

## BRACHIOPOD-BASED OXYGEN-ISOTOPE THERMOMETER: UPDATE AND REVIEW

UWE BRAND<sup>1\*</sup>, M. ALEKSANDRA BITNER<sup>2</sup>, ALAN LOGAN<sup>3</sup>, KAREM AZMY<sup>4</sup>, GAIA CRIPPA<sup>5</sup>,  
LUCIA ANGIOLINI<sup>5</sup>, PATRICK COLIN<sup>6</sup>, ERIKA GRIESSHABER<sup>7</sup>, ELIZABETH M. HARPER<sup>8</sup>,  
EMMA TADDEI RUGGIERO<sup>9</sup> & VRENI HÄUSSERMANN<sup>10</sup>

<sup>1\*</sup>Corresponding author: Department of Earth Sciences, Brock University, 1812 Sir Isaac Brock Way, St. Catharines, Ontario L2S3A1 Canada.  
E-mail: ubrand@brocku.ca

<sup>2</sup>Institute of Paleobiology, Polish Academy of Science, Twarda 51/55, 00-818 Warsaw, Poland

<sup>3</sup>Centre for Coastal Studies, University of New Brunswick, Saint John, New Brunswick E2L 4L5, Canada

<sup>4</sup>Department of Earth Sciences, Memorial University of Newfoundland, St. John's, Newfoundland A1B3X5, Canada

<sup>5</sup>Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano, Via Mangiagalli 34, 20133 Milano, Italy

<sup>6</sup>Coral Reef Research Foundation, P.O. Box 1765, Koror 96940, Palau

<sup>7</sup>Department of Earth and Environmental Sciences, Ludwig-Maximilians-Universität München, Theresienstr. 41, 80333 Munich, Germany

<sup>8</sup>Department of Earth Sciences, University of Cambridge, Cambridge, U.K.

<sup>9</sup>Dipartimento di Scienze della Terra, Università di Napoli Federico II, 801380 Napoli, Italy

<sup>10</sup>Pontificia Universidad Católica de Valparaíso, Facultad de Recursos Naturales, Escuela de Ciencias del Mar, Avenida Brasil, 2950, Valparaíso, Chile & Huinay Scientific Field Station, Puerto Montt, Chile

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*Abstract.* In the early 1950's, McCrea and Epstein and co-workers laid the foundation for the oxygen isotope-based thermometers. Many variations of the thermometer have been since formulated based on synthetic and biogenic carbonates. Overall, the use and application of oxygen isotope thermometers must consider and be specific as to the mineralogy, and whether it is synthetic, abiogenic, abiogenic or biogenic carbonate.

Here, we propose an updated and refined oxygen-isotope thermometer based on a large database of articulated brachiopods from high to low latitudes, cold to warm and shallow to deep-water regimes. In general, brachiopod-based oxygen isotopes are offset from abiogenic calcite precipitated in thermodynamic equilibrium by about -1 ‰. They maintain this offset and that allows for the determination of robust ambient water temperatures over the full marine spectrum. Thus, the specific brachiopod-based oxygen-isotope thermometer applies, with few exceptions, to most modern articulated brachiopods, and potentially their ancient counterparts, and it is as follows:

$$T^{\circ}\text{C} = 17.3750 - 4.2535 (\delta\text{c}-\delta\text{w}) + 0.1473 (\delta\text{c}-\delta\text{w})^2 \quad (\text{N}=578, r^2 = 0.980)$$

Furthermore, it is imperative that mineralogy and taxa be considered for their appropriateness in the application of oxygen isotope thermometers on synthetic, abiogenic and biogenic marine carbonates. Articulated brachiopods are ideal recorders of oceanographic parameters due to their sessile nature, widespread distribution, high abundance in the Paleozoic and Mesozoic, high resilience to most environmental stresses (e.g., climate change - global warming, ocean acidification), and the resistance of the calcite shell - the archive - to post-depositional diagenetic alteration.

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## INTRODUCTION

In 1950, McCrea published a paper on the first oxygen isotope - water temperature relationship based on synthetically precipitated calcite. The idea followed the natural progressing of the principles on stable isotope geochemistry outlined by Urey (1947). His study was followed in quick succession by the paper of Epstein *et al.* (1951) and the presentation of another oxygen isotope thermometer, but this one was based on well-constrained biogenic carbonates and their ambient seawater temperatures. This study included brachiopods, bivalves, and gastropods from environments with detailed information of water temperature and oxygen isotope composition. In their follow-up study (Epstein *et al.* 1953), the authors dropped the brachiopods from their investigation of marine biogenic carbonates, instead relying mostly on mollusc material. It was not until the 1980's, when the study by Lowenstam (1961) on modern brachiopods and their shell geochemistry sparked renewed interest in this group of marine organisms (Morrison & Brand 1986). He proposed that brachiopods incorporate oxygen isotopes into shell carbonate in equilibrium with ambient seawater. Subsequently, it was realized that there may be differences in carbon and oxygen isotope compositions between aragonite and calcite (e.g., Tarutani *et al.* 1969), as well as some potential for a vital effect in their compositions in biogenic carbonates (e.g., Wefer 1985).

