Element/Ca, C and O isotope ratios in modern brachiopods: species-specific signals of biomineralization

C.V. ULLMANN[1,*], R. FREI[2], C. KORTE[2], C. LÜTER[3]

[1]University of Exeter, Camborne School of Mines & Environment and Sustainability Institute, Penryn Campus, Penryn, TR10 9FE, United Kingdom

[2]University of Copenhagen, Department of Geoscience and Natural Resource Management, Øster Voldgade 10, 1350 Copenhagen, Denmark

[3]Museum für Naturkunde, Leibniz-Institut für Evolutions- und Biodiversitätsforschung, Invalidenstraße 43, 10115 Berlin, Germany

[*]*Correspondence:* c.v.ullmann@gmx.net; Tel: 0044 1326 259165

Abstract: Fossil brachiopods are of major importance for the reconstruction of palaeoenvironmental conditions, particularly of the Palaeozoic. In order to better understand signals of ancient shell materials, modern analogue studies have to be conducted.

Here we present C and O isotope data in conjunction with Mg/Ca, Sr/Ca, Mn/Ca and Fe/Ca data for nine modern rhynchonellid and terebratulid brachiopod species from tropical to intermediate latitudes and shallow to very deep marine settings. C and O isotope signals of most species suggest formation of secondary shell layers near or in isotopic equilibrium with ambient seawater. Some species – especially in the suborder Terebratellidina – show partly distinct disequilibrium signals, suggesting some degree of phylogenetic control on the expression of vital effects.

Mn/Ca and Fe/Ca ratios measured in the modern species form a baseline to assess fossil preservation, but also yield environmental information Mg/Ca and Sr/Ca ratios follow previously observed patterns, with all studied brachiopod species comprising low-Mg calcite. Strong covariation of Sr/Ca ratios with Mg/Ca ratios is only observed in rhynchonellids and possibly one terebratulid species, potentially linking the incorporation behaviour of alkaline earth metals to phylogeny.

Sr/Ca show a strong negative correlation with δ^{13}C values in terebratellidinid species which exhibit major isotopic disequilibrium and also combined data from three localities for which two species were studied indicate such a negative relation. The observed covariation of Sr/Ca ratios with δ^{13}C values may therefore become a useful tool to detect δ^{13}C disequilibrium and to robustly estimate δ^{13}C values of ambient DIC in deep time.

1. Introduction

Geochemical information derived from brachiopod shell calcite is of major importance for understanding past environmental conditions (e.g., Popp et al., 1986; Grossman et al., 1993; Bickert et al., 1997; Veizer et al., 1999; Korte et al., 2008; Rasmussen et al., 2016). Carbon and oxygen isotope ratios have traditionally been the primary focus of such palaeoenvironmental studies, because these proxies allow the most direct insights into local palaeotemperatures and carbon cycle dynamics. The combination of C and O isotope data with element/Ca ratios forms the backbone of palaeoenvironmental studies employing fossil brachiopod shells. Element/Ca data are most commonly used as one means of informing about the preservation state of the shell material (e.g., Brand and Veizer, 1980; Veizer, 1983; Al-Aasm and Veizer, 1986; Ullmann and Korte, 2015). They can, however, also be used to give insights into the chemical composition of seawater (Steuber and Veizer, 2002; Lee et al., 2004; Ullmann et al., 2016) and supplement isotopic data to more robustly constrain palaeotemperatures (Brand et al.,

2013, 2015; Butler et al., 2015). Despite the potential value of this supplementing information, the chemical composition of brachiopod shell material has received comparatively little attention.

Shell carbon and oxygen isotope ratios as well as element concentration data of extant brachiopods has been presented for compilations of multiple species (Lowenstam, 1961; Brand et al., 2003, 2013), but large datasets for single species are rare. Studies of brachiopod calcite chemistry have mostly focused on the distribution of single elements in the different shell layers and areas (Cusack et al., 2008a; Pérez-Huerta et al., 2008). In particular, biomineralisation aspects have been prominent in this research (Griesshaber et al., 2007; Cusack et al., 2008b). Major controls of phylogeny, shell layer, ontogeny and functional morphology on the isotopic ratios and elements recorded in brachiopod shell calcite have been documented (e.g., Carpenter and Lohmann, 1995; Parkinson et al., 2005; Cusack et al., 2008a, 2012).

The chemical and isotopic patterns observed in brachiopod calcite have been generalized to

the assumption that the secondary shell layer of brachiopods is precipitated near isotopic equilibrium with ambient seawater, whereas the primary shell layer is not (Brand et al., 2013, 2015; see also Carpenter and Lohmann, 1995). Element concentrations and isotopic ratios derived from the secondary shell layer of adult brachiopods are therefore thought to yield the most robust results for environmental reconstructions.

While it is well-established that brachiopod shell calcite is chemically and isotopically heterogeneous, studies presenting isotopic data alongside element concentration data for a multitude of samples from single modern brachiopods are very rare. It is therefore not clear in which way isotopic and chemical variability in the shell calcite relate to each other and whether they are governed by common control mechanisms. In this study, combined element/Ca data and $\delta^{13}C$ and $\delta^{18}O$ values measured for 267 samples from nine brachiopod species of the orders Rhynchonellida and Terebratulida are presented. The covariations of the element and isotope data are discussed in the light of potential controlling factors and their meaning for palaeoenvironmental studies.

2. Materials and Methods

One to three valves of nine modern brachiopod species from different localities ranging from northern intermediate latitudes to southern intermediate latitudes and shallow waters to ~1600 m depth were studied in detail (Table 1). Differences in sample numbers for each species are due to specimen size, allowing for only five samples to be analysed for a small specimen of *Frenulina sanguinolenta* and 60 samples for *Liothyrella neozelanica*. Multiple valves could be studied for most species, but for *Magellania venosa* and *Liothyrella neozelanica* only one ventral valve was available. Most specimens were devoid of organic tissues, but for

the specimens from Friday Harbour (*Terebratalia transversa* and *Terebratulina* sp.) organic material was removed applying 5 % NaClO solution for 24h and subsequent washing with deionised water. Samples of 1-2 mg were extracted from the shell using a stainless steel scalpel (Supplementary Figure 1). Owing to their thin shells, samples for *Frenulina sanguinolenta*, *Notosaria nigricans* and *Terebratulina* sp. were taken from the inner shell surface. For *Calloria inconspicua*, *Compsothyris racovitzae*, *Liothyrella neozelanica*, *Magellania venosa*, *Stenosarina crosnieri* and *Terebratalia transversa*, the epifauna, detrital contamination and outer shell layer were removed using a stainless steel scalpel previous to sample extraction. In most instances the primary shell layer was removed entirely during this process, but for comparatively thin shells of *M. venosa* and the shell of *T. transversa* which has relatively strong surface relief, its removal was not always quantitative. Samples were extracted parallel to growth lineaments from the outer surface of the valves starting near the umbo and progressed towards later growth increments (Supplementary Figure 1).

Resulting sample powders were split into two batches, one for element concentration analysis and one for determination of $\delta^{13}C$ and $\delta^{18}O$ values. Element ratios were determined on ~ 0.6 mg of shell powder using an Optima 7000 DV ICP-OES at the Department of Geosciences and Natural Resource Management, University of Copenhagen. Samples were dissolved with 2 % HNO_3 in a ratio of ~1.5 ml per 100 µg of calcite to achieve a sample solution with Ca concentration close to 25 µg/g. Quantification of element concentrations was done employing a multi-point calibration using a blank solution and three matrix-matched calibration solutions covering the expected range of analyte concentrations. Reproducibility and accuracy of the analyses were controlled by interspersed aliquots of JLs-1

Table 1: Localities and taxonomic data for sampled species.

locality	latitude	longitude	water depth m	material	Order/Suborder	sampled material
Friday Harbour, Washington State, U.S.A.	48°32' N	123°00' W	20	*Terebratalia transversa*	Terebratulida/Terebratellidina	ventral, dorsal, loop
Friday Harbour, Washington State, U.S.A.	48°32' N	123°00' W	20	*Terebratulina* sp.	Terebratulida/Terebratulidina	ventral, dorsal, loop
tropical Pacific				*Frenulina sanguinolenta*	Terebratulida/Terebratellidina	ventral, dorsal, loop
Walvis Ridge So233 St. 57	26°18'08" S	6°26'20" E	1600	*Stenosarina crosnieri*	Terebratulida/Terebratulidina	dorsal
Walvis Ridge So233 St. 57	26°18'08" S	6°26'20" E	1600	*Stenosarina crosnieri*	Terebratulida/Terebratulidina	ventral
Walvis Ridge So233 St. 57	26°18'08" S	6°26'20" E	1600	*Stenosarina crosnieri*	Terebratulida/Terebratulidina	ventral
Walvis Ridge, So233 St.57	26°18'08" S	6°26'20" E	1600	*Compsothyris racovitzae*	Rhynchonellida	dorsal
Walvis Ridge, So233 St.57	26°18'08" S	6°26'20" E	1600	*Compsothyris racovitzae*	Rhynchonellida	ventral
Walvis Ridge, So233 St.57	26°18'08" S	6°26'20" E	1600	*Compsothyris racovitzae*	Rhynchonellida	ventral
near Chatham Islands	44°36' S	176°31' W	421-563	*Liothyrella neozelanica*	Terebratulida/Terebratulidina	ventral
Porpoise Bay, New Zealand	46°39' S	169°07' W	shallow	*Calloria inconspicua*	Terebratulida/Terebratellidina	ventral
Porpoise Bay, New Zealand	46°39' S	169°07' W	shallow	*Notosaria nigricans*	Rhynchonellida	dorsal
Porpoise Bay, New Zealand	46°39' S	169°07' W	shallow	*Notosaria nigricans*	Rhynchonellida	ventral
Porpoise Bay, New Zealand	46°39' S	169°07' W	shallow	*Notosaria nigricans*	Rhynchonellida	ventral
South American shelf (prob. Chile)				*Magellania venosa*	Terebratulida/Terebratellidina	ventral

