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A Stable Isotope Test for the Origin of Fossil Brown Bodies in Trepostome Bryozoans from the Ordovician of Estonia

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Abstract

This study provides a novel test of the brown body origin of brown deposits in fossil bryozoans. We use C stable isotopes of inorganic carbonate from separate samples of brown deposits, skeletal walls, matrix, and diagenetic cements from trepostome bryozoans from the Ordovician of Estonia. Our sampling technology improves on the spatial resolution of previous studies to minimize contamination from the various carbonate sources. Samples from brown deposits display lower $\delta^{13}C$ values indicating the presence of originally organic material. The granular texture, reddish-brown color, 80 µm diameter size, and circular cross-sectional shape of the deposits as well as their location in the zooecial chambers relative to diaphragms support the isotope results in demonstrating the brown deposits are the diagenetic remnants of original brown bodies.

Introduction

A brown body in an extant bryozoan is the degenerated cellular residue of the soft tissues of a polypide (Bassler 1953; Ryland 1970; Boardman and Cheetham 1983). In stenolaemate bryozoans like cyclostomes, multiple brown bodies can accumulate in the zooecium in response to repeated cycles of polypide generation-degeneration (Borg 1923; Ryland 1970; Hayward and Ryland 1985; Barnes and Clarke 1998). The polypide degenerates and is encapsulated within a membrane to form a brown body (Gordon 1977; Boardman 1998). The cellular and histological degradation that leads to the formation of brown bodies has been well documented by Gordon (1973). The cause of polypide generation-degeneration cycles and the resulting brown bodies has been variously linked to polypide aging, accumulation of residual waste products in the stomach, exposure to adverse environmental conditions (e.g., temperature, salinity, food supply, etc.), as well as reproductive activity (see Gordon [1977] for a review).

A brown deposit is the fossilized remains of organic material from a bryozoan whose original source may have been functional organs or a brown body proper (Boardman 1971, 1999; Utgaard 1973; Boardman and Cheetham 1983). This paper will use brown deposit in a more restrictive sense to refer to an encapsulated fossil brown body (e.g., Boardman 1983, Fig. 40.1), not simply the diagenetic remains of functional organs (e.g., Boardman 1983, Fig. 46.4a) termed brown residues by Ernst and Voigt (2002). Based on their similar position in the zooecium, size, shape, number and color, brown deposits have traditionally been interpreted as the diagenetic remnants of brown bodies (Cumings and Galloway 1915). In extinct stenolaemates, the brown deposits are associated with polypide generation-degeneration cycles as they are often found sealed off from the zooecial living chamber by diaphragms (Cumings and Galloway 1915; Boardman 1971, 1983, 2001; Utgaard 1973, 1983; Corneliussen and Perry 1973; Ernst and Voigt 2002).

Some studies have suggested that changes, including encapsulation, calcification, and phosphatization, may occur in brown bodies prior to diagenesis. Cummings (1973) reported, at least for one extant cheilostome, that brown bodies become encapsulated in a non-cellular material that calcifies before the colony dies. Similarly, Utgaard (1968, 1973) found evidence that brown deposits in cystoporates

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are encapsulated in membranes, and Bigey (1991) noted some cyst-like structures that contained brown deposits. This is similar to the calcification of other organic membranes during the dormant stage of trepostome zooids (Boardman and McKinney 1976). Other studies have indicated that brown bodies and other organs may be phosphatized as part of the early polypide degeneration cycle. This was first suggested by Oakley (1934, 1966) and Spjeldnæs (1950) who reported phosphatic brown body-like spheres in Silurian cystoporates. Eisenack (1964) renamed them Oakleyites. Martinssson (1965) found phosphatized zooecial linings from Paleozoic cryptostomes. Boardman (1971) and Conti and Serpagli (1988) suggested that brown deposits, in at least some extinct trepostomes, were phosphatized while the colony was alive. This was reaffirmed more recently by Fedorov and Krusanov's (1997) work on the phosphatized remains of extinct trepostomes. Bacteria likely use the availability of Ca along with P in the organic matter to generate the phosphate (Emslie and Patterson 2007).