The paper by Carpenter & Lohmann (1995) initiated a second resurgence in the geochemical study of brachiopods, but they advocated caution about the suitability of some of their shell components such as the primary layer as a reliable recorder of ambient environmental conditions. This resurgence continues unabated to this day, with comprehensive geochemical works, just to name a few, for example, Buening & Carlson (1992), Buening & Spero (1996), Auclair *et al.* (2003), Brand *et al.* (2003, 2013, 2015), Parkinson *et al.* (2005), Cusack *et al.* (2008), Perez-Huerta *et al.* (2008), Yamamoto *et al.* (2010), Takayanagi *et al.* (2013), Came *et al.* (2017), Ullmann *et al.* (2017a, 2017b), and Bajnai *et al.* (2018). Unfortunately, these and many other studies did not resolve the issue of whether articulated brachiopods incorporate carbon and oxygen isotopes in equilibrium or not with ambient seawater. Instead, it is becoming increasingly clear that

thermodynamic equilibrium is not the norm for oxygen and clumped isotope incorporation into modern brachiopod calcite shells (Bajnai *et al.* 2018) and potentially other biogenic carbonates (e.g., Erez & Luz 1983; McConnaughey 2003).

Despite the on-going issue of whether articulated brachiopods precipitate their calcite shells in thermodynamic equilibrium or not, they are unsurpassed marine-water temperature recorders because their history extends back to the Cambrian, and they occur in all depth and temperature regimes of mostly normal marine salinity. Furthermore, their sessile nature and diagenetically resistant low-Mg calcite mineralogy make them ideal archives of recording and storing information about spatially-fixed but temporally changing oceanographic conditions. With a change in oceanographic conditions, marine organisms must either migrate to a more favourable location, adapt to the changing environmental conditions or become extinct. It appears that brachiopods, as a group, are quite resilient in coping with environmental changes such as moderate (Peck *et al.* 2009) but not excessive increases in water temperature (e.g., Brand *et al.* 2012, 2016) or ocean acidification (Cross *et al.* 2018). Thus brachiopods, a group of marine invertebrates able to survive mass and smaller extinctions, are invaluable in recording changes in past and present oceanographic conditions.

The objective of this study is a re-evaluation of the applicability of low-Mg calcite articulated brachiopod shells as archives of oxygen isotope and thus of ambient water temperatures (Epstein *et al.* 1951, 1953; Brand *et al.* 2013). This evaluation and review are important in light of the fact that brachiopods, apparently do not incorporate oxygen and clumped isotopes in thermodynamic equilibrium with ambient seawater (Bajnai *et al.* 2018). We aim to quantify this offset and formulate a relationship that allows for the calibration of ambient seawater temperatures using modern articulated brachiopods.

## STUDY MATERIAL AND METHODS

The study material consists of modern articulated and some inarticulated brachiopods and their ambient seawater. In addition, presentations and evaluations will consider the results of the pre-