(limestone; n = 163; see Rasmussen et al., 2016 for further details), which yielded averages ± two standard deviations of 14.0 ± 0.4 mmol/mol for Mg/Ca, 0.344 ± 0.008 mmol/mol for Sr/Ca, 0.07 ± 0.04 mmol/mol for Fe/Ca and 0.029 ± 0.009 mmol/mol for Mn/Ca. These results are in good agreement with published values giving averages (± 2 err) of Mg/Ca = 15.3 ± 0.7 mmol/mol, Sr/Ca = 0.343 ± 0.009 mmol/mol, Fe/Ca = 0.2 ± 0.1 mmol/mol, and Mn/Ca = 0.030 ± 0.004 mmol/mol (Imai et al., 1996). Uncertainty of Fe/Ca and Mn/Ca analyses is mostly related to baseline variability of the ICP-OES due to low Fe and Mn concentrations in JLs-1. Raw element ratios of the calibration solution with highest Fe/Ca (2.86 mmol/mol) and Mn/Ca (0.724 mmol/mol) reproduced within 4 % for Fe (2 sd) and 2 % for Mn (2 sd) for repeated calibrations within sample batches, evidencing much lower relative uncertainties at higher concentration levels.

Carbon and oxygen isotope ratios were determined using an IsoPrime GS-IRMS in continuous flow setup and a Delta V GS-IRMS coupled with a Kiel IV device, both at the Department of Geosciences and Natural Resource Management, University of Copenhagen. For the IsoPrime analyses (samples 1893-1979; see Supplementary Table 1), ~0.6 mg of powder was analysed using protocols described in Ullmann et al. (2013, 2014). Reproducibility (2 sd) was monitored through multiple measurement of the in-house standard LEO (Carrara Marble) and was found to be 0.07 ‰ for $\delta^{13}C$ values and 0.19 ‰ for $\delta^{18}O$ values (n = 105).

For analyses using the Delta V (samples 973-1132; see Supplementary Table 1), 40 to 60 μg of calcite were used. Samples were processed automatically using the Kiel IV device and isotopic ratios corrected using averages of multiple analyses of NBS-18 and NBS-19 as anchor points. Adjustment of isotopic ratios was only done for batches where results for the NBS standards significantly deviated from certified or recommended values. As an independent monitor of stability, an in-house reference material from Freie Universität Berlin (LM; Laaser Marble, $\delta^{13}C$ = +1.51 ‰; $\delta^{18}O$ = -5.17 ‰) was run interspersed with the samples and gave averages ± 2 standard deviations of 1.50 ± 0.03 ‰ for $\delta^{13}C$ values and -5.15 ± 0.10 ‰ for $\delta^{18}O$ values (n = 28).

3. Results

Geochemical data for different valves of the investigated species are either not statistically significant, smaller than internal variability encountered in single shells, and/or do not indicate consistent, strong differences between dorsal and ventral valves. The geochemical results of the species are therefore not discussed in light of possible inter-valve differences.

3.1 $\delta^{13}C$ and $\delta^{18}O$ values

A wide range of δ13C values (-5.8 to +3.7 ‰) and $\delta^{18}O$ values (-2.9 to +5.7 ‰) is observed in the studied specimens (Fig. 1). The lightest and most variable carbon and oxygen isotope ratios are observed in *M. venosa*, which also shows the highest variability in Sr/Ca ratios. The heaviest $\delta^{13}C$ values (> +3 ‰) are observed in *L. neozelanica* and the tropical *F. sanguinolenta*. The most positive $\delta^{18}O$ values (> +5 ‰) are seen in the two species from 1.6 km depth at Walvis Ridge, *C. racovitzae* and *S. crosnieri*. Strong covariation of carbon and oxygen isotope ratios in the studied species is limited to the suborder Terebratellidina, where three of four species show strong correlations between these isotope ratios (r^2 = 0.77 to 0.92; Fig. 2). The slopes of the linear regression lines for these correlations range from 0.4 (*M. venosa*; stronger effect on carbon) to 1.4 (*C. inconspicua*; stronger effect on oxygen).

3.2 Mn/Ca and Fe/Ca ratios

Mn/Ca ratios in the nine species range from detection limit to 0.13 mmol/mol and Fe/Ca ratios from detection limit to 0.75 mmol/mol (Supplementary Table 1). Within single species the observed ranges are usually much smaller. Mn/Ca ratios > 0.05 mmol/mol are only encountered in *T. transversa*, *M. venosa* and rarely in *S. crosnieri* (two samples) and *L. neozelanica* (one sample). Enrichments of Fe are more common, with Fe/Ca ratios > 0.2 mmol/mol observed in *T. transversa*, *L. neozelanica* (particulary near the umbo) and rare samples of *C. racovitzae* (two samples), *M. venosa* (two samples) and *S. crosnieri* (one sample).

Correlation coefficients of linear regressions between Mn/Ca and Fe/Ca in single species range from r^2= 0.00 to 0.80, whereby the three species showing r2 values > 0.4 were collected from localities close to large landmasses - *C. inconspicua* and *N. nigricans* from Porpoise Bay, New Zealand and *T. transversa* from Friday Harbor, U.S.A.

Average Mn/Fe ratios in different species from the same locality can differ significantly. At Friday Harbor, U.S.A., *T. transversa* has an average Mn/Fe ratio of 0.3 mol/mol and Terebratulina sp. an average Mn/Fe ratio of 1.5 mol/mol. At Porpoise Bay, New Zealand, *N. nigricans* has an average Mn/Fe ratio of 0.2 mol/mol and *C. inconspicua* an average Mn/Fe ratio of 1.2 mol/mol. At the Walvis Ridge site, *C.*

racovitzae (0.11 mol/mol) and *S. crosnieri* (0.13 mol/mol) show very similar average Mn/Fe ratios and low concentrations of these elements.
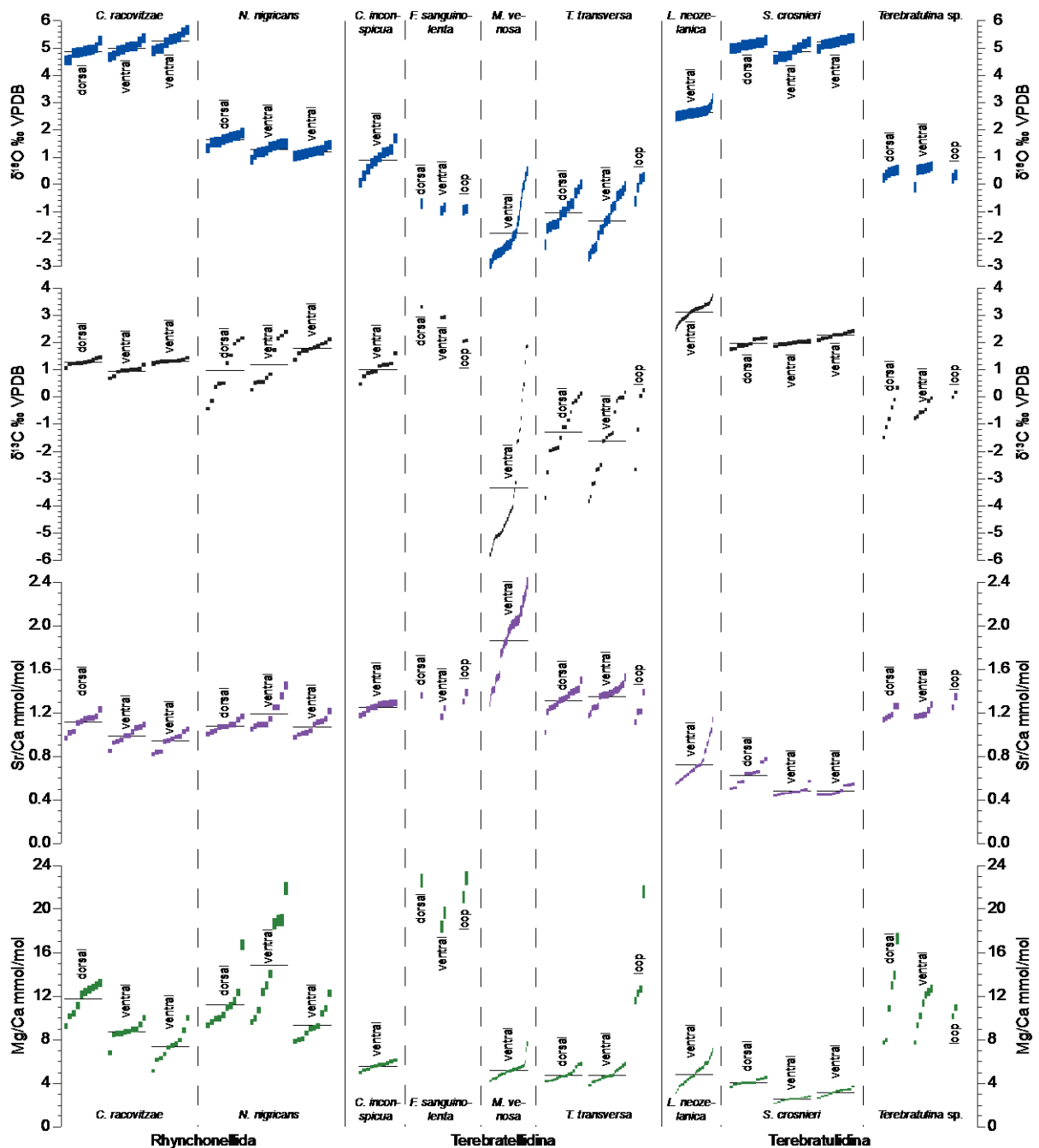