Following the death of a colony, the textural, chemical, and mineralogical changes of diagenesis begin. Little work has been conducted on the composition and diagenesis of brown deposits in fossils. The earliest speculation on the composition of brown deposits was based on their reddish-brown color, which is suggestive of oxidized Fe. Cumings and Galloway (1915) suggested that during diagenesis the original organic matter was replaced by Fe-sulfide or Fe-oxide. Oakley (1934) interpreted their yellowish-brown color as indicative of iron-oxide. McKinney (1969) also interpreted their color to indicate the presence of iron minerals. Boardman (1971, 1983) and Boardman and McKinney (1976) construed the reddish-brown color to imply the presence of Fe-sulfide or Fe-oxide.

Instead of using color as a proxy for indirectly inferring the composition of brown deposits, Oakley (1934) was the first to use more quantitative techniques. He determined the refractive index using petrographic light microscopy and the ammonium molybdate test to determine the presence of Ca-phosphate in brown body-like spheres in Silurian cystoporates. Boardman (1971) used a simple HCl and HF acid-digestion test, to conclude that the residual brown deposits in Devonian trepostomes contained organic matter. He also did an electron-microprobe analysis and documented an elevated concentration of P relative to the skeletal walls and diagenetic cements but could not rule out a diagenetic origin of the P. The most recent work on the composition of brown deposits was done by Morrison (1975) and Morrison and Anstey (1979). They used histological staining, electron-microprobe analysis, and transmission electron microscopy to document the abundance of organic C and the presence of Fe and S in the now permineralized brown deposits of Ordovician trepostomes (Morrison and Anstey 1979). The organic matter could either be replaced by pyrite (an Fe-sulfide) under reducing conditions or be preserved in glauconite (an Fe-aluminosilicate) under more oxidizing conditions (Morrison 1975). They concluded that brown deposits are fossilized brown bodies.

Compared to inorganic carbonate, brown bodies should have a different diagenetic history owing to their original organic composition. Lower inorganic $\delta^{13}C$ values are indicative of diagenetic carbonates derived from degradation of original organic matter (Patterson and Walter 1994a; Wakeham 2004). This results from isotopic fractionation associated with oxidation of organic C during diagenesis (McArthur 1989). Organic matter in the brown body is degraded by bacteria, generating CO_2 that becomes a component of the dissolved inorganic C (DIC). This process results in the microenvironmental waters around the brown body becoming acidified. This dissolves the adjacent skeletal carbonate thereby buffering the system, increasing alkalinity and carbonate saturation (via contribution of the dissolved components to the microenvironmental water), forcing the reprecipitation of carbonate to occur (Walter et al. 1993; Patterson and Walter 1994a,b). Finally, the reprecipitated carbonate incorporates the more negative DIC generated by breakdown of the organic matter resulting in carbonate in the brown body with lower inorganic $\delta^{13}C$ values (Bickert 2000). This transformation occurs within the organic component of sediments on many carbonate platforms (Patterson and Walter 1994a,b; Immenhauser et al. in press).

The goal of this study is to apply a new independent geochemical test to the brown-body origin of fossilized brown deposits in trepostome bryozoans. It is hypothesized that if the brown deposits are the diagenetic remnants of brown bodies originally containing organic C, they should have lower inorganic $\delta^{13}C$ values than the inorganic C preserved in the skeletal walls, matrix, and cements.

Geologic Setting

Middle to Late Ordovician rocks of Estonia were chosen for this study as they contain well-preserved fossil bryozoans with well-preserved brown deposits. These rocks are also thought to be diagenetically pristine based on their undeformed bedding and shallow burial. The Baltic Platform was chosen for this study site as Baltica had a cooler post-burial thermal history resulting from its more stable tectonic history (Nikishin et al. 1996). During the Ordovician, the Baltic basin experienced a period of regional intracratonic platform subsidence (Nikishin et al. 1996). As sea level rose, there was progressive overstepping of the basin's margins, and shallow marine carbonates and shales were deposited on the platform (Hints et al. 1989).