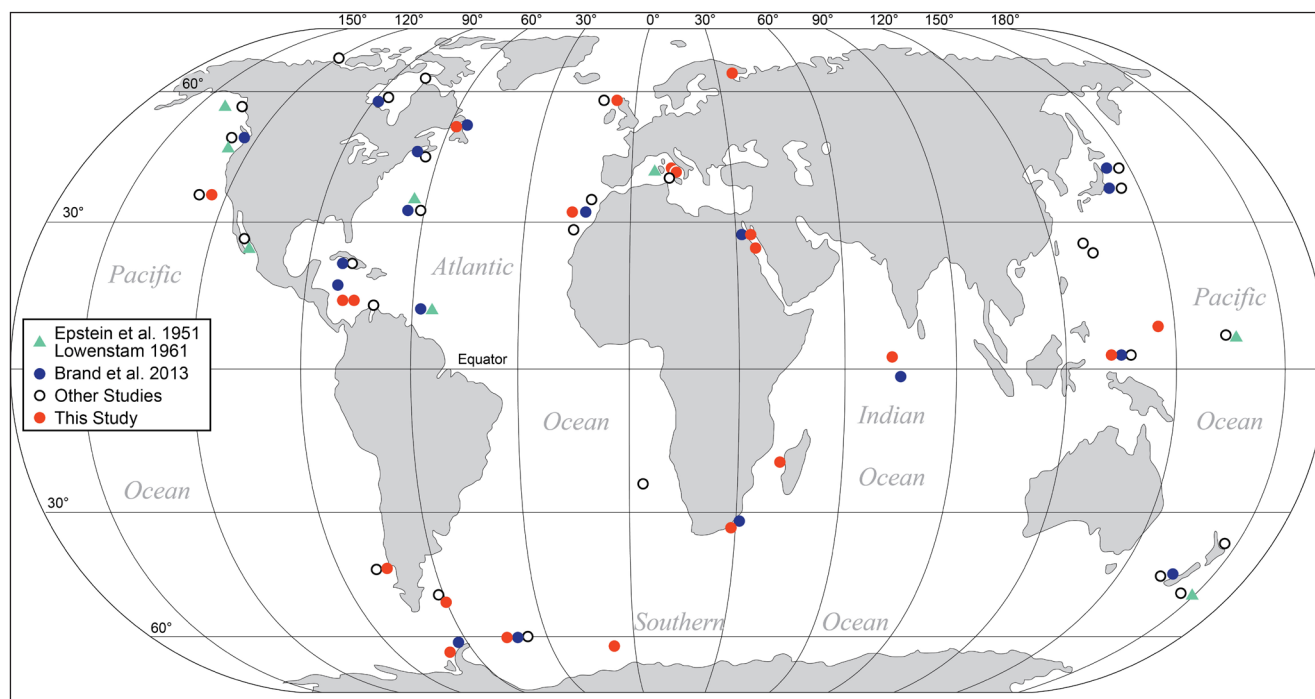


Fig. 1 - Localities of modern articulated brachiopods examined in this study (Supplement 1) and of other studies mentioned in Brand et al. (2013), for example Lowenstam (1961) and of Epstein et al. (1951). Seawater information and chemistry are presented in Supplement 2.

vious study by Brand et al. (2013) and the results of others contained therein. Furthermore, studies of other authors published since 2013 will be also considered in this evaluation (e.g., Ullmann et al. 2017a, 2017b; Bajnai et al. 2018).

### Modern Brachiopods

This study consists of a total of 164 specimens belonging to 17 species from 22 localities covering high to low latitudes, from cold to warm, and from shallow to deep depths for geochemical evaluation (Fig. 1). With ontogenetic sampling, the geochemical results include 328  $\text{MgCO}_3$  determinations, which include 26 results of the inarticulated brachiopod *Novocrania anomala* from the Mediterranean, whereas the total oxygen isotope results number 324 analyses from all shell layers/areas (except for the primary layer; Supplement 1).

### Modern Seawater

In conjunction with the brachiopods, whenever feasible, we collected seawater for isotope and chemical analyses to complement the shell chemistry. For some select localities such as Signy Island (Antarctica), the Weddell Sea (Antarctica) or off California (U.S.A.), we had to rely on information from published sources (Marshall et al. 1997; Pierre

1999; Bigg & Rohling 2000; Mackensen 2001; Bass et al. 2014; Supplement 2).

### Analytical Methods - Sample Preparation

All brachiopod shells were cleaned of organic tissue by physical and chemical means (cf. Brand et al. 2003; Zaky et al. 2015). All sufficiently large specimens were sampled along the ontogenetic growth axis – from the umbo to the shell edge (cf. Romanin et al. 2018). For small specimen, we had to use the whole shell for trace chemistry and stable isotope analyses. Prior to powdering and/or milling, the primary layer, as much as possible, was physically and chemically removed from the underlying layer(s) by leaching shells with 10 % hydrochloric acid. In addition, specialized areas, such as umbo and muscle scars were sampled separately for individual analysis and evaluation.

### Analytical Methods - Sample Imaging

EBSD (electron backscatter diffraction) imaging of the modern brachiopods was carried out on a Hitachi SU 5000 field emission scanning electron microscope (SEM) equipped with an Oxford detector. The instrument was operated at 20kV and measurements were indexed with the CHANNEL 5 HKL software.