Fig. 1. Geochemical results for specimens analysed in this study. Data are sorted separately for each proxy from the lowest to highest value. Black lines through data sets of at least 8 analyses indicate average values.

3.3 Sr/Ca and Mg/Ca ratios

Sr/Ca ratios from 0.4 to 2.4 mmol/mol and Mg/Ca ratios from 2.2 to 22.8 mmol/mol are found in the nine brachiopod species. All investigated species can be classified as low Mg calcite (Figs. 1-3; Veizer, 1983; Morrison and Brand, 1986).

The lowest Sr/Ca ratios were observed in the *L. neozelanica* and *S. crosnieri*, both living at depths > 400 m and belonging to the suborder Terebratulidina. The highest Sr/Ca ratios were measured in brachiopods of the suborder Terebratellidina, particularly in *M. venosa*. Variability of Sr/Ca ratios within single valves averages 20 % (2 relative standard deviations; RSD), but *M. venosa* (33 %) and *L. neozelanica* (41 %) show considerably higher within-shell

variability. Variability of Sr/Ca ratios of multiple valves of the same species (25 %, 2 RSD) is only slightly larger than average variability within single valves of these species (17 %, 2 RSD). Differences in Sr/Ca ratios of ventral and dorsal valves, as well as the loop are generally minor (Fig. 1).
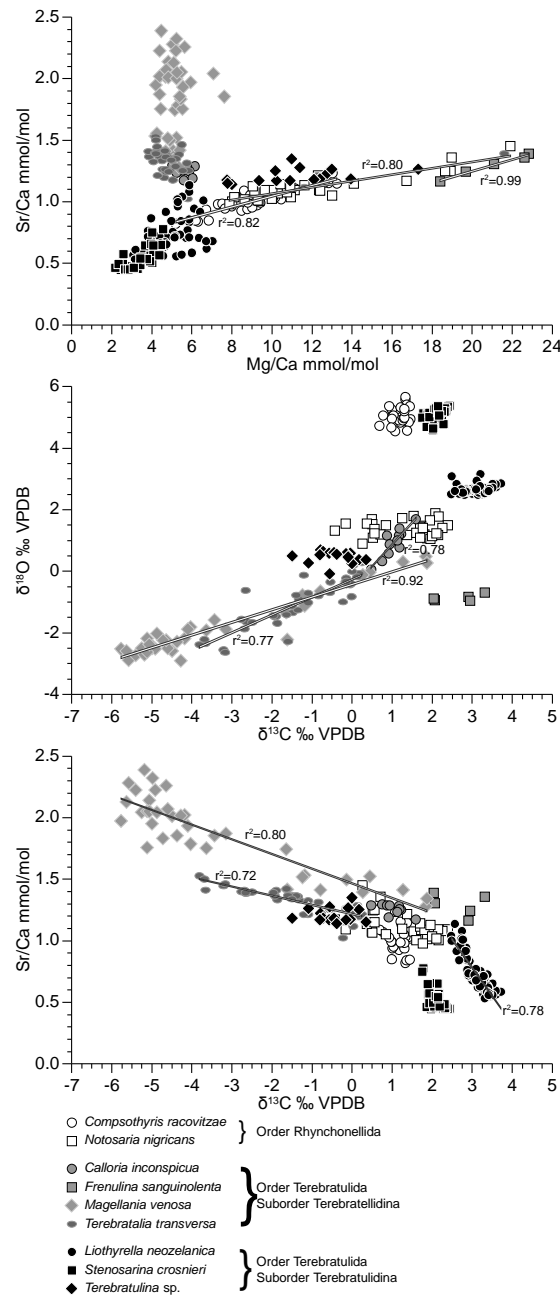

Fig. 2. Cross plots of element and isotope proxies in the studied shell materials.

Similar patterns as for Sr/Ca ratios are observed for Mg/Ca ratios. Lowest Mg/Ca ratios are measured in *S. crosnieri*, and most investigated terebratulids apart from *F. sanguinolenta* and *Terebratulina* sp. show low average Mg/Ca ratios < 6 mmol/mol. The highest Mg/Ca ratios are observed in *F. sanguinolenta*.

Average within-shell variability of Mg/Ca ratios (29 %, 2 RSD) is higher than for Sr/Ca. Also differences between Mg/Ca ratios of different valves of a single species are larger, resulting in a larger variability of Mg/Ca for whole species (51 %, 2 RSD) than for single valves of these species (29 %, 2 RSD). While data for dorsal and ventral valve agree well with data for the loop of F. sanguinolenta and Terebratulina sp., the loop of T. transversa is considerably enriched in Mg with respect to the secondary layer of the valves.
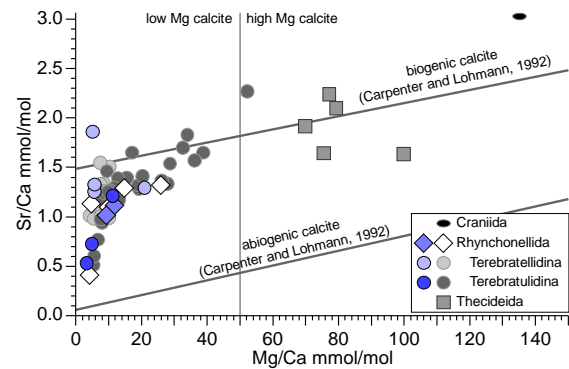

Fig. 3. Cross plot of average Sr/Ca and Mg/Ca ratios in the studied brachiopod species (blue colours) supplemented with results from Lowenstam (1961), Carpenter and Lohmann (1992, 1995), Brand et al. (2003, 2013), Lee et al. (2004), Pérez-Huerta et al. (2008) (white, grey, and black). The approximate limit of low-Mg calcite as well as proposed trend lines for abiogenic and biogenic calcite (Carpenter and Lohmann, 1992) are also indicated.

Very strong covariance (r2 >= 0.80) of Sr/Ca ratios with Mg/Ca ratios is observed for both investigated species of the order Rhynchonellida, whereas for the order Terebratulida covariance between Sr/Ca and Mg/Ca is generally weak (r2 = 0.25 or lower) (Fig. 2). Also in *S. crosnieri* the covariation is strong (r^2 = 0.55), but mostly defined by the difference in concentrations of Sr and Mg measured between the valves in this species. The very strong covariance of Sr and Mg (r^2 = 0.99) in *F. sanguinolenta* points to a possible biomineralisation control common to both of these elements. The correlation is not taken as robustly defined here, however, because it is based on only five analyses.

For two of the species recording strong covariation of carbon and oxygen isotope ratios also Sr/Ca is linearly linked with the isotopic signals (*M. venosa*; r^2 = 0.80 for δ^{13}C and 0.74 for δ^{18}O, and *T. transversa*; r2 = 0.72 for δ^{13}C and 0.57 for δ^{18}O; Fig. 2). In *L. neozelanica* Sr/Ca is linearly correlated with δ^{13}C (r^2 = 0.78), but not with δ^{18}O. None of the investigated species, however, exhibits a strong covariation of Mg/Ca ratios with δ^{18}O values.

5

4. Discussion
4.1 Isotopic equilibrium and disequilibrium signals
4.1.1 Previous reports
Disequilibrium incorporation of O and C isotopes into the primary layer of brachiopods is a widespread phenomenon common to nearly all modern brachiopods (Carpenter and Lohmann, 1995; Auclair et al., 2003; Parkinson et al., 2005; Jean et al., 2015). The isotopic composition of the secondary layer of brachiopod shells on the other hand tends to be more often compatible with O and C isotope equilibrium (e.g., Carpenter and Lohmann, 1995; Parkinson et al., 2005; Brand et al., 2015). Disagreements with expected isotopic ratios, however, have also been reported in this shell layer. Some of the non-articulated craniids and one thecideid species have been described to have secondary layers enriched in 18O (Carpenter and Lohmann, 1995; Parkinson et al., 2005), an effect which has been related to their comparatively high Mg content (Brand et al., 2013).