The Ordovician strata lie almost flat with a regional southward dip of 2.5 to 3.5° (Männil 1990). No subsequent orogenies occurred after deposition, and the study location is situated on the stable southern portion of the Baltic shield therefore maintaining its undeformed bedding (Ainsaar et al. 1999).

Carbonate deposition in the Baltic basin extended over Scandinavia and East Baltic (Ainsaar et al. 1999). Deposition in the basin is characterized by concentric lithofacies belts (Jaanusson 1976, 1995). The Northern Estonia belt is characterized by laminar, nodular, argillaceous, bioclastic limestones and pure biomicritic limestones (Ainsaar et al. 1999). Burial of Ordovician rocks in Estonia did not exceed 2 km depth (Ainsaar et al. 2004). The conodont color alteration index of these rocks indicates the Ordovician rocks reached a maximum burial temperature of 80°C (Bergström 1980). Thus, the carbonate minerals should not have been recrystallized owing to exposure to hot fluids associated with subsequent orogenies.

Materials and Methods

Eight stratigraphic stages from the Middle and Late Ordovician of northern Estonia were sampled at 15 quarries and road cuts (Fig. 1). This yielded 150 colonies that were sectioned, from which four, representing four stratigraphic stages (Table 1), were selected based on the most abundant brown deposits. All four are hemispherical dome-shaped massive colonies of *Diplotrypa petropolitana*. The fossilized bryozoan colonies were longitudinally sectioned to 100 μm thickness, polished, and cleaned in an ultrasonic bath. Micromilling was performed (sensu Wurster et al. 1999) on a robotic, computer-controlled, three-dimensional positioning stage set under a fixed, high-precision dental drill that results in <1 μm spatial-sampling resolution. This fine sampling resolution minimized mixing of carbonate from brown deposits (mean diameter 80 μm), skeletal walls, matrix, and cements. Despite this fine-sampling resolution, the intergrowth of the crystalline microspar of the brown deposits with the surrounding coarser infilling sparry calcite cement (sensu McKinney 1969) precludes the complete isolation of carbonate from these four sources. Morrison's (1975) and Morrison and Anstey's (1979) studies were constrained by the technology available at the time as their electron beam was >4 μm wide. This study improves on that with 1 μm spatial-sampling precision. Sufficient carbonate was milled to generate powder samples of approximately 10 to 40 μg for each stable isotope analysis.