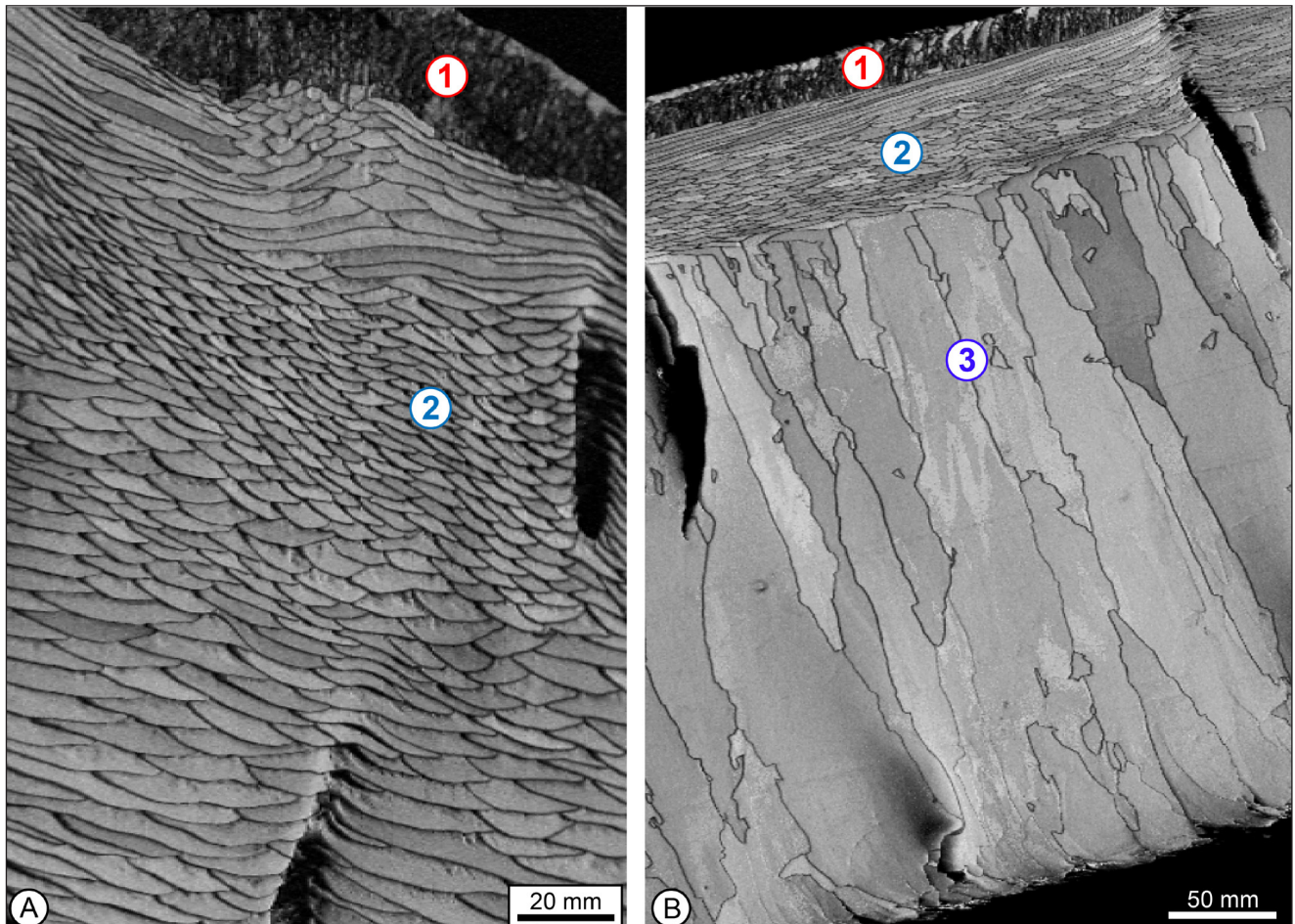


Fig. 2 - EBSD band contrast-images of shell microstructures of primary, secondary and tertiary layers in some modern brachiopods. A: Microstructure of primary (1) and secondary (2) layers within calcite shell of *Liothyrella uva*. B: Microstructure of primary (1), secondary (2) and tertiary (3) layers within the calcite shell of *Gryphus vitreus*.

#### Analytical Methods - Elemental chemistry

Most samples were analysed for Ca, Mg, Sr, Na, Mn and Fe by atomic absorption spectrometer; but, here we report only on the Mg results (Supplement 1). All results were adjusted to a 100 % carbonate basis (cf. Brand & Veizer 1980). Reproducibility consisting of accuracy and precision of elemental results (Mg) compared to certified NBS (NIST) SRM 633 value was better than  $\pm 0.8$  and 6.2 %, respectively.

#### Analytical Methods - Stable Isotopes

All brachiopod powder material was analysed for carbon and oxygen isotope compositions at Memorial (Canada) and Milan (Italy) Universities. A small quantity of weighed powder was reacted with anhydrous phosphoric acid at 70°C prior to introduction into the mass spectrometer. All results are normalized and reported in VPDB in permil (‰). Reproducibility compared to NBS 19 and IAEA-

603 calibrated with internal standards was better than 0.05 ‰. All brachiopod trace chemistry (Mg) and isotope ( $\delta^{18}\text{O}$ ) results are reported in Supplement 1.

Seawater samples collected in the field were filtered and stored in 50 mL amber borosilicate glass vials. They were kept cool for as long as possible during shipment. Water temperature was measured with a Fish Hawk TD probe on an aliquot of the shipped sample. Salinity was measured immediately upon receipt of sample in the lab at Brock University (Canada), which was followed by trace chemistry analysis at Brock on an atomic absorption spectrometer. Seawater oxygen isotope composition was determined by the G.G. Hatch laboratory at the University of Ottawa (Canada) following the procedure and protocol listed in Brand et al. (2013) and reported in VSMOW. Replicate analyses and reproducibility were better than 0.01 ‰, and all geochemical results are presented in Supplement 2.

