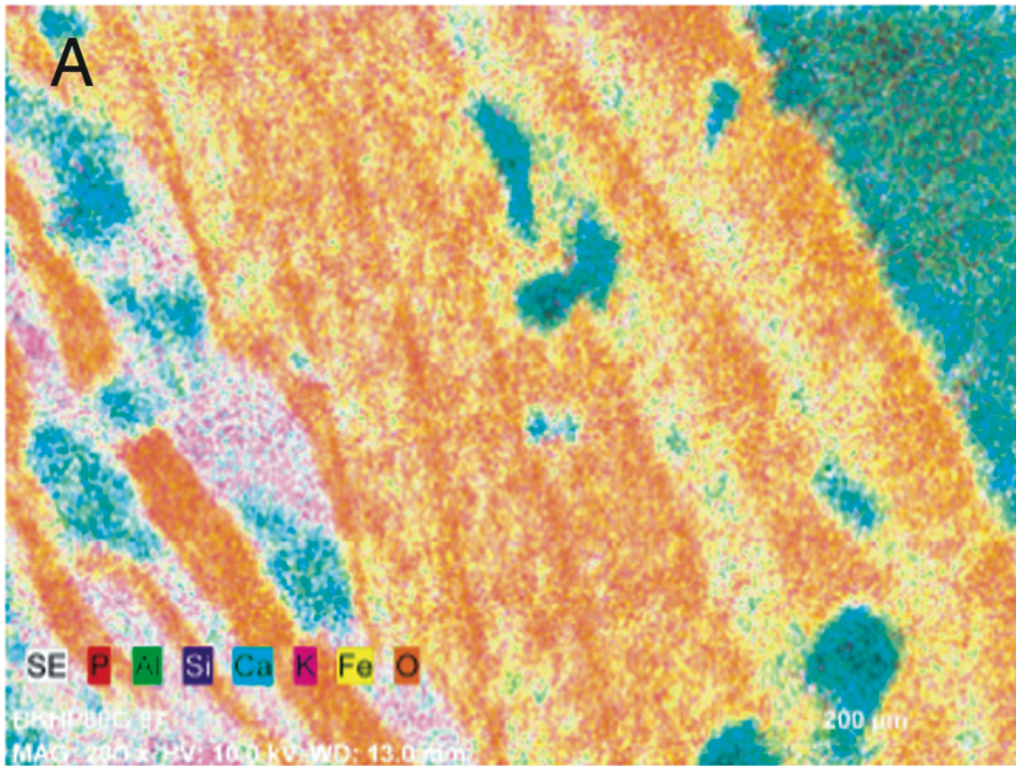
Figure 18 – Graph of $\delta^{18}O$ of individual growth line sets from five different lingulid brachiopod valves (*L. ampla*)(+/- 0.21‰).
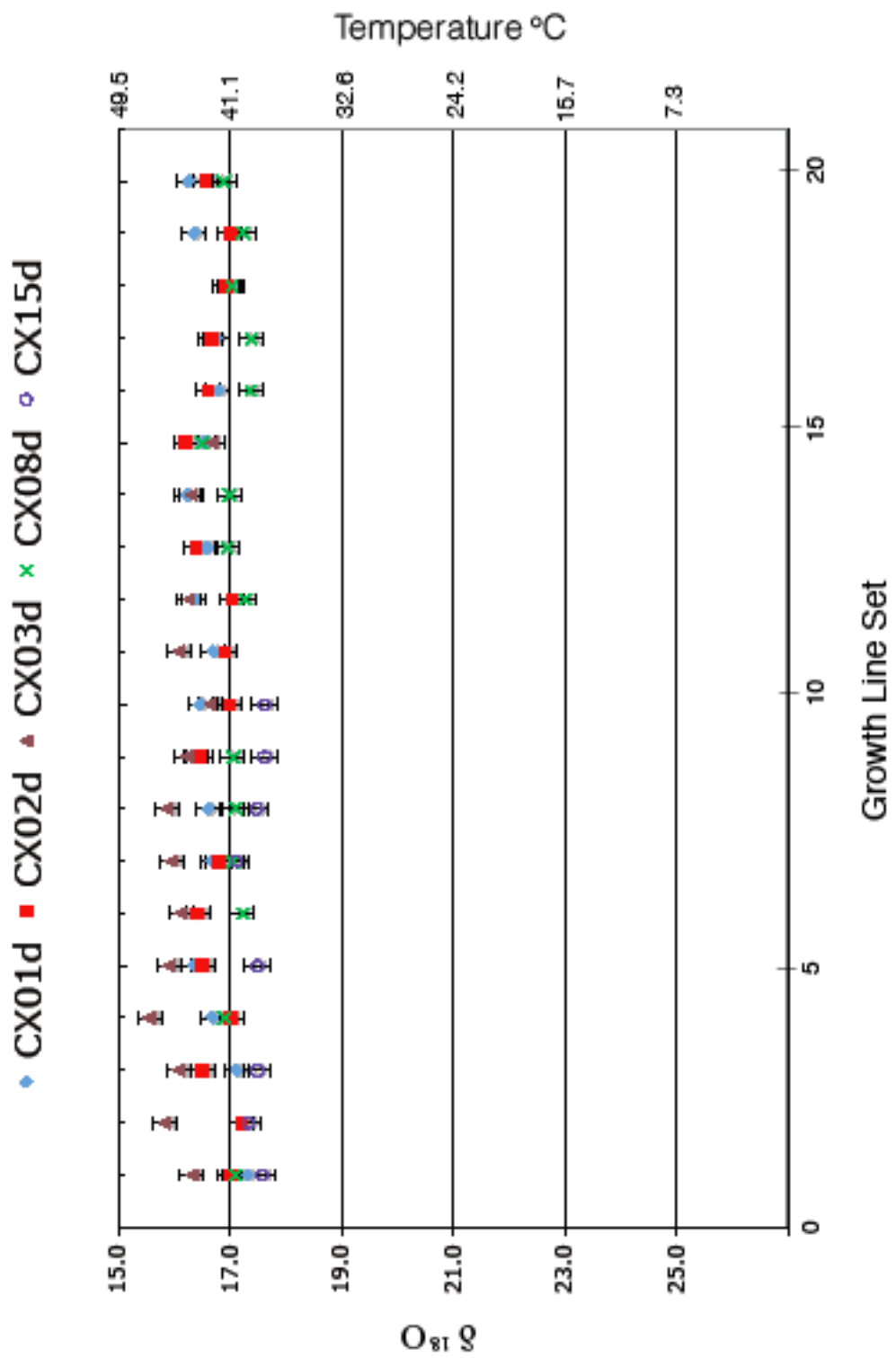
Table 1 - Eau Claire formation brachiopod biofacies. Adapted from Aswasereelert (2008). Ichnofabric index from Droser and Botjer (1986)