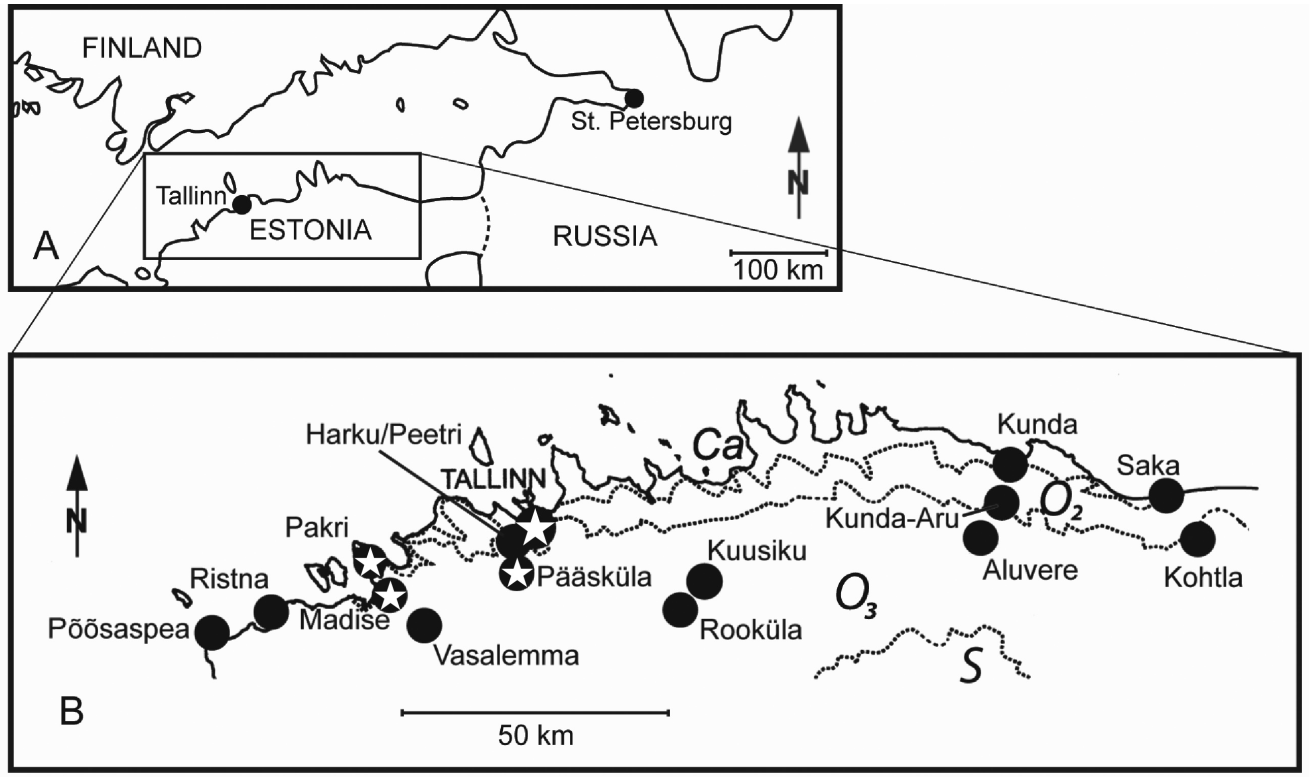

Figure 1. Schematic geologic map of northern Estonia showing collecting localities. Stars indicate sites of colonies selected for this study. *Ca* = Cambrian, O_2 = Middle Ordovician, O_3 = Upper Ordovician, *S* = Silurian. Modified from Wyse Jackson and Key (2007, Fig. 1).

Table 1. Sample, location, and stratigraphic information for the bryozoans analyzed.

Sample #	Sources sampled	Location (see Fig. 1)	Formation (member)	Regional age/stage	Global age/stage	Global epoch/series
TCD. 58257b	brown deposits, skeletal walls, cements	Pääskula Hillock	Kahula	Keila (D_{II})	Caradoc	Upper Ordovician
TCD. 58301b	brown deposits, skeletal walls, matrix, cements	Madise Village	Kahula (Madise)	Upper Haljala (D_I)	Caradoc	Upper Ordovician
TCD. 58006b	brown deposits, skeletal walls, matrix, cements	Väo Quarry (in Tallinn)	Väo	Lower Uhaku (C_{Ic})	Darriwilian	Middle Ordovician
TCD. 58206b	brown deposits, skeletal walls, cements	Pakri Peninsula	Pakri	Middle Kunda (B_{III})	Darriwilian	Middle Ordovician

The carbonate samples were roasted *in vacuo* at 200°C for 1 hr to remove any water and volatile organic contaminants that could interfere with the carbonate analyses. Stable isotope values were obtained using a Finnigan Kiel-III automated carbonate preparation system directly coupled to the inlet of a Finnigan MAT 253 gas-ratio mass spectrometer. Carbonate was reacted at 70°C with two drops of anhydrous phosphoric acid for 90 sec. Isotope ratios were corrected for acid fractionation and ^{17}O contribution and reported as $\delta^{13}C_{(CaCO_3)}$ and $\delta^{18}O_{(CaCO_3)}$ in per mil notation relative to the VPDB standard (‰ VPDB). Precision and calibration of data were monitored through daily analysis of NBS-18 and NBS-19 carbonate standards. Precision was better than ± 0.05 ‰ VPDB for $\delta^{13}C$ and ± 0.1 ‰ VPDB for $\delta^{18}O$. All micromilling and mass spectrometer analyses were performed at the Saskatchewan Isotope Laboratory in the Department of Geological Sciences, University of Saskatchewan, Saskatoon, Canada. All thick sections are housed in the Geological Museum at Trinity College, Dublin (TCD).