Location	Species	Latitude	Depth	N	Mean	Error	Min	Max	Range
Palau (Pacific)	<i>Thecidellina congregata</i>	7°N	1-2 m	9	-2.51	0.03	-2.61	-2.30	0.31 (1)
Beaufort Sea (Arctic)	<i>Glaciarcula spitsbergensis</i>	70°N	~55	2	+2.20		+2.05	+2.34	0.29 (2)
Rothera (Antarctica)	<i>Liothyrella uva</i>	67°S	5-25	28	+4.38	0.05	+3.75	+4.72	0.97 (3)
Alboran Sea (Mediterranean)	<i>Terebratulina retusa</i>	36°N	100	11	+0.87	0.06	+0.56	+1.11	0.55 (4)
"	<i>Mergelia truncata</i>	"	"	14	+0.38	0.06	+0.05	+0.65	0.60 (5)
"	<i>Megathyris detruncata</i>	"	"	17	+0.39	0.07	-0.18	+1.05	1.23 (6)
Doubtful Sound (New Zealand)	<i>Liothyrella neozelanica</i>	45°S	15-22	13	+1.23	0.04	+0.83	+1.44	0.61 (7)
"	<i>Notosaria nigricans</i>	"	"	6	+1.21	0.05	+1.07	+1.41	0.34 (8)
"	<i>Magasella sanguinea</i>	"	"	11	+0.63	0.07	+0.22	+0.92	0.70 (9)
Friday Harbor (Washington State, U.S.A.)	<i>Hemithiris psittacea</i>	48°N	80	22	-0.37	0.06	-0.88	+0.15	1.03 (10)
"	<i>Terebratalia transversa</i>	"	"	22	-0.40	0.07	-1.21	+0.25	1.46 (11)
"	<i>Terebratulina unguicula</i>	"	"	20	-0.08	0.03	-0.38	+0.17	0.55 (12)
Comau Fjord (Chile)	<i>Magellania venosa</i>	42°S	15-60	58	+1.70	0.03	+1.16	+2.12	0.96 (13)
Weddell Sea (Antarctica)	<i>Magellania fragilis</i>	70°S	215	9	+4.38	0.14	+3.88	+4.98	1.10 (14)
Caribbean Sea	<i>Chlidonophora incerta</i>	13°N	3445	16	+3.37	0.02	+3.24	+3.50	0.26 (15)
"	<i>Chlidonophora incerta</i>	"	4010	10	+3.39	0.01	+3.33	+3.44	0.11 (16)

Tab. 1 - Summary statistics ( $\delta^{18}\text{O}$  ‰, VPDB; seawater- $^{18}\text{O}$  corrected values) of select modern articulated brachiopods from low to high latitudes, from warm to cold and shallow to deep environmental settings. Note: Number (in brackets) corresponds to numbers in Fig. 3.

## RESULTS

Shells of the studied articulated brachiopods consist of either a two-layer or three-layer sequence. The outer, primary layer has a microgranular fabric, whereas the secondary layer generally consists of elongated mesocrystal fibers, whereas the tertiary layer (if present) consists of prismatic columns (Fig. 2; Garbelli et al. 2012; Schmahl et al. 2012; Casella et al. 2018). In all instances, the outer primary layer was removed prior to elemental and isotope analyses, because of the inherent vital effect recorded by it (cf. Carpenter & Lohmann 1995). Extraction and removal of the primary layer must be followed through on fossil material to avoid extraneous signals not representative of the ambient environment (cf. Brand et al. 2012). It is equally desirable that all fossil material be inspected and tested for preservation of primary values including the brachiopod archive (e.g., Brand 1982, 2004; Popp et al. 1986; Veizer et al. 1999; Angiolini et al. 2012). Because of the many deviations from apparent thermodynamic equilibrium of marine biogenic carbonates, here, we will concentrate on the articulated brachiopods.