Lithofacies	Body Fossils	Inchofabric Index	Depositional Environment
A: Mudstone and siltstone with minor sandstone	Brachiopod fragments	3-4	Offshore below storm wave base
B: Thin bedded micro-hummocky cross-stratification sandstone with siltsone and mudstone	Brachiopod fragments	3	Offshore transition zone between storm and fair weather wave base
C: Thick- to very thick-bedded hummocky to swaley cross-stratification and low angle to planar laminated sandstone with minor siltstone and mudstone (divided into 4 lithofacies: Ca, Cb, Cc, Cd)	Brachiopod fragments throughout; hyolithid and trilobite casts in Cb	2	Lower shoreface Ca: just below fair weather wave base Cb: at fair weather wave base Cc: Just above fair weather wave base Cd: above fair weather wave base
D: Thick- to very thick-bedded trough cross-stratification sandstone	Brachiopod fragments	1-2	Upper shoreface below low tide
E: Very thick-bedded, planar laminated sandstone	Brachiopod fragments	1	Forshore within intertidal zone

Table 2 - $\delta^{18}O$ data from five individual valves of *Lingulella ampla* from Colfax Quarry, WI. Growth Line Sets indicate successive drill progression from commissure to umbo (*indicates adjusted temperatures for -2‰ $\delta^{18}O_{ecns}$)