Many brachiopod species of the order Terebratulida have been found to show vital effects enriching the light O and C isotopes in the secondary shell layer (Carpenter and Lohmann, 1995; Auclair et al., 2003; Yamamoto et al., 2010a, 2011; Cusack et al., 2012; Takayanagi et al., 2012, 2015).

Isotopic signals in the secondary shell material of rhynchonellids are least indicative of isotopic disequilibrium and no consistent vital effect has so far been described for rhynchonellid species. Observations of partial disequilibrium in *Hemithiris psittacea* and *Notosaria* sp. exist, however (Carpenter and Lohmann, 1995; Cusack et al., 2012).

4.1.2 Observed isotope ratios
Approximate equilibrium ranges of oxygen isotope ratios can be computed for most of the investigated species (Table 2). Seawater at Friday Harbor (*T. transversa* and *Terebratulina* sp.) and possibly Porpoise Bay (*C. inconspicua* and *N. nigricans*) is depleted in 18O due to admixture of freshwater (Brand et al., 2013), but other localities are expected to have seawater δ18O values near 0 ‰ VSMOW (Bigg and Rohling, 2000). Approximate seasonal temperature variability estimates are available for most specimens apart from M. venosa and *F. sanguinolenta* and a maximum expected temperature range for *M. venosa* can be deduced from ecological studies (McCammon, 1973).

Figure 4 shows the expected equilibrium δ18O values for the eight species with known temperature ranges according to a series of published temperature equations. A correction for Mg concentrations was only applied for calculations according to Brand et al. (2013), because most of the calibrations were done on natural calcite with unknown Mg concentration and the expected Mg-effect on calcite δ18O (Jimenez-Lopez, 2004) is < 0.25 ‰ in 95 % of the samples.

The observed patterns in Figure 3 broadly confirm reports from previous studies: All rhynchonellids and the species of the suborder Terebratulidina studied here show δ18O values compatible with or heavier than predicted values using recent (Coplen, 2007) and brachiopod specific (Brand et al., 2013) calibrations. Larger biases are documented for the other calibrations, which predict significantly more negative δ18O values. It may be argued that the disagreement of the two deep sea species C. racovitzae and *S. crosnieri* with the calibration of Coplen (2007) is related to the low ambient temperatures of +2 to +5°C at Walvis ridge, ~30°C lower than the calibration point constrained by Coplen (2007). Reasons for the offset from the calibration of Brand et al. (2013) which covers the temperature range from 0 to +30°C are less obvious, however. Core-top benthic foraminifer δ18O from IODP site 1264 at Walvis Ridge (Bell et al., 2015) are in agreement with Coplen (2007) and Brand et al. (2013) but more than 1 ‰ lighter than δ18O values of *C. racovitzae* and *S. crosnieri*. Preferential uptake of heavy oxygen isotopes into the shell of these two brachiopod species as described for very slowly growing Terebratulina crossei (Takayanagi et al., 2015) is therefore indicated.

In contrast to the studied rhynchonellids, all three sampled terebratellidinid species show clear indications of oxygen isotope disequilibrium with ambient waters, as expressed in variable and low δ18O values that correlate strongly with δ13C values (Fig. 2). Even for the terebratulidinid species for which no clear indication of vital effects affecting δ18O values were found in the present study, previous studies documented some evidence for C and O isotope disequilibrium in the secondary/tertiary shell layer: Some species of Terebratulina have yielded partly too light C or O isotope ratios (Yamamoto et al., 2011; Cusack et al., 2012; Takayanagi et al., 2015). Also, strong covariation of C and O isotope ratios grading into isotopically depleted values of the primary layer have been observed in *Liothyrella uva* and *Liothyrella neozelanica* (Parkinson et al., 2005, their Appendix A).

Table 2: Isotopic composition and temperature range observed and the different sample localities.

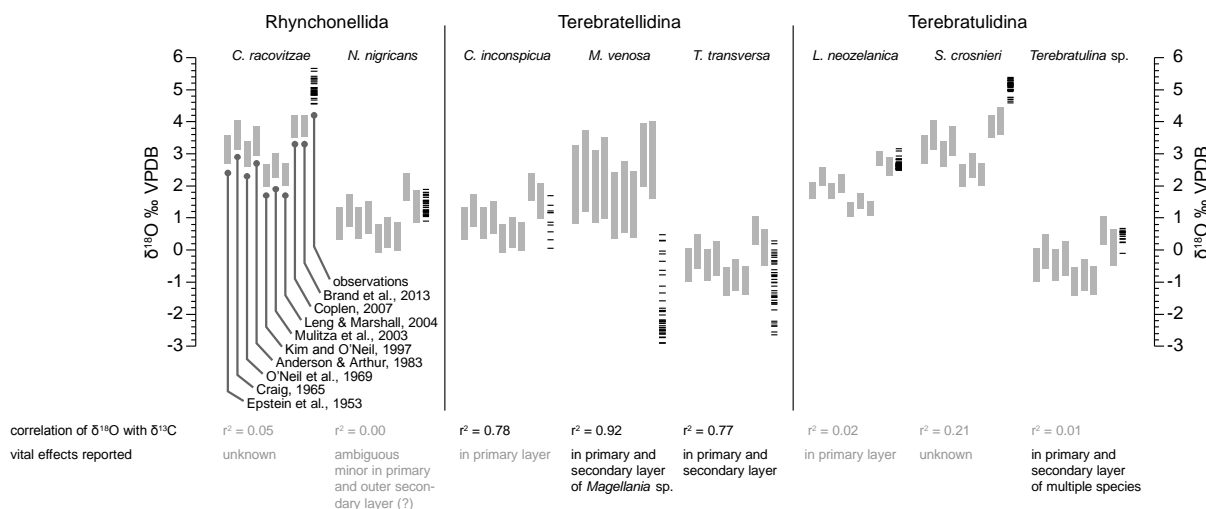| locality	water depth	material	$\delta^{18}O$ water ‰	$\delta^{13}C$ water ‰	expected T	seawater estimates		Temperature estimate
	m		SMOW	PDB	°C			
Friday Harbour, Washington State, U.S.A.	20	*Terebratalia transversa*	-1.8		+8 to +12	Brand et al., 2013		Sutherland et al., 2011
Friday Harbour, Washington State, U.S.A.	20	*Terebratulina* sp.	-1.8		+8 to +12	Brand et al., 2013		Sutherland et al., 2011
tropical Pacific		*Frenulina sanguinolenta*						
Walvis Ridge So233 St. 57	1600	*Stenosarina crosnieri*	0.0	0.8	+2 to +5	Bigg and Rohling, 2000	Kroopnick, 1980	Raitzsch et al., 2008
Walvis Ridge, So233 St.57	1600	*Compsothyris racovitzae*	0.0	0.8	+2 to +5	Bigg and Rohling, 2000	Kroopnick, 1980	Raitzsch et al., 2008
near Chatham Islands	421-563	*Liothyrella neozelanica*	0.0		+7 to +9	Bigg and Rohling, 2000		Heath, 1980
Porpoise Bay, New Zealand	shallow	*Calloria inconspicua*			+10 to +14			Chiswell, 1994
Porpoise Bay, New Zealand	shallow	*Notosaria nigricans*			+10 to +14			Chiswell, 1994
South American shelf (prob. Chile)		*Magellania venosa*			+3 to +12			McCammon, 1973

Fig. 4. Observed $\delta^{18}O$ values in the brachiopod species in comparison with calculated, expected equilibrium $\delta^{18}O$ values according to various palaeotemperature equations. Information about isotopic equilibrium and disequilibrium is derived from Carpenter and Lohmann (1995), Rahimpour-Bonab et al. (1997), Auclair et al. (2003), Parkinson et al. (2005), Yamamoto et al. (2010a,b, 2011), Cusack et al. (2012), Takayanagi et al. (2012, 2013, 2015), Jean et al. (2015).

4.1.3 Does Mg concentration resolve apparent isotopic disequilibrium?

C and O isotope data for most modern brachiopod species are shifted towards apparent equilibrium, if an empirical calibration including the Mg concentration of the shell calcite is employed (Jimenez-Lopez et al., 2004, 2006; Brand et al., 2013, 2015). Whether this fit is truly indicative of isotopic equilibrium is unclear at present, however. In the case of carbon isotopes, the relationship between the isotope fractionation factor and the Mg concentration of calcite is currently poorly defined ($r^2 = 0.29$; Jimenez-Lopez et al., 2006). For oxygen isotope ratios, the most recent calibration is derived from a best-fit line through an array of data that have been recalculated according to their Mg concentrations (Brand et al., 2013). While incorporating experimental data on effects of Mg on calcite precipitation (Jimenez-Lopez et al., 2004), this approach does not take information from established calcite precipitation experiments into account. The resulting slope of the fit (~3.5°C per ‰, Brand et al., 2013) indeed differs significantly from slopes constrained by inorganic precipitation experiments of Mg-free calcite in the relevant temperature range (4.4-4.6°C per ‰; O'Neil et al., 1969; Kim and O'Neil, 1997). This discrepancy remains unresolved at present.