Results

The four colonies revealed numerous brown deposits (Fig. 2.1). In cross-sectional view, they form granular circular masses (Fig. 2.2) with reddish-brown mottled appearance in reflected light with a mean diameter of 80 μm (n = 8; range: 63-91 μm; standard deviation: 12 μm). They are typically preserved in coarser-infilling sparry calcite cement with no matrix present. They are found bracketed between successive diaphragms in zooecial living chambers (Fig. 2.2) and often immediately distal to a basal diaphragm (Fig. 2.3). There is typically one brown deposit between successive diaphragms (Fig. 2.3), but there can be more when the diaphragms are more widely spaced (Fig. 2.2).

The four colonies yielded 44 separate isotope analyses. Ten brown deposits, five skeletal walls, two samples of matrix, and five cements were each analyzed for C and O isotope values (Table 2). $\delta^{13}C$ values ranged from −2.0 to 1.2 ‰ VPDB, and the $\delta^{18}O$ values ranged from −6.5 to −2.6 ‰ VPDB (Fig. 3). The brown deposits had significantly lower $\delta^{13}C$ values (mean = −0.24 ‰ VPDB) than the skeletal walls, matrix, and cements (mean = 0.64 ‰ VPDB) (Mann-Whitney U Test, $p = 0.03$). Three of the $\delta^{13}C$ values of brown deposits are more negative than the rest (Fig. 3). This may be due to contamination, so each colony was separately tested for differences in $\delta^{13}C$ values between brown deposits and skeletal walls, matrix, and cements. The brown deposits had lower $\delta^{13}C$ values relative to the skeletal walls, matrix, and cements in eight of the 10 comparisons. The two exceptions were with the matrix of TCD.58006b and the skeletal walls of TCD.58206. In contrast, the brown deposits did not have significantly different $\delta^{18}O$ values (mean = −4.1 ‰ VPDB) than the skeletal walls, matrix, and cements (mean = −4.2 ‰ VPDB) (Mann-Whitney U Test, $p = 0.89$). The summary statistics for brown deposits, skeletal walls, matrix, and cements are separately reported in Table 2.