Sample ID	Growth Line Set		$\delta^{18}O$ (vs. VSMOW)	$\Delta\delta^{18}O$	Temp°C	Δ°C	*Temp°C
CX01d	1	Commissure	17.3		39.8		35.1
	3		17.1	-0.192	40.6	0.8	36.0
	4		16.7	-0.432	42.4	1.8	37.8
	5		16.3	-0.326	43.8	1.4	39.2
	7		16.7	0.322	42.4	-1.4	37.8
	8		16.6	-0.072	42.7	0.3	38.1
	9		16.4	-0.200	43.6	0.8	38.9
	10		16.5	0.059	43.3	-0.2	38.7
	11		16.7	0.241	42.3	-1.0	37.7
	12		16.3	-0.369	43.9	1.6	39.2
	13		16.6	0.241	42.9	-1.0	38.2
	14		16.2	-0.344	44.3	1.5	39.7
	15		16.5	0.301	43.0	-1.3	38.4
	16		16.8	0.263	41.9	-1.1	37.3
	17		16.7	-0.043	42.1	0.2	37.5
	18		17.0	0.253	41.1	-1.1	36.4
	19		16.3	-0.653	43.8	2.8	39.2
	20	~1 mm from Umbo	16.3	-0.097	44.2	0.4	39.6
CX02d	1	Commissure	17.0		41.1		36.4
	2		17.2	0.200	40.2	-0.8	35.6
	3		16.5	-0.700	43.2	3.0	38.5
	4		17.0	0.517	41.0	-2.2	36.3
	5		16.5	-0.517	43.2	2.2	38.5
	6		16.4	-0.086	43.5	0.4	38.9
	7		16.8	0.379	41.9	-1.6	37.3
	9		16.4	-0.350	43.4	1.5	38.8
	10		17.0	0.542	41.1	-2.3	36.5
	11		16.9	-0.079	41.4	0.3	36.8
	12		17.0	0.126	40.9	-0.5	36.3
	13		16.4	-0.645	43.6	2.7	39.0
	15		16.2	-0.187	44.4	0.8	39.8
	16		16.6	0.400	42.7	-1.7	38.1
	17		16.6	0.048	42.5	-0.2	37.9
	18		16.9	0.268	41.4	-1.1	36.8
	19		17.0	0.084	41.1	-0.4	36.4
	20	~1 mm from Umbo	16.6	-0.443	42.9	1.9	38.3
CX03d	1	Commissure	16.3		44.0		39.4
	2		15.8	-0.488	46.1	2.1	41.4
	3		16.1	0.258	45.0	-1.1	40.3
	4		15.6	-0.519	47.2	2.2	42.5
	5		15.9	0.349	45.7	-1.5	41.1
	6		16.1	0.208	44.8	-0.9	40.2
	7		15.9	-0.167	45.5	0.7	40.9
	8		15.9	-0.079	45.9	0.3	41.2
	9		16.2	0.368	44.3	-1.6	39.7
	10		16.6	0.404	42.6	-1.7	38.0
	11		16.1	-0.547	44.9	2.3	40.3
	12		16.3	0.172	44.2	-0.7	39.5
	14		16.3	0.039	44.0	-0.2	39.4
	15	~1 mm from Umbo	16.7	0.366	42.5	-1.5	37.8
CX08d	1	Commissure	17.1		40.7		36.0
	4		16.9	-0.205	41.5	0.9	36.9
	6		17.2	0.333	40.1	-1.4	35.5
	7		17.0	-0.177	40.9	0.7	36.2
	8		17.1	0.057	40.6	-0.2	36.0
	9		17.0	-0.051	40.9	0.2	36.2
	12		17.3	0.207	40.0	-0.9	35.3
	13		16.9	-0.304	41.3	1.3	36.6
	14		17.0	0.030	41.1	-0.1	36.5
	15		16.5	-0.482	43.2	2.0	38.5
	16		17.4	0.872	39.5	-3.7	34.9
	17		17.4	0.002	39.5	0.0	34.8
	18		17.0	-0.342	40.9	1.4	36.3
	19		17.2	0.198	40.1	-0.8	35.5
	20	~1 mm from Umbo	16.9	-0.341	41.5	1.4	36.9
CX15d	1	Commissure	17.6		38.6		34.0
	2		17.3	-0.241	39.7	1.0	35.0
	3		17.5	0.156	39.0	-0.7	34.4
	5		17.5	0.000	39.0	0.0	34.4
	7		17.1	-0.370	40.6	1.6	35.9
	8		17.5	0.359	39.1	-1.5	34.4
	9		17.6	0.136	38.5	-0.6	33.8
	10	~1 mm from Umbo	17.6	0.004	38.5	0.0	33.8
Strum Dp 7-1	4	Whole Valve	16.2		44.3		39.7
Strum Dp 7-2	5	Whole Valve	16.9	0.7	41.4	2.9	36.8
Strum Dp 7-3	6	Whole Valve	15.4	-1.5	47.8	-6.4	43.3