Significant differences between $\delta^{13}C$ values in multiple valves from the two deep-sea species collected during the same dredge from Walvis Ridge (+0.7 to +1.5 ‰ *C. racovitzae*; +1.8 to +2.4 ‰ *S. crosnieri*, Fig. 1) cannot easily be reconciled in the framework of equilibrium precipitation. If applied, a Mg correction of $\delta^{13}C$ of these two species would even slightly increase this disagreement. Minor isotopic disequilibrium of C and O isotope ratios (-1 ‰ to +1 ‰) is thus indicated for *C. racovitzae* and *S. crosnieri*, where the very positive oxygen isotope ratios in these species might be related to slow precipitation rates (cf. Takayanagi et al., 2015).

Overall, strong vital effects, however, seem to be a more common feature in the order

Terebratulida, in particular in the suborder Terebratellidina (Fig. 4).

4.2 Element/Ca ratios

4.2.1 Intra-shell variability of element/Ca ratios

Unsoluble organic matter in biogenic carbonate which has not or cannot be removed before sampling can contain extreme element/Ca ratios (Schöne et al., 2010) and is therefore potentially of concern for the results presented here. Element concentrations within this organic matter, however are expected to be too low to dictate the observed elemental heterogeneity: organic matter contents on the order of 50 % would be required to shift Mg/Ca ratios by ca. 1 mmol/mol and Sr concentrations are even less sensitive to organic matter admixture (Schöne et al., 2010, see also Watanabe et al., 2001).

Relatively large intraspecimen heterogeneity of biogenic calcite is a common phenomenon and for alkaline earth elements it is usually Mg that shows the more pronounced variability (Table 3). With respect to intra-specimen variability of element/Ca ratios modern brachiopods are comparable to other calcifying species and such variability should thus not be viewed as atypical.

Even larger heterogeneity is to be expected when analysing specimens from a variety of localities with a wider range of physical conditions and species assemblages than are covered by the current dataset. The data presented here furthermore relates to shell splinters of ca. 1 mm^3, which will not capture some of the heterogeneity associated with functional morphology (Parkinson et al., 2005) and specific portions of the different shell layers of brachiopods (Cusack et al., 2008a,b). The sampling approach adopted here, however, directly relates to commonly employed sampling protocols for studies on fossil materials, ensuring direct comparability of the analytical results.

4.2.2 Phylogenetic control on Mg/Ca and Sr/Ca

Even though the dataset for the chemical composition of modern brachiopod species is still sparse – especially the craniids and rhynchonellids require further study – a general pattern of shell geochemistry in brachiopods is emerging (Fig. 3). Average Sr/Ca and Mg/Ca ratios provide further evidence for a chemical divide between terebratulids and rhynchonellids on the one hand and thecideids and craniids on the other. The former comprise mostly low Mg calcite whereas the latter all form high Mg calcite shells. Most terebratulids and rhynchonellids fall below the trend line for Mg and Sr ratios in biogenic calcite proposed by Carpenter and Lohmann (1992) with some species showing very low Sr/Ca and Mg/Ca ratios approaching the composition of abiogenic calcite (Fig. 3). Nearly all of these species characterized by particularly low Sr/Ca ratios are part of the suborder Terebratulidina, but also one deep-sea rhynchonellid shows this pattern. Within the order Terebratulina, the terebratulidinids exhibit a trend towards higher Mg/Ca ratios than the terebratellidinids, the latter showing average Mg/Ca ratios > 20 mmol/mol only in the specimen of *F. sanguinolenta* analysed in the present study.

4.2.3 Controls on Mn/Ca and Fe/Ca ratios

Mn and Fe concentrations in fossil shell calcite are most commonly employed to gauge the preservation of palaeoenvironmental proxies, because the concentrations of these elements are often found to be elevated in altered fossil specimens (e.g., Ullmann and Korte, 2015 for a review). Usually, modern analogue Mn and Fe concentrations (e.g., Brand et al., 2003) are used to inform these preservation limits. Appraising covariation of element and isotope proxies in conjunction with an assessment of the depositional and diagenetic environments, however, is necessary to understand primary and diagenetic trends in fossil datasets. A variety of Mn-Fe trends and substantial intra-specimen heterogeneity are observed in the present dataset, where specimens from the Chatham Rise (*L. neozelanica*) and Walvis Ridge (S. crosnieri, *C. racovitzae*) show elevated Fe/Ca ratios but very little Mn (Fig. 5). The specimen of *M. venosa* from the South American shelf, on the other hand incorporated nearly equal amounts of Fe and Mn and *T. transversa* from Friday Harbor shows an intermediate trend between these extremes. (Fig. 5).

Table 3: Average intra-specimen variability of Mg/Ca and Sr/Ca ratios (2 relative standard deviations; rsd) in various calcite secreting species.

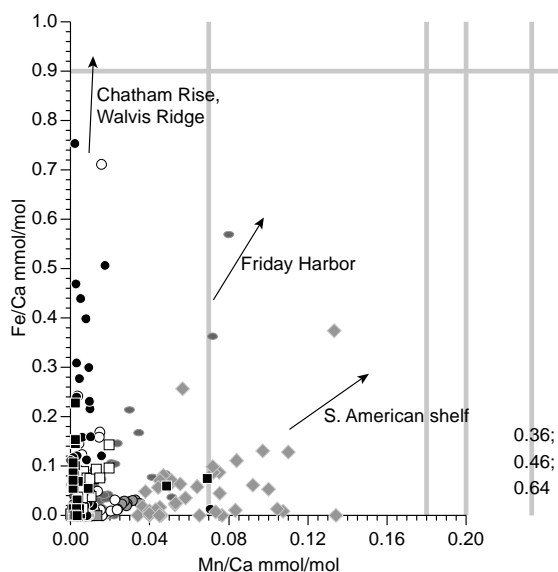| Phylum	Order	Species	Mg/Ca 2 rsd (%)	Sr/Ca 2 rsd (%)	source
Mollusca	Ostreida	*Pinna nobilis*	18	15	Freitas et al., 2005
Mollusca	Ostreoida	*Crassostrea gigas*	32	10	Almeida et al., 1998
Mollusca	Pectinata	*Pecten maximus*	58	25	Freitas et al., 2016
Mollusca	Belemnitida	*Passaloteuthis bisulcata*	24	18	Ullmann et al., 2015
Mollusca	Belemnitida	*Belemnellocamax mammillatus*	16	13	Sørensen et al., 2015
Echinodermata	Forcipulatida	*Asterias rubens*	13	3	Borremans et al., 2009
Echinodermata	Clypeasteroida	*Dendraster excentricus*	8	6	Pilkey and Hower, 1960

Fig. 5: Crossplot of Fe/Ca ratios and Mn/Ca ratios in the analysed specimens. Arrows indicate tentative element trends in brachiopods at the studied localities. For legend of the symbols, see Figure 2. Vertical grey bars denote limiting Mn/Ca and Fe/Ca ratios employed in the literature for culling altered samples from fossil brachiopod datasets (Ullmann and Korte, 2015 and references therein).

Substantial intra-specimen variability observed here could potentially be mistaken for differential preservation, if only Mn and Fe as alteration proxies are employed. Additionally, different species from the same locality show different Mn/Ca and Fe/Ca patterns, which may in part relate to the sampled shell portions (inner surface, secondary layer, amount of organic matter present). Species-specific diagenetic enrichments of Mn, however, have been observed (Harlou et al., 2016), suggesting that Mn enrichment may be driven by shell ultrastructure as well.

Besides its use as marker for diagenesis, Mn has been inferred to respond to a variety of environmental influences, e.g., water depth in the tidal zone (Bourget, 1974), shore line proximity and infections of the shell forming animal (Almeida et al., 1998), freshwater and nutrient supply (Lazareth et al., 2003). Such proxies employing the very short oceanic residence time of Mn (Li, 1982) may become interesting to understand depositional environments in deep time, warranting further study of the distribution of Mn and Fe in extant species.

4.3. Covariation of isotope and element ratios
Element concentration data for brachiopod calcite are used mostly for addressing questions of biomineralization in modern species (e.g., Cusack et al., 2008b; Pérez-Huerta et al., 2008). Palaeo-environmental studies on the other hand almost exclusively use these data to control

sample preservation (see Ullmann and Korte, 2015 for a review). Only very few studies have attempted to use the chemical information retrieved from brachiopod calcite to infer the composition of past seawater (Steuber and Veizer, 2002; Ullmann et al., 2016) and very little is known about the covariation of $\delta^{13}C$ and $\delta^{18}O$ values with element/Ca ratios in brachiopod calcite.

Geochemical profiles through three specimens, where 20 or more samples could be collected from a single shell, are presented in Figure 6. Approximate ages for the studied specimens were derived from the respective von Bertalanffy growth curves (von Bertalanffy, 1934, 1938) for these species (Paine (1969) for T. transversa; Baird et al. (2013) for *L. neozelanica*; Baumgarten et al. (2014) for *M. venosa*). The profiles lack a clear expression of seasonality, in part because of little seasonal change in ambient conditions (*L. neozelanica*). More importantly it was not always possible to sample secondary shell material from the same depth within the shell throughout the transects, such that no strict chronological order of the samples can be assumed. Strong geochemical heterogeneity throughout the transect and covariation of Sr/Ca with isotopic proxies (Fig. 6) are especially clear for *M. venosa*, which grows comparatively fast and is the largest known modern brachiopod (Baumgarten et al., 2014).