## ENVIRONMENTAL DISTRIBUTION

The summary statistics of oxygen isotope composition, corrected for seawater- $^{18}\text{O}$ , of modern brachiopods from low to high latitudes, shallow to deep settings, and changing depths provide insight into the incorporation process. No specific but some general relationships exist between environmental settings and oxygen isotope compositions as well as specimens inhabiting the same environment (Tab. 1). The  $\delta^{18}\text{O}$  values of brachiopods from the tropics (e.g., Palau) are more negative than those of high latitude counterparts (Beaufort Sea, Rothera [Antarctica]; Tab. 1). However, the values of the two high latitude specimens differ by about 2.1 ‰ reflecting strong isotopic differences between the waters of the Arctic and Southern Oceans. Low ambient water temperatures are also encountered in tropical but abyssal regimes such as the Caribbean (Tab. 1). A comparison of mid-latitude brachiopod populations from Friday Harbor (48°N) and Doubtful Sound (45°S), similarly, shows an average difference of about 1.3 ‰ (Tab. 1). Some of the smallest ranges in  $\delta^{18}\text{O}$  values are recorded in

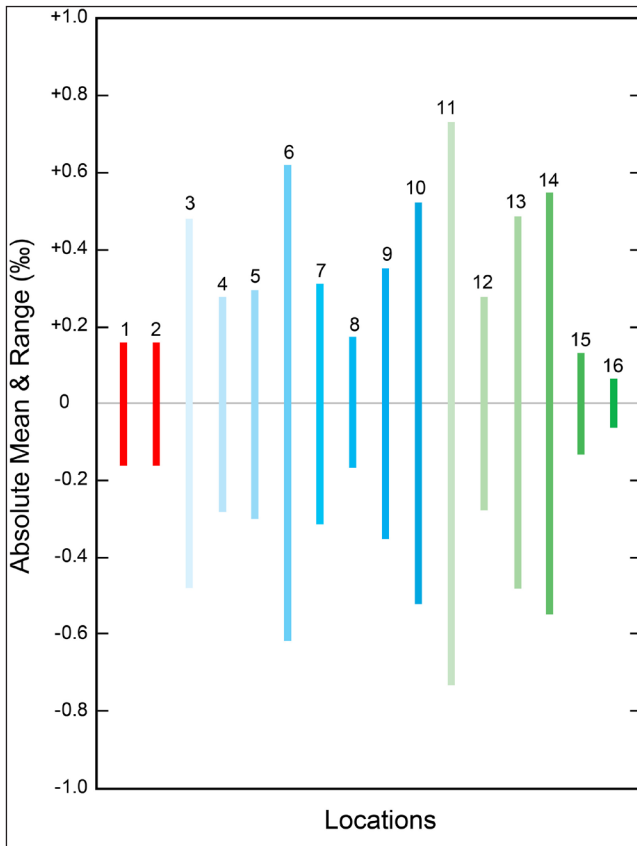


Fig. 3 - Absolute  $\delta^{18}\text{O}$  mean values and ranges of modern articulated brachiopods from low to high latitudes, cold to warm and from shallow to deep environments. For additional details see Tab. 1.

both warm and cold water brachiopods, for example, from Palau, Caribbean Sea, and Beaufort Sea, whereas the opposite of large ranges are recorded

in counterparts from Rothera (Antarctica), Weddell Sea, Alboran (Mediterranean), and Friday Harbor (North Pacific, Washington State, U.S.A.; Fig. 3). Thus, it is quite clear that a simple latitudinal model does not adequately address the isotopic variation recorded by modern brachiopods. Instead, it must give way to a more realistic and complex oceanographic relationship (Fig. 3) when dealing with modern and deep-time brachiopods.

Individual brachiopod groups complicate matters, by incorporating and/or growing at different times during the year, which is clearly documented by the groups from the Alboran Sea, Doubtful Sound (New Zealand) and Friday Harbor (Tab. 1, Fig. 3). Thus in addition to latitudinal variation(s), environmental assessments must give due consideration to species-specific growth conditions (cf. Ullmann et al. 2017a) during isotope evaluations of brachiopods.

### $\text{MgCO}_3$ CONTENTS AND THE GLOBAL BRACHIOPOD Mg LINE

The Mg content of brachiopods has garnered great interest in being a potential proxy of seasonality (Butler et al. 2015; Clark et al. 2016) as well as a water-independent thermometer (e.g., Perez-Huerta et al. 2008). Several concepts need to be considered before we can implement its full potential, such as growth rate, species-specific biomineralization, and