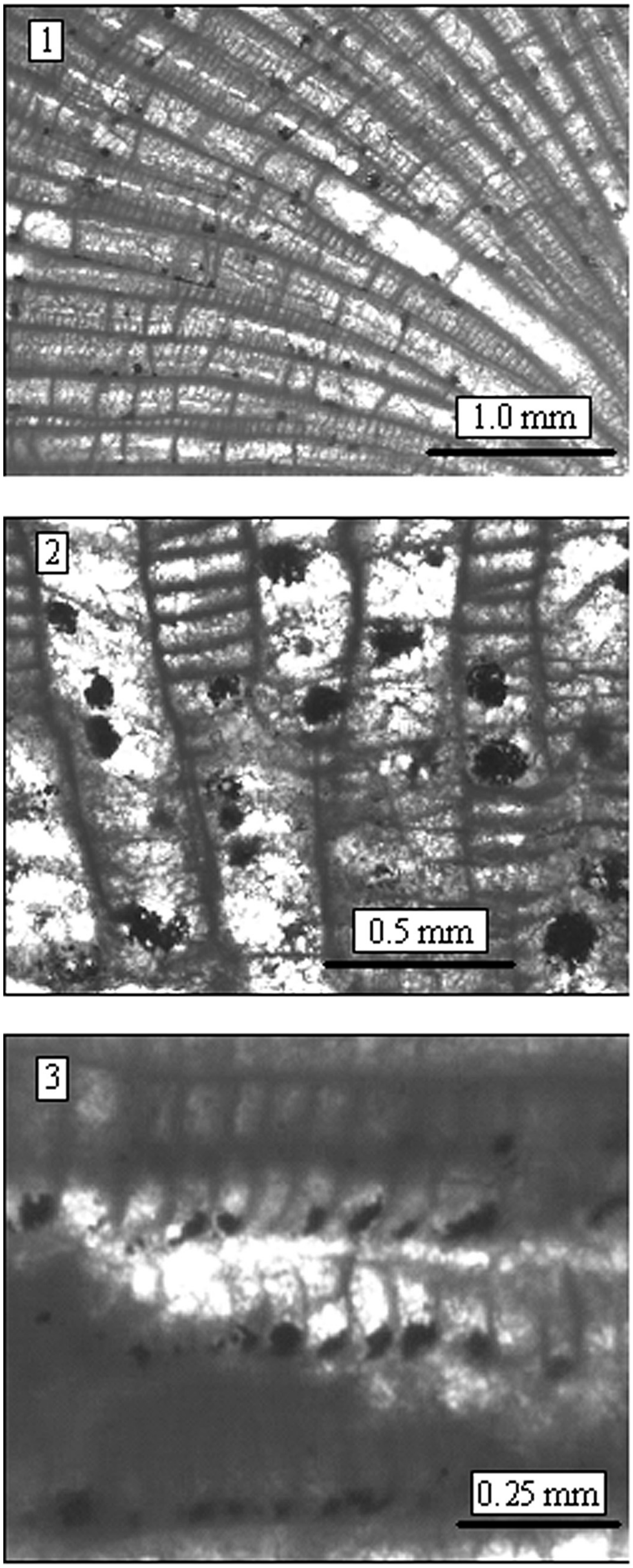

Figure 2. Photomicrographs of brown deposits in longitudinal sections of *Diplotrypa petropolitana*. 1) Abundance of brown deposits shown in transmitted light, TCD.58206b. 2) Irregular-circular shapes of brown deposits shown in transmitted light, TCD.58257b. 3) Relationship of brown deposits to basal diaphragms shown in transmitted light, TCD.58206b.