4.4. Sr as a monitor for growth rate and isotopic disequilibrium?
A positive relationship between precipitation rate and Sr concentration in calcite is well-established from abiogenic precipitation experiments (Lorens, 1981; Tesoriero and Pankow, 1996; Gabitov and Watson, 2006; Tang et al., 2008; Gabitov et al., 2014) and theoretical considerations (DePaolo, 2011; Gabitov et al., 2014). Also for biogenic calcite such a relationship has been proposed, e.g. for bivalves (Richardson et al., 2004; Lorrain et al., 2005), belemnites (Ullmann et al., 2015), coccoliths (Stoll and Schrag, 2000) and foraminifers (Lea et al., 1999; Kisakürek et al., 2008). It is therefore probable that also brachiopods may show growth rate-related enrichments in Sr.

Sr/Ca ratios in the brachiopods shells are indeed particularly high where low $\delta^{13}C$ and $\delta^{18}O$ ratios indicate growth rate-induced kinetic isotope effects (*M. venosa*, *T. transversa*, Fig. 2). In the near-shore settings, Sr/Ca and $\delta^{13}C$ data show a similar pattern with *N. nigricans* lower in Sr/Ca and higher in $\delta^{13}C$ than *C. inconspicua* from the same locality and Friday Harbor data of Terebratulina sp. overlapping with *T. transversa* (Fig. 2). Also in the deep-water sites such a trend

is indicated. *L. neozelanica* (water depth ~ 500m) shows a negative correlation of $\delta^{13}C$ with Sr/Ca ratios and at Walvis Ridge (water depth $\sim 1,600$ m) *S. crosnieri* has much lower Sr/Ca and higher $\delta^{13}C$ than *C. racovitzae*.

In addition to already established controls on $\delta^{13}C$ and $\delta^{18}O$ values (e.g., Carpenter and Lohmann, 1995; Auclair et al., 2003; Parkinson et al., 2005) also Sr/Ca ratios in the shell material therefore seem to respond to metabolic processes, potentially tracking growth rate.

The resulting negative correlation of Sr/Ca ratios with $\delta^{13}C$ values opposes a generally observed positive correlation of these proxies related to diagenesis (e.g., Brand and Veizer, 1981; Ullmann and Korte, 2015). It may thus be possible to use this relationship in fossil brachiopod samples to address disequilibrium isotope incorporation in the shell calcite, where the samples with lowest Sr/Ca ratios and highest $\delta^{13}C$ values would be most likely to reflect the palaeoenvironmental signal.
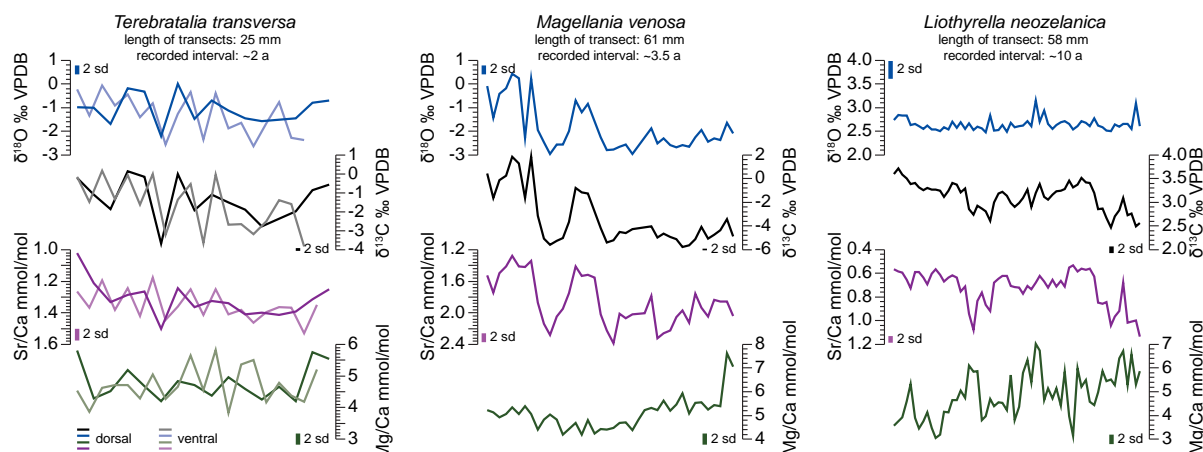

Fig. 6. Geochemical transects through three brachiopod species for which profiles of at least 20 samples could be prepared. The direction is from umbo (left) to margin (right).

Conclusions

Combined $\delta^{13}C$ values, $\delta^{18}O$ values, Mg/Ca, Sr/Ca, Mn/Ca and Fe/Ca ratio measurements are presented for nine modern brachiopod species of the orders Rhynchonellida and Terebratulida.

Isotopic signals of most brachiopod materials indicate formation of the studied shell calcite in or near isotopic equilibrium, but partly strong disequilibrium signals are observed in brachiopods of the suborder Terebratellidina.

All studied terebratulids and rhynchonellids comprise low-Mg calcite, with strong correlations of Mg/Ca ratios with Sr/Ca ratios restricted to rhynchonellid species and possibly one terebratulid (*F. sanguinolenta*).

A negative correlation of Sr/Ca ratios with δ13C is recorded in multiple species and localities where partial isotopic disequilibrium in the shell calcite is indicated. This relationship may find future use in fossil materials for more robust reconstruction of $\delta^{13}C$ values of DIC in past seawater.

References

Al-Aasm, I., Veizer, J., 1986. Diagenetic stabilization of aragonite and low-Mg calcite, I. Trace elements in rudists. Journal of Sedimentary Petrology 56 (1), 138-152.

Almeida, M.J., Machado, J., Moura, G., Azevedo, M., Coimbra, J., 1998. Temporal and local variations in biochemical composition of Crassostrea gigas shells. Journal of Sea Research 40, 233–249.

Anderson, T.F., Arthur, M.A., 1983. Stable isotopes of oxygen and carbon and their application to sedimentologic and

palaeoenvironmental problems, Society of Economic Paleontologists and Mineralogists Short Course 10, I.1-I-151.

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

Baird, M.J., Lee, D.E., Lamare, M.D., 2013. Reproduction and growth of the terebratulid brachiopod Liothyrella neozelanica Thomson, 1918 from Doubtful Sound, New Zealand. Biol. Bull. 225, 125-136.

Baumgarten, S., Laudien, J., Jantzen, C., Häussermann, V., Försterra, G., 2014. Population structure, growth and production of a recent brachiopod from the Chilean fjord region. Marine Ecology 35, 401-413. doi: 10.1111/maec.12097.

Bell, D.B., Jung, S.J.A., Kroon, D., 2015. The Plio-Pleistocene development of Atlantic deep-water circulation and its influence on climate trends. Quaternary Science Reviews 123, 265-282. doi: 10.1016/j.quascirev.2015.06.026.

Bickert, T., Pätzold, J., Samtleben, C., Munnecke, A., 1997. Paleoenvironmental changes in the Silurian indicated by stable isotopes in brachiopod shells from Gotland, Sweden. Geochimica et Cosmochimica Acta 61 (13), 2717-2730.

Bigg, G.R., Rohling, E.J., 2000. An oxygen isotope data set for marine waters. Journal of Geophysical Research 105, 8527-8535.

Borremans, C., Hermans, J., Baillon, S., André, L., Dubois, P., 2009. Salinity effects on the Mg/Ca and Sr/Ca in starfish skeletons and the echinoderm relevance for paleoenvironmental reconstructions. Geology 37 (4), 351–354. doi:10.1130/G25411A.1.

Bourget, E., 1974. Environmental and structural control of trace elements in barnacle shells. Marine Biology 28, 27–36.

Brand, U., Veizer, J., 1980. Chemical diagenesis of a multicomponent carbonate system-1: Trace elements. Journal of Sedimentary Petrology 50 (4), 1219–1236.

Brand, U., Veizer, J., 1981. Chemical diagenesis of a multicomponent carbonate system-2: stable isotopes. Journal of Sedimentary Petrology 51 (3), 987-997.

Brand, U., Logan, A., Hiller, N., Richardson, J., 2003. Geochemistry of modern brachiopods: applications and implications for oceanography and paleoceanography. Chemical Geology 198, 305–334.

Brand, U., Azmy, K., Bitner, M.A., Logan, A., Zuschin, M., Came, R., Ruggiero, E., 2013. Oxygen isotopes and MgCO3 in brachiopod calcite and a new paleotemperature equation. Chemical Geology 359, 23–31.

Brand, U., Azmy, K., Griesshaber, E., Bitner, M.A., Logan, A., Zuschin, M., Ruggiero, E., Colin, P.L., 2015. Carbon isotope composition in modern brachiopod calcite: A case of equilibrium with seawater? Chemical Geology 411, 81-96. doi: 10.1016/j.chemgeo.2015.06.021.

Butler, S., Bailey, T.R., Lear, C.H., Curry, G.B., Chems, L., McDonald, I., 2015. The Mg/Ca-temperature relationship in brachiopod shells: Calibrating a potential palaeoseasonality proxy. Chemical Geology 397, 106–117.