References

Aswasereelert, W., Simo (Toni), J.A., and LePain D.L., 2008. Deposition of the Cambrian Eau Claire Formation, Wisconsin: Hydrostratigraphic Implications of Fine Grained Cratonic Sandstones. Wisconsin Geological and Natural History Survey, in Geoscience Wisconsin, 19.

Auclair, A.C., Joachimski, M.M., and Lecuyer, C., 2003. Deciphering kinetic, metabolic and environmental controls on stable isotope fractionations between seawater and the shell of Terabratalia transversa (Brachiopoda). Chemical Geology, 202, 59-78

Azmy K., Veizer J., Wenzel B., Bassett M. G., and Copper P.,1999. Silurian strontium isotope stratigraphy. GSA Bulletin, 111, 475–483.

Barker, S., Knorr, G., Edwards, L.R., Parrenin, F., Putnam, A.E., Skinner, L.C., Wolff, E., and Ziegler, M., 2011. 800,000 years of abrupt climate variability. Science, 334, 347-351

Bassett, D., Macleod, K.G., Miller, J.F., and Ethington, R.L., 2007. Oxygen isotopic composition of biogenic phosphate and the temperature of early Ordovician seawater. Palaios, 22(1), 98-103

Battey, M. H., 1981. Mineralogy for Students. Longman, London. 355

Berner, R.A., 1990. Atmospheric Carbon Dioxide levels over Phanerozoic Time. Science. 21, 1382-1386.

Billings, E., 1861. On some new or little known species of Lower Silurian fossils from the Potsdam group (Primordial zone). *Palaeozoic Fossils* 1(1), 1-18

Brand, U., 1982. The oxygen and carbon isotope composition of Carboniferous fossil components: sea water effects. Sedimentology. 29, 139-147

Buening, N., 2001. Brachiopod Shells: Recorders of the Present and Keys to the Past. in Brachiopods Ancient and Modern., Paleontological Society Papers; editors Carlson S.J., and Sandy, M.R., 7, 117-143

Chase, C.G., and Gilmer, T.H., 1973. Precambrian plate tectonics: The mid-continent gravity high. Earth and Planetary Science Letters, 21, 70-78

Cowan, C.A., Fox, D.L., Runkel, A.C., and Saltzman, M.R., 2005. Terrestrial-marine carbon coupling in ~500 my-old phosphatic brachiopods. Geology. 33, 661-664

Dott, R.H., Jr., Byers, C.W., Fielder, G.W., Stenzel, S.R., and Winfree, K.E., 1986. Aeolian to marine transition in Cambro-Ordovician cratonic sheet sandstones of the northern Mississippi Valley, USA: Sedimentology, 33, 345-367

Elrick, M., Reiboldt, S., Saltzman, M., and McKay, R.M., 2011. Oxygen Isotope trends and seawater temperature changes across the Late Cambrian Steptoean postitive-isotope excursion (SPICE event). Geological Society of America. 39, 987-990

Finnegan, S., Bergmann, K., Eiler, J.M., Jones, D.S., Fike, D.A., Eisemanman, I., Hughes, N.C., Tripati, A.K., and Fischer, W.W., 2011. The magnitude and duration of late Ordovician-early Silurian Glaciation. Science. 331, 903-906