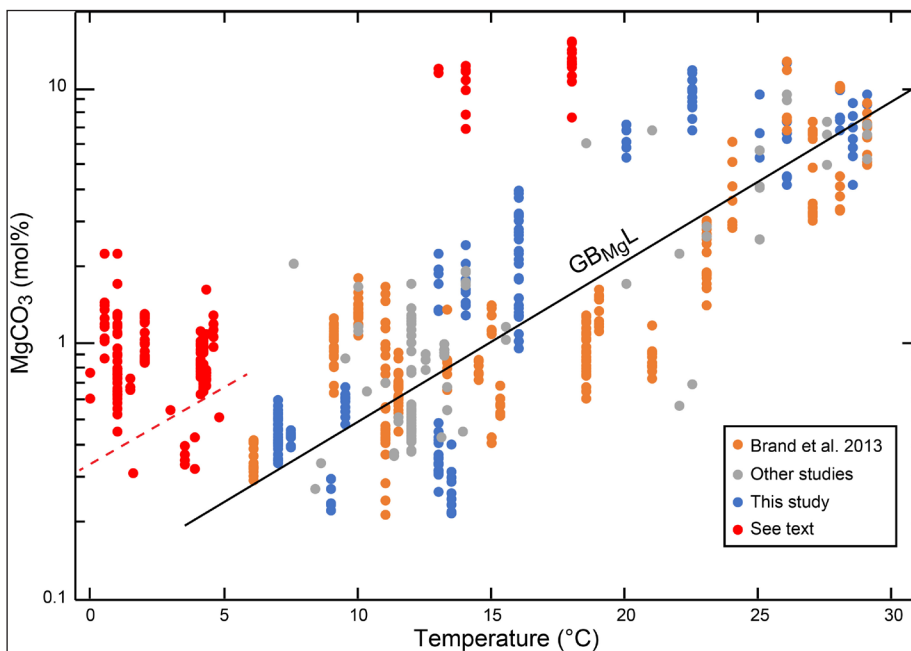
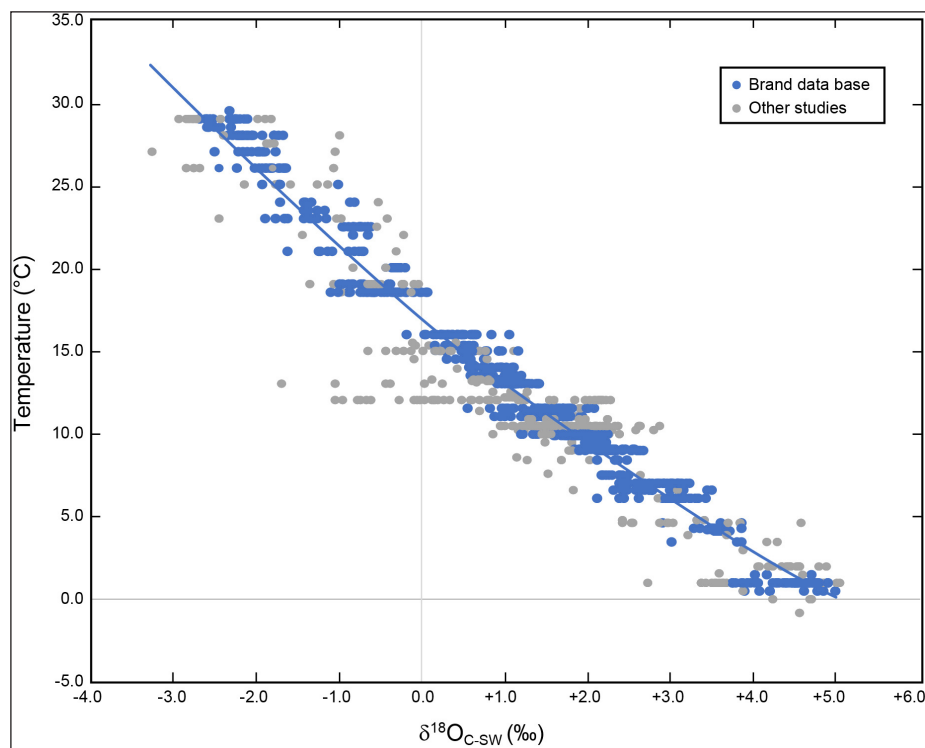


Fig. 4 - Plot of  $\text{MgCO}_3$  contents of modern brachiopods supplemented by those of Brand et al. (2013) and of other studies. Samples in 'red' symbols and above the dashed line fall outside the expected content and range typical for articulated brachiopods and their concurrence with the 'Global Brachiopod Mg Line' (Brand et al. 2013). The 'red' specimens include the inarticulated species *Novocrania anomala* from the Mediterranean, and most articulated brachiopods from environments with ambient water temperatures of less than  $5^\circ\text{C}$  (cf. *L. notorcadensis*, *L. wa*, *M. fragilis*, *C. incerta*, and *C. racovitzæ*).