Carpenter, S.J., Lohmann, K.C., 1992. Sr/Mg ratios of modern marine calcite: Empirical indicators of ocean chemistry and precipitation rate. Geochimica et Cosmochimica Acta 56, 1837–1849.

Carpenter, S.J., Lohmann, K.C., 1995. δ18O and δ13C values of modern brachiopod shells. Geochimica et Cosmochimica Acta 59 (18), 3749–3764.

Chiswell, S.M., 1994. Variability in sea surface temperature around New Zealand from AVHRR images. New Zealand Journal of Marine and Freshwater Research 28 (2), 179–192.

Coplen, T.B., 2007. Calibration of the calcite-water oxygen-isotope geothermometer at Devils Hole, Nevada, a natural laboratory. Geochimica et Cosmochimica Acta 71, 3948-3957. doi: 10.1016/j.gca.2007.05.028.

Craig, H., 1965. The measurement of oxygen isotope paleotemperatures. In: Tongiorgi, E. (Ed.), Stable Isotopes in Oceanographic Studies and Paleotemperatures. Consiglio Nazionale delle Ricerche Laboratorio di Geologia Nucleare, Pisa, pp. 161–182.

Cusack, M., Pérez-Huerta, A., Janousch, M., Finch, A.A., 2008a. Magnesium in the lattice of calcite-shelled brachiopods. Chemical Geology 257, 59–64.

Cusack, M., Dauphin, Y., Cuif, J.-P., Salomé, M., Freer, A., Yin, H., 2008b. Micro-XANES mapping of sulphur and its association with magnesium and phosphorus in the shell of the brachiopod, Terebratulina retusa. Chemical Geology 253, 172-179.

Cusack, M., Pérez-Huerta, A., EIMF, 2012. Brachiopods recording seawater temperature – A matter of class or maturation? Chemical Geology 334, 139-143. doi: 10.1016/j.chem.geo.2012.10.021.

DePaolo, D.J., 2011. Surface kinetic model for isotopic and trace element fractionation during precipitation of calcite from aqueous solution. Geochimica et Cosmochimica Acta 75, 1039-1056. doi: 10.1016/j.gca.2010.11.020.

Epstein, S., Buchsbaum, R., Lowenstam, H.A., Urey, H.C., 1953. Revised carbonate-water isotopic temperature scale. Bulletin of the Geological society of America 64, 1315-1326.

Freitas, P., Clarke, L., Kennedy, H., Richardson, C., Abrantes, F., 2005. Mg/Ca, Sr/Ca, and stable-isotope (δ18O and δ13C) ratio profiles from the fan mussel Pinna nobilis: Seasonal records and temperature relationships. Geochemistry Geophysics Geosystems 6 (4), Q04D14. doi: 10.1029/2004GC000872.

Freitas, P.S., Clarke, L.J., Kennedy, H., Richardson, C.A., Abrantes, F., 2006. Environmental and biological controls on elemental (Mg/Ca, Sr/Ca and Mn/Ca) raios in the shells of the king scallop Pecten maximus. Geochimica et Cosmochimica Acta 70, 5119–5133. doi: 10.1016/j.gca.2006.07.029.

Gabitov, R.I., Watson, E.B., 2006. Partitioning of strontium between calcite and fluid. Geochemistry, Geophysics, Geosystem 7 (11), Q11004. doi: 10.1029/2005GC001216.

Gabitov, R.I., Sadekov, A., Leinweber, A., 2014. Crystal growth rate effect on Mg/Ca and Sr/Ca partitioning between calcite and fluid: An in situ approach. Chemical Geology 367, 70-82. doi: 10.1016/j.chemgeo.2013.12.019.

Griesshaber, E., Schmahl, W., Neuser, R., Pettke, T., Blüm, M., Mutterlose, J., Brand, U., 2007. Crystallographic texture and microstructure of terebratulide brachiopod shell calcite: An optimized materials design with hierarchical architecture. American Mineralogist 92, 722-734.

Grossman, E.L., Mii, H.-S., Yancey, T.E., 1993. Stable isotopes in Late Pennsylvanian brachiopods from the United States: Implications for Carboniferous paleoceanography. Geological Society of America Bulletin 105, 1284-1296.

Harlou, R., Ullmann, C.V., Korte, C., Lauridsen, B.W., Schovsbo, N.H., Surlyk, F., Thibault, N., Stemmerik, L., 2016. Geochemistry of Campanian-Maastrichtian brachiopods from the Rørdal-1 core (Denmark): Differential responses to environmental change and diagenesis. Chemical Geology 442, 35–46. doi:10.1016/j.chemgeo.2016.08.039.

Heath, R.A., 1980. Oceanic fronts around southern New Zealand. Deep-Sea Research 28A (6), 547–560.

Imai, N., Terashima, S., Itoh, S., Ando, A., 1996. 1996 compilation of analytical data on nine GSJ geochemical reference samples, "Sedimentary Rock Series". Geostandards Newsletter 20 (2), 165-216.

Jean, C.B., Kyser, T.K., James, N.P., Stokes, M.D., 2015. The Antarctic brachiopod Liothyrella uva as a proxy for ambient oceanographic conditions at McMurdo Sound.

Journal of Sedimentary Research 85, 1492-1509. doi: 10.2110/jsr.2015.94.

Jiménez-López, C., Romanek, C.S., Huertas, F.J., Ohmoto, H., Caballero, E., 2004. Oxygen isotope fractionation in synthetic magnesian calcite. Geochimica et Cosmochimica Acta 68 (16), 3367-3377.

Jiménez-López, C., Romanek, C.S., Caballero, E., 2006. Carbon isotope fractionation in synthetic magnesian calcite. Geochimica et Cosmochimica Acta 70, 1163-1171. doi: 10.1016/j.gca.2005.11.005.

Lazareth, C.E., Vander Putten, E., André, L., Dehairs, F., 2003. High-resolution trace element profiles in shells of the mangrove bivalve Isognomon ephippium: a record of environmental spatio-temporal variations? Estuarine, Coastl and Shelf Science 57, 1103–1114.

Lea, D.W., Mashiotta, T.A., Spero, H.J., 1999. Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing. Geochimica et Cosmochimica Acta 63 (16), 2369-2379.

Lee, X., Hu, R., Brand, U., Zhou, H., Liu, X., Yuan, H., Yan, C., Cheng, H., 2004. Ontogenetic trace element distribution in brachiopod shells: an indicator of original seawater chemistry. Chemical Geology 209, 49-65. doi: 10.1016/j.chemgeo.2004.04.029.

Leng, M.J., Marshall, J.D., 2004. Palaeoclimate interpretation of stable isotope data from lake sediment archives. Quat. Sci. Rev. 23, 811–831.

Li, Y.-H., 1982. A brief discussion on the mean oceanic residence time of elements. Geochimica et Cosmochimica Acta 46, 2671–2675.

Lorens, R.B., 1981. Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite precipitation rate. Geochimica et Cosmochimica Acta 45, 553-561.

Lorrain, A., Gillikin, D.P., Paulet, Y.-M., Chauvaud, L., Mercier, A.L., Navez, J., André, L., 2005. Strong kinetic effects on Sr/Ca ratios in the calcitic bivalve Pecten maximus. Geology 33 (12), 965-968. doi: 10.1130/G22048.1.

Lowenstam, H.A., 1961. Mineralogy, O18/O16 ratios, and strontium and magnesium contents of recent and fossil brachiopods and their bearing on the history of the oceans. The Journal of Geology 69 (3), 241-260.

Kim, S.-T., O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. Geochimica et Cosmochimica Acta 61 (16), 3461-3475.

Kisakürek, B., Eisenhauer, A., Böhm, F., Garbe-Schönberg, D., Erez, J., 2008. Controls on shell Mg/Ca and Sr/Ca in cultured planktonic foraminiferan, Globigerinoides ruber (white). Earth and Planetary Science Letters 273, 260-269. doi: 10.1016/j.epsl.2008.06.026.

Korte, C., Jones, P.J., Brand, U., Mertmann, D., Veizer, J., 2008. Oxygen isotope values from high-latitudes: Clues for Permian sea-surface temperature gradients and Late Palaeozoic deglaciation. Palaeogeography, Palaeoclimatology, Palaeoecology 269, 1–16.

Kroopnick, P., 1980. The distribution of 13C in the Atlantic Ocean. Earth and Planetary Science Letters 49, 469–484.

McCammon, H.M., 1973. The ecology of Magellania venosa, and articulate brachiopod. Journal of Paleontology 47 (2), 266-278.

Morrison, J.O., Brand, U., 1986. Paleoscene #5. Geochemistry of recent marine invertebrates. Geoscience Canada 13 (4), 237-254.

Mulitza S., Donner B., Fischer G., Paul A., Pätzold J., Rühlemann C., Segl M., 2003. The South Atlantic oxygen isotope record of planktic foraminifera. In The South Atlantic in the Late Quaternary: Reconstruction of Material budgets and Current Systems (eds. G. Wefer, S. Mulitza and V. Ratmeyer). Springer-Verlag, Berlin, pp. 121–142.