Gill, B.C., Lyons, T.W., and Saltzman, M.R., 2007. Parallel high-resolution carbon and sulfur isotope records of the evolving Paleozoic marine sulfur resevoir. Paleogeography, Paleoclimatology, Paleoecology, 256, 156-173

Gill, B.C., Lyons, T.W., Young, S.A., Kump, L.R., Knoll, A.H., and Saltzman, M.R., 2011. Geochemical evidence for widespread euxinia in the Later Cambrian ocean. Nature. 469, 80-83

Hagadorn, J.W. and Bottjer, D.J., 1997. Wrinkle structures: Microbially mediated sedimentary structures common in subtidal siliciclastic settings at the Proterozoic-Phanerozoic transition, 25, 1047-1050

Hall, J., 1861. Descriptions of New Species of Fossils; from the Investigations of the Survey. Geological Survey of Wisconsin, Report of the Superintendent, Jan. 1: 9-52

Holland, H.D., 2006. The oxygenation of the atmosphere and oceans. Phil. Trans. R. Soc. 361, 903-915

Holmden, C., Creaser, R.A., Muehlenbachs, K., Leslie, S.A., and Bergström, S.M., 1998. Isotopic evidence for geochemical decouple between ancient epeiric seas and bordering oceans: implications for secular curves, 56, 567-570

Huybers, P. & Curry, W., 2006. Links between annual, Milankovitch and continuum temperature variability. Nature Letters, 441, 329-332

Hyodo, A., Kozdon, R., Pollington, A.D., and Valley, J., 2011. Burial history of the Cambrian Eau Claire Formation based on in situ oxygen isotope analysis of quartz overgrowths and healed fractures. Geological Society of America *Abstracts* with programs. 43, 442.

Jaffres, J.B.D., Sheilds, G.A., and Wallmann, K., 2007. The oxygen evolution of seawater: A critical review of a long-standing controversy and an improved geologic water cycle model for the past 3.4 billion years. Earth Science Reviews, 83, 83-112

Joachimski, M.M., Breisig, S., Buggisch, W., Talent, J.A., Mawson, R., Gereke, M., Morrow, J.R., Day, J., and Weddige, K., 2009. Devonian climate and reef evolution: insights from oxygen isotopes in apatite. Earth and Planetary Science Letters, 284, 599-609

Johnston, T.C., Barry, S.L., Chan, Y., and Wilkinson, P., 2012. Decadal record of climate variability spanning the past 700 yr in the Southern Tropics of East Africa. Geology 2001, 29, 83-86

Kemp D.B., Coe A.L., Cohen A.S., and Schwark L., 2005. Astronomical Pacing of Methane Release in the Early Jurassic Period. Nature. 437, 396

Kocsis, L., Dulai, A., Bitner, M.A., Vennemann, T., and Cooper, M., 2012. Geochemical compositions of Neogene phosphatic brachiopods: Implications for ancient environmental and marine conditions. Paleogeography, Paleoclimatology, Paleoecology, 326-328, 66-67

Kowalewski, M. and Flessa, K.W., 1996. Improving with age: The fossil record of lingulide brachiopods and the nature of taphonomic megabiases. Geology, 24, 977-980

Lhomme, N., Clarke, G.K.C., and Ritz, C., 2005. Global budget of water isotopes inferred from polar ice sheets. Geophys. Res. Lett. 32,

Longinelli, A., and Nuti, S., 1968a. Oxygen isotope composition of phosphates from marine formations. Earth Planet. Sci. Lett. 5, 13–16.

Longinelli, A., and Nuti, S., 1968b. Oxygen-isotope ratios in phosphate from fossil marine organisms. Science 160, 879–881.

Lécuyer, C., Grandjean, P., Barrat, J.A., Nolvak, J., Emig, C., Paris, F., and Robardet, M., 1998. $\delta^{18}O$ and REE Contents of Phosphatic Brachiopods: A Comparison Between Modern and Lower Paleozoic Populations. Elsevier Sciences Ltd. Geochimica et Cosmochimica Acta. 59. 3749-3764.