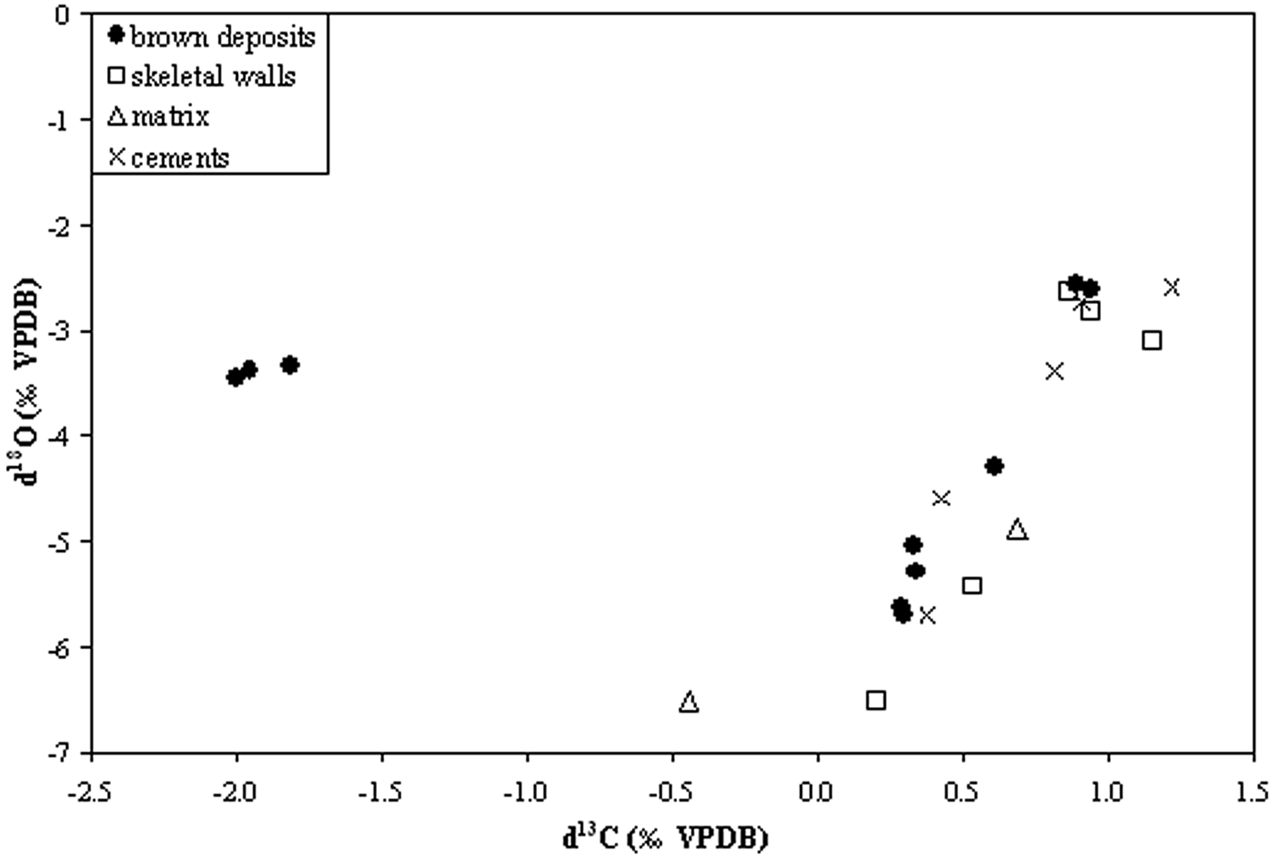

Figure 3. Plot of C and O isotope values for the 22 samples of brown deposits, skeletal walls, matrix, and cement from *Diplotrypa petropolitana* from the Ordovician of Estonia.

Discussion

There are several possible sources of variation affecting the stable isotope results of the brown deposits: (1) other diagenetic effects, (2) vital effects of the bryozoans themselves, (3) temporal sources of variation, and (4) real differences in the preservational history of the brown bodies owing to their original compositional differences as hypothesized in this study.

(1) Carbonate minerals in bryozoans are notoriously susceptible to diagenesis (see review in Key et al. 2005a). Carbonate diagenesis includes compaction, dissolution, neomorphism (i.e., recrystallization), as well as cementation, all variably significant in lithification of carbonate sediment. Inorganic C isotopes are less susceptible to alteration than O isotopes (Marshall 1992). Fortunately these stenolaemate trepostome bryozoans were probably constructed of the diagenetically more stable low Mg calcite (LMC) as the primitive state of biomineralization in the entire bryozoan clade is LMC. This is based on the fact that all five orders of the more primitive class Stenolaemata had calcitic skeletons (Lowenstam 1963; Boardman and Cheetham 1987; Taylor 1999) and the surviving descendants of the stratigraphically oldest bryozoans, the cyclostomes, are all calcitic and mostly LMC (Smith et al. 2006). In addition, as reviewed in the introduction, the Ordovician rocks of northern Estonia experienced minimal diagenetic alteration during their history. Thus, the isotope values reported here were unlikely to be significantly overprinted by some diagenetic signal other than original compositional differences of the brown bodies.

(2) C isotope fractionation is complex, affected by a variety of factors (i.e. vital effects) including kinetic effects, that are controlled by growth and calcification rates, as well as metabolic effects, that are controlled by respiration and photosynthetic rates (Norris 1998). In contrast, δ^{18}O fractionation is relatively simple as it is predominantly correlated with water temperature and salinity (Norris 1998). A few bryozoans do not secrete their skeletons in isotopic equilibrium with their surrounding water (Crowley and Taylor 2000; Smith et al. 2004), but fortunately the majority do (see review in Key et al. 2005b). Thus, the isotope values reported here were probably not altered by vital effects.

(3) Funding constraints limited this initial study to one colony containing brown deposits per stratigraphic interval sampled. Therefore each colony is from a different stratigraphic level (Table 1). C and O isotope values of the world's oceans have varied over time. During the Middle and Upper Ordovician, the range of δ^{13}C values of the global oceans was −2.5 to 6.1 ‰ VPDB (Veizer et al. 1999, Fig. 10).

Table 2. Summary data for C and O isotope values of brown deposits, skeletal walls, matrix, and cements from Ordovician trepostomes of Estonia. N = number, SD = standard deviation.