O'Neil, J.R., Clayton, R.N., Mayeda, T.K., 1969. Oxygen isotope fractionation in divalent metal carbonates. The Journal of Chemical Physics 51 (12), 5547-5558.

Paine, R.T., 1969. Growth and size distribution of the brachiopod Terebratalia transversa Sowerby. Pacific Science 23, 337-343.

Parkinson, D., Curry, G.B., Cusack, M., Fallick, A.E., 2005. Shell structure, patterns and trends of oxygen and carbon stable isotopes in modern brachiopod shells. Chemical Geology 219, 193–235.

Pérez-Huerta, A., Cusack, M., Jeffries, T.E., Williams, C.T., 2008. High resolution distribution of magnesium and strontium and the evaluation of Mg/Ca thermometry in recent brachiopod shells. Chemical Geology 247, 229–241.

Pilkey, O.H., Hower, J., 1960. The effect of environment on the concentration of skeletal magnesium and strontium in Dendraster. The Journal of Geology 68 (2), 203–214.

Popp, B.N., Anderson, T.F., Sandberg, P.A., 1986. Brachiopods as indicators of original isotopic compositions in some Paleozoic limestones. Geological Society of America Bulletin 97, 1262–1269.

Rahimpour-Bonab, H., Bone, Y., Moussavi-Harami, R., 1997. Stable isotope aspects of modern molluscs, brachiopods, and marine cements from cool-water carbonates, Lacepede Shelf, South Australia. Geochimica et Cosmochimica Acta 61 (1), 207-218.

Raitzsch, M., Kuhnert, H., Groeneveld, J., Bickert, T., 2008. Benthic foraminifer Mg/Ca anomalies in south Atlantic core top sediments and their implications for paleothermometry. Geochemistry Geophysics Geosystems 9 (5), Q05010. doi: 10.1029/2007GC001788.

Rasmussen, C.M.Ø., Ullmann, C.V., Jakobsen, K.G., Lindskog, A., Hansen, J., Hansen, T., Eriksson, M.E., Dronov, A., Frei, R., Korte, C., Nielsen, A.T., Harper, D.A.T., 2016. Onset of main Phanerozoic marine radiation sparked by emerging Mid Ordovician icehouse. Scientific Reports 6:18884. doi:10.138/srep18884.

Richardson, C.A., Peharda, M., Kennedy, H., Kennedy, P., Onofri, V., 2004. Age, growth rate and season of recruitment of Pinna nobilis (L) in the Croatian Adriatic determined from Mg:Ca and Sr:Ca shell profiles. Journal of Experimental Marine Biology and Ecology 299, 1-16. 10.1016/j.jembe.2003.08.012.

Schöne, B.R., Zhang, Z., Jacob, D., Gillikin, D.P., Tütken, T., Garbe-Schönberg, D., McConnaughey, T., Soldati, A., 2010. Effect of organic matrices on the determination of the trace element chemistry (Mg, Sr, Mg/Ca, Sr/Ca) of aragonite bivalve shells (Arctica islandica) – comparison of ICP-OES and LA-ICP-MS data. Geochemical Journal 44, 23–37.

Steuber, T., Veizer, J., 2002. Phanerozoic record of plate tectonic control of seawater chemistry and carbonate sedimentation. Geology 30, 1123–1126.

Stoll, H.M., Schrag, D.P., 2000. Coccolith Sr/Ca as a new indicator of coccolithophorid calcification and growth rate. Geochemistry, Geophysics, Geosystems 1 (10), 1006. doi: 10.1029/1999GC000015.

Sutherland, D.A., MacCready, P., Banas, N.S., Smedstad, L.F., 2011. A model study of the Salish Sea estuarine circulation. Journal of Physical Geography 41, 1125–1143. doi: 10.1175/2011JPO4540.1.

Sørensen, A.M., Ullmann, C.V, Thibault, N., Korte, C., 2015. Geochemical signatures of the early Campanian belemnite Belemnellocamax mammillatus from the Kristianstad Basin in Scania, Sweden. Palaeogeography, Palaeoclimatology, Palaeoecology 433, 191–200. doi: 10.1016/j.palaeo.2015.05.025.

Takayanagi, H., Asami, R., Abe, O., Kitagawa, H., Miyajima, T., Iryu, Y., 2012. Carbon- and oxygen-isotope compositions of a modern deep-water brachiopod Campagea japonica collected off Aguni-jima, Central Ryukyu Islands, southwestern Japan. Geochemical Journal 46, 77-87.

Takayanagi, H., Asami, R., Abe, O., Miyajima, T., Kitagawa, H., Sasaki, K., Iryu, Y., 2013. Intraspecific variations in carbon-isotope and oxygen-isotope compositions of a brachiopod Basiliola lucida collected off Okinawa-jima, southwestern Japan. Geochimica et Cosmochimica Acta 115, 115-136.

Takayanagi, H., Asami, R., Otake, T., Abe, O., Miyajima, T., Kitagawa, H., Iryu, Y., 2015. Quantitative analysis of

intraspecific variations in the carbon and oxygen isotope compositions of the modern cool-temperate brachiopod Terebratulina crossei. Geochimica et Cosmochimica Acta 170, 301-320. doi: 10.1016/j.gca.2015.08.006.

Tang, J., Köhler, S.J., Dietzel, M., 2008. Sr2+/Ca2+ and 44Ca/40Ca fractionation during inorganic calcite formation: I. Sr incorporation. Geochimica et Cosmochimica Acta 72, 3718-3732. doi: 10.1016/j.gca.2008.05.031.

Tesoriero, A.J., Pankow, J.f., 1996. Solid solution partitioning of Sr2+, Ba2+, and Cd2+ to calcite. Geochimica et Cosmochimica Acta 60 (6), 1053-1063.

Ullmann, C.V., Korte, C., 2015. Diagenetic alteration in low-Mg calcite from macrofossils: a review. Geological Quarterly 59 (1), 3–20.

Ullmann, C.V., Campbell, H.J., Frei, R., Hesselbo, S.P., Pogge von Strandmann, P.A.E., Korte, C., 2013. Partial diagenetic overprint of Late Jurassic belemnites from New Zealand: Implications for the preservation potential of δ7Li values in calcite fossils. Geochimica et Cosmochimica Acta 120, 80-96.

Ullmann, C.V., Thibault, N., Ruhl, M., Hesselbo, S.P., Korte, C., 2014. Effect of a Jurassic oceanic anoxic event on belemnite ecology and evolution. PNAS 111, 10073-10076. doi: 10.1073/pnas.1320156111.

Ullmann, C.V., Frei, R., Korte, C., Hesselbo, S.P., 2015. Chemical and isotopic architecture of the belemnite rostrum. Geochimica et Cosmochimica Acta 159, 231-243. doi: 10.1016/j.gca.2015.03.034.

Ullmann C.V., Campbell, H.J., Frei, R., Korte, C., 2016. Oxygen and carbon isotope and Sr/Ca signatures of high-latitude Permian to Jurassic calcite fossils from New Zealand and New Caledonia. Gondwana Research 38, 60-73. doi: 10.1016/j.gr.2015.10.010.

Veizer, J., 1983. Chapter 3. Chemical diagenesis of carbonates: Theory and application of trace element technique. In: Stable isotopes in sedimentary geology. SEPM Short Course Notes 10, 1983, 3-1-3-100. doi: 10.2110/scn.83.01.0000.

Veizer, J., Ala, D., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Carden, G.A.F., Diener, A., Ebneth, S., Godderis, Y., Jasper, T., Korte, C., Pawellek, F., Podlaha, O.G., Strauss, H., 1999. 87Sr/86Sr, δ13C and δ18O evolution of Phanerozoic seawater. Chemical Geology 161, 59–88.

von Bertalanffy, L., 1934. Untersuchungen über die Gesetzlichkeit des Wachstums. I. Teil: Allgemeinde Grundlage der Theorie; mathematische und physiologische Gesetzlichkeiten des Wachstums bei Wassertieren. Development Genes and Evolution 131 (4), 613-652.

von Bertalanffy, L., 1938. A quantitative theory of organic growth (inquiries on growth laws. II). Human Biology 10 (2), 181-213.

Watanabe, T., Minagawa, M., Oba, T., Winter, A., 2001. Pretreatment of coral aragonite for Mg and Sr analysis: Implications for coral thermometers. Geochemical Journal 35, 265–269.

Yamamoto, K., Asami, R., Iryu, Y., 2010a. Within-shell variations in carbon and oxygen isotope compositions of two modern brachiopods from a subtropical shelf environment off Amami-o-shima, southwestern Japan. Geochemistry, Geophysics, Geosystems 11(10), 1–16.

Yamamoto, K., Asami, R., Iryu, Y., 2010b. Carbon and oxygen isotopic compositions of modern brachiopod shells from a warm-temperature shelf environment, Sagami Bay, central Japan. Palaeogeography, Palaeoclimatology, Palaeoecology 291, 348-359. doi: 10.1016/j.palaeo.2010.03.006.

Yamamoto, K., Asami, R., Iryu, Y., 2011. Brachiopod taxa and shell portions reliably recording past ocean environments: Toward establishing a robust paleoceanographic proxy. Geophysical Research Letters 38, 1–5.