Norris. R.D., Bice, K.L., Magno, E.A., and Wilson, P.A., 2002. Jiggling the tropical thermostat in the Cretaceous hot house. Geological Society of America, 30, 299-302

Ostrom, M.E., 1978. Stratigraphic Relationships of Lower Paleozoic Rocks of Wisconsin in Lithostratigraphy, Petrology, and Sedimentation of Late Cambrian-Early Ordovician Rocks Near Madison, Wisconsin, Field Trip Guide Book, 3, 3-22.

Ogg, J.G., Ogg, G., and Gradstein, F.M., 2008. The Concise Geologic Time Scale, by J.G. Ogg, G. Ogg, and F.M. Gradstein. Cambridge: Cambridge University Press.

Over, D.J., 1988. Lingulid brachiopods and *Lingulichnus* from a Silurian shelf–slope carbonate sequence, Delorme Group, Mackenzie Mountains, Northwest Territories D. Jeffrey Over*Canadian Journal of Earth Sciences*, 25(3), 465-471

Owen, D.D., 1852. Description of New and Imperfectly Known Genera and Species of Organic Remains, Collected During the Geological Surveys of Wisconsin, Iowa and Minnesota and Incidentally of a Portion of Nebraska Territory. Report of a Geological Survey of Wisconsin, Iowa and Minnesota. Lippincott, Grambo & Co. Philadelphia. P. 537-587, pl. 1-3, 5, 7-8.

Palmer, A.R., 1965. Trilobites of the Late Cambrian Pterocephaliid Biomere in the Great Basin, United States: U.S. Geological Survey, Professional Paper 493, 105 p.

Palmer, A.R., 1979. Biomere boundaries re-examined. Alcheringa: An Australasian Journal of Paleontology. 3:1, 33-41

Pearson, P.N., Ditchfield, P.W., Singano, J., Harcourt-Brown, K.G., Nicholas, C.J., Olsson, R.K., Shackleton, N.J., Hall, M.A., 2001. Warm tropical sea surface temperatures in the Late Cretaceous and Eocene epochs. Nature, *Articles*. 413, 481-487

Pemperton, G.S., and Kobluk, D.R., 1978. Oldest known brachiopod burrow: Lower Camrbian of Labrador. Canadian Journal of Earth Science, 15, 1385-1389

Peters, S.E. and Gaines, R.R., 2012. Formation of the 'Great Unconformity' as a trigger for the Cambrian exolosion, Nature, 484, 363-366

Poulsen, C., 1932. The Lower Cambrian faunas of East Greenland. *Meddelelser om Grønland* 87(6):1-66 [P. Wagner/P. Wagner]

Popov, L.E., Holmer, L.E., and Miller, J.F., 2002. Lingulate brachipods from the Cambrian-Ordovician boundary beds of Utah. Journal of Paleontology, 76, 211-228.

Pörtner, H.O., 2001. Climate change and temperature-dependent biogeography: Oxygen limitation of thermal tolerance in animals. Naturwissenschaften. 88, 137-146

Pucéat, E., Joachimski, M.M., Bouilloux, A., Monna F., Bonin, A., Motreuil, S., Moriniere, P., Henard, S., Mourin, J., Dera, G., and Quesne, D., 2010. Revised Water-Phosphate Fractionation Equation Reassessing Paleotemperatures Derived from Biogenic Apatite. Earth and Planetary Science Letters, 298, 135-142.

Puura, I. and Nemliher, J., 2001. Apatite Varieties in Recent and Fossil Linguloid Brachiopod   Shells. Brachiopods Past and Present. edited by C. Howard C. Brunton, L. Robin M. Cocks, and Sarah L. Long. 7-16.

Ramanathan, V. and Collins W., 1991. Thermodynamic regulation of ocean warming by cirrus clouds deduced from observations of the 1987 El Niño. Nature Articles, 351, 27-32

Roberts, J., and Jell, P.A., 1990. Early Middle Cambrian (Ordian) brachiopods of the Coonigan Formation, western New South Wales. Alcheringa,14, 257-309.

Rodland, D.L., Kowalewski, M., Dettman, D.L., Flessa, K.W., Atudorei, V., and Sharp, Z.D., 2003. High Resolution Analysis of $\delta^{18}O$ in the Biogenic Phosphate of Modern and Fossil Lingulid Brachiopods. Journal of Geology 111, 441-453.