		$\delta^{13}C$ ‰ VPDB			$\delta^{18}O$ ‰ VPDB		
Sample	N	Range	Mean	SD	Range	Mean	SD
brown deposits	10	−2.0 to 0.89	−0.24	1.2	−5.7 to −2.6	−4.1	1.2
skeletal walls	5	0.21 to 1.2	0.74	0.37	−6.5 to −2.6	−4.1	1.8
matrix	2	−0.44 to 0.69	0.12	0.80	−6.5 to −4.9	−5.7	1.2
cements	5	0.38 to 1.2	0.75	0.35	−5.7 to −2.6	−3.8	1.3
all non-brown deposits combined	12	−0.44 to 1.2	0.64	0.46	−6.5 to −2.6	−4.2	1.5

Our $\delta^{13}C$ values (range: −2.0 to 1.2 ‰ VPDB; mean: 0.24 ‰ VPDB) fall well within this range. During the Middle and Upper Ordovician, the range of $\delta^{18}O$ values of the global oceans was −9.5 to −2.5 ‰ VPDB (Veizer et al. 1999, Fig. 13). Our $\delta^{18}O$ values (range: −6.5 to −2.6 ‰ VPDB; mean: −4.2 ‰ VPDB) fall well within this range. Even if the differences in isotope values between colonies resulted entirely from temporal (i.e., stratigraphic) variation in the composition of global sea water, our results show a consistent trend within colonies of significantly lower $\delta^{13}C$ values and insignificantly different $\delta^{18}O$ values. This indicates the presence of a non-stratigraphic C isotope signal.

(4) If the previous three sources of variation are ruled out or at least minimized, then the lower $\delta^{13}C$ values of the brown deposits compared to the skeletal walls, matrix, and cements reflect real differences in the diagenetic history of the brown bodies due to the presence of original organic C. Thus, the C isotopes support the hypothesis that the brown deposits are formed from organic components of the original brown bodies.

Are brown bodies the same as conodont pearls? The brown body-like spheres reported by Sollas (1879), Oakley (1934, 1966), Spjeldnæs (1950), Eisenack (1964), and Snell (2004) in the zooecial chambers of Silurian cystoporates were interpreted by these authors to be have been (bio)chemically precipitated inside zooecial chambers sealed off by subsequent basal diaphragms. These were reinterpreted by Glenister et al. (1976, 1978) as conodont pearls formed by the conodont animal around a particulate or organic irritant. This interpretation was based partly on their Cambrian-Carboniferous stratigraphic range that overlaps with conodonts (Stauffer 1940; Youngquist and Miller 1948), their abundance which is proportional to that of associated conodonts (Youngquist and Miller 1948), and they have a similar apatite composition as conodonts (Leuteritz et al. 1972; Glenister et al. 1976; Wang and Chatterton 1993). Conodont pearls have also been attributed to egg cases from an undetermined animal (Stauffer 1935), egg cases from the conodont animal itself (Stauffer 1940), conodont otoliths (Youngquist and Miller 1948), cnidarian statoliths (Bischoff 1973), and nautiloid uroliths (McConnell and Ward 1978). Donoghue (1995, 1996, 1998) has repeatedly argued against the conodont origin as conodont pearls are not found in all conodont residues. Most recently, Giles et al. (2002) argued for a fish otolith origin.

Even though they have the same general size and shape, conodont pearls are not brown deposits as described here as they have different compositions as well as internal and external morphologies. Conodont pearls are made of apatite with radially aligned crystallites arranged in concentric bands with a smooth external surface (Glenister et al. 1976; Wang and Chatterton 1993; Giles et al. 2002), whereas the brown deposits found in most bryozoans are made of calcite with randomly arranged crystallites arranged in a granular texture with an irregular external surface.

Conclusions

The brown deposits in these Ordovician trepostomes from Estonia are interpreted as the diagenetic remnants of brown bodies, which were the degenerated remnants of polypides. This is based on the following five lines of evidence: (1) There is a general morphologic resemblance between brown deposits in fossil bryozoans and brown bodies in extant bryozoans. They have a similar granular texture and reddish-brown color. (2) They have a similar size (i.e., diameter of 80 µm). (3) They have a similar shape (i.e., roughly circular in cross-section view). (4) They have a similar position in the zooecial living chambers. They are typically preserved in coarser infilling sparry calcite cement with no matrix present and bracketed between adjacent diaphragms. This location proximal to at least one diaphragm resulted in isolation of the parent brown body from the colony's external environment and makes their origin from a source external of the zooid unlikely. (5) Their C isotopic composition is indicative of diagenesis of original organic matter.

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