Rosenzweig, C., Karoly, D., Vicarelli, M., Neofotis, P., Wu, Q., Casassa, G., Menzel, A., Root, T.L., Estrella, N., Seguin, B., TryJanowski, P., Liu, C., Rawlins, S., and Imeson, A., 2008. Attributing physical and biological impacts to anthropogenic climate change. Nature Articles, 453, 353-357

Runkel, A.C., 1994. Deposition of the upper-most Cambrian (Croixan) Jordan Sandstone, and the nature of the Cambrian-Ordovician boundary in the Upper Mississippi Valley. Geological Society of America Bulletin, 106, 492-506

Runkel, A.C., Miller, J.F., McKay, R.M., Palmer, A.R., and Taylor, J.F., 2007. high-resolution sequence stratigraphy of lower Paleozoic sheet sandstones in central North America: The role of special conditions of cratonic interiors in development of stratal architecture. Geological Society of America Bulletin, 119, 860-881

Runkel, A. C., Mackey, T. J., Cowan, C. A. and Fox, D. L., 2010. Tropical shoreline ice in the late Cambrian: Implications for Earth's climate between the Cambrian Explosion and the Great Ordovician Biodiversification Event. GSA Today, 20, 4 – 10.

Rush, P.F. and Chavetz, H.S., 1990. Fabric-retentive, non-luminescent brachiopods as indicators of original $\delta13C$ and $\delta18O$ compositions: A test. Journal of Sedimentary Petrology, 60, 968-981

Saltzman, M.R., Runnegar, B., and Lohmann, K.C., 1998. Carbon isotope stratigraphy of Upper Cambrian sequences of the eastern Great Basin: Record of global oceanographic event. Geological Society of America Bulletin, 110, 285-297

Saltzman, M.R., Ripperdan, R.L., Brasier, M.D., Lohmann, K.C., Robinson, R.A., Chang, W.T., Peng, S., Ergaliev, E.K., and Runnegar, B., 2000. A global carbon isotope excursion (SPICE) during the Late Cambrian: relation to trilobite extinctions, organic-matter burial and sea level, Palaeogeography, Palaeoclimatology, Palaeoecology, 162, 211-223

Saltzman, M.R.,Cowan,C.A., Runkel, A.C.,Runnegar, B., Stewart,M.C., and Palmer, A.R., 2004. The Late Cambrian SPICE ($\delta13C$) event and the Sauk II–Sauk III regression: new evidence from Laurentian basins in Utah, Iowa, and Newfoundland. J. Sediment. 74, 366–377.

Schulte, P., Alegret, L., Arenillas, I., Arz, J.A., Barton, P.J., Bown, P.R., Bralower, T.J., Christeson, G.L., Claeys, P., Cockell, C.S., Collins, G.S., Deutsch, A., Goldin, T.J., Goto, K., Grajales-Nishimura, J.M., Grieve, R.A.F., Gulick, J.P.S., Johnson, K.R., Kiessling, W., Koeberl, C., Kring, D.A., MacLeod, K.G., Matsui, T., Melosh, J., Montanari, A., Morgan, J.V., Neal, C.R., Nichols, D.J., Norris, R.D., Pierazzo, E., Ravizza, G., Rebolledo-Vieyra, M., Reimold, W.U., Robin, E., Salge, T., Speijer, R.P., Sweet, A.R., Urrutia-Fucugauchi, J., Vajda, V., Whalen, M.T., and Willumsen, P.S., 2010. The Chicxulub asteroid impact and mass extinction at the Cretaceous-Paleogene Boundary. Science, 327, 1214-1218

Scott, C., Lyons, T.W., Bekker, A., Shen, Y., Poulton, S.W., Chu, X., and Anbar, A.D., 2008. Tracing the step-wise oxygenation of the Proterozoic ocean, Nature Letters, 452, 456-459

Scotese, C.R., 2001. Atlas of Earth History, Volume 1, Paleogeography, PALEOMAP Project, 52

Seillacher, A. and Pflüger, F., 1994. From biomats to benthic agriculture: A biohistoric revolution. In Krumbein, W.E., et al., eds. Biostabilization of Sediments, 97-105

Shields G.A., Giles C.A.F., Veizer J., Meidla T., Rong J., and Li R., 2003. Sr. and O isotope geochemistry of Ordovician brachiopods: A major isotopic event around the Middle-Late Ordovician Transition

Shen, S., Crowley, J.L., Wang, Y., Bowring, S.A., Erwin, D.H., Sadler, P.M., Cao, C., Rothman, D.H., Henderson, C.M., Ramezani, J., Zhang, H., Shen, Y., Wang, X., Wang, W., Mu, L., Li, W., Tang, Y., Liu, X., Liu, L., Zeng, Y., Jiang, Y., and Jin Y., 2011. Calibrating the end-Permian mass extinction. Science 334, 1367-1372

Simoes, M., Rodrigues, S.C., De Morales J., and Bissaro Jr., M.C., 2005. The settling pattern of brachiopod shells: Stratigraphic and taphonomic implications to shell bed formation and paleoecology. Revisita Brasileria de Geociencias. vol. 35. pp. 383-391

Sloss, L.L., 1963. Sequences in the cratonic interior of North America. Geological Society of America Bulletin. vol. 74. no. 2. pp. 93-114

Stitt, J.H., 1977. Late Cambrian and earliest Ordovician trilobites Wichita Mountains area, Oklahoma, Oklahoma Geological Survey, 124, 1-79

Trotter, J.A., Williams, I.S., Barnes, C.R., Lecuyer, C., and Nicoll, R.S., 2008. Did cooling oceans trigger Ordovician biodiversification? Evidence from conodont thermometry: Science, 321, 550–554.

Thayer, C.W., and Steele-Petrovic, M., 1975. Burrowing of the lingulid brachiopod *Glottidia pyramidata*: its ecological and paleoecologic significance. Lethaia, 8, 209-221

Veizer, J., Fritz, P., and Jones, B., 1996. Geochemistry of brachiopods: Oxygen and carbon isotopic records of Paleozoic oceans. Geochimica et Cosmochimica Acta, 50, 1679-1696

Vennemann, T.W., Fricke, H.C., Blake, R.E., O'Neil, J.R., and Colman, A., 2002. Oxygen isotope analysis of phosphates: a comparison of techniques for analysis of Ag_3PO_4. Chemical Geology, 185, 321–336.

Wallmann, K., 2001. The geological water cycle and the evolution of marine $\delta^{18}O$ values. Geochimica et Cosmochimica Acta, 65, 2469-2485

Wenzel, B., Lécuyer, C., and Joachimski, M., 2000. Comparing oxygen isotope records of Silurian calcite and phosphate — δ18O compositions of brachiopods and conodonts. Geochimica Cosmochimica Acta 64, 1859–1872.

Williams, A., Mackay, S., and Cusack, M., 1992. Structure of the Organo-Phosphatic Shell of the Brachiopod Discina. Philisophical Transactions: Biological Sciences, 337, 83-104.

Williams, A., Cusack, M., and Mackay, S., 1994. Collagenous chitinophosphatic shell of the brachipod lingula, Philisophical Transactions: Biological Sciences, 346, 223-236.

Williams, A., Cusak, M., and Buckman, J.O.,1998. Chemico-structural phylogeny of discinoid brachiopod shell. Phil. Trans. R. Soc. Lond. B., 353, 2005-2038

Williams, A., Cusack, M., Buckman. J.O., and Stachel, T., 1998a. Siliceous tablets in the larval shell of apatitic Discinid brachiopods. Science, New Series, 279, 2094-2096

Williams, A., 1977. Differentiation and growth of the brachiopod mantle, American Zoologist, 17, 107-120

Williams, A., 2003. Microscopic imprints on the juvenile shells of Paleozoic Linguliform brachiopods. Paleontology, 46, 67-92

Yugan, J., Xianguang, H., and Huayu, W., 1993. Lower Cambrian pediculate Lingulids from Yunnan, China, Journal of Paleontology, 67, 788-798