Fig. 5. - Plot of water-corrected oxygen isotope compositions of modern brachiopods and ambient seawater temperature (this study and Brand et al. 2003, 2013) supplemented by results of other studies (N=1227). Other results from Epstein et al. (1951), Henkes et al. (2013), Came et al. (2014), Rollion-Bard et al. (2016), Wacker et al. (2014), Butler et al. (2015), Ullmann et al. (2017a, 2017b), Bajnai et al. (2018). The results were not filtered for position on the shell, but it excludes results of the primary layer.



an appropriate group-specific thermometer. Brand et al. (2013) presented the  $\text{MgCO}_3$  content of the global population on modern brachiopods (Fig. 4), with most other modern material falling within the parameters of the LINE. Most Mg results of the new brachiopod database also fall within the confines of the LINE; with few exceptions (Fig. 4). The articulated species *Liothyrella uva*, *Liothyrella notorcadensis* (old description => *uva*), *Magellania fragilis*, *Chlidonophora incerta*, and *Compsothyris racovitzae*, and the inarticulated *Novocrania anomala* fall above the GBMgL (Fig. 4). Based on analogous faster growth of the umbo and its correspondingly higher Mg content it was concluded that faster growth rate due to higher temperatures and/or productivity may be responsible for this 'positive' Mg offset (e.g., Buening & Carlson 1992; Perez-Huerta et al. 2008; Brand et al. 2013; Butler et al. 2015). Many modern brachiopods have a life span of 5 -10 years (e.g., Thayer 1977; Baumgarten et al. 2013), with a few such as *Liothyrella neozelandica* have life spans of about 17 years (Baird et al. 2013). Even fewer such as *L. uva* and *M. fragilis* have life spans in excess of 50 years (Brey et al. 1995; Peck & Brey 1996), and with a similar life span observed for the inarticulated brachiopod *N. anomala* (Taddei Ruggiero 2001). Based on the observed long life spans, it is not fast growth rate, but indeed the opposite, a 'slow' one that is responsible for their 'positive' Mg offset from the

GBMgL (Fig. 4). Thus, a re-evaluation of the Mg content for brachiopods, in concert, with this revised thinking is highly warranted for its unrealized potential as a seawater-independent thermometer.

## DISCUSSION

### Brachiopod-based oxygen-isotope thermometer

For decades, researchers used the Epstein et al. (1953) oxygen-isotope thermometer on various carbonates archives from foraminifera to molluscs to brachiopods. But diversification and the realization of species influences saw the proliferation of a multitude of paleothermometers; among them synthetic (Kim & O'Neil 1997) and biogenic carbonates (e.g., Brand et al. 2013). However, the question of equilibrium, more precisely of thermodynamic equilibrium, remains an elusive goal (Bajnai et al. 2018).

The work of Coplen (2007) and Bajnai et al. (2018) on abiogenic and brachiopod calcite clearly highlights the difference in isotopic compositions at perceived slow growth rates. Brand et al. (2013) invoked a Mg-influence on the oxygen isotope composition and ultimately a relationship to water temperature. Since this was based on Mg impacts recorded in synthetically precipitated carbonates, another

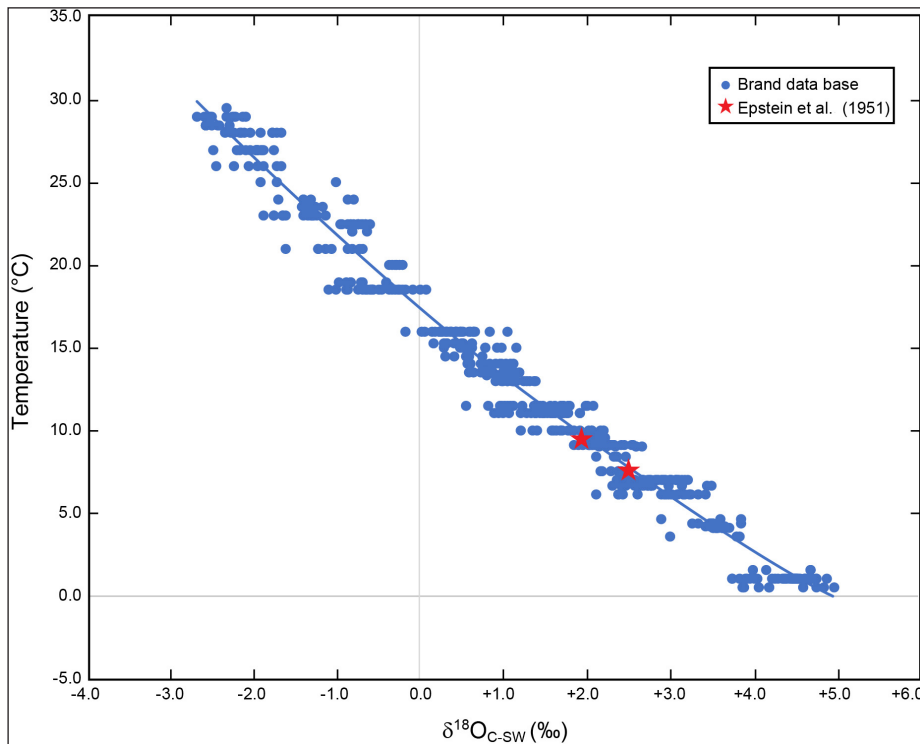


Fig. 6 - Plot of water-corrected oxygen isotope composition of modern brachiopods based solely on the collections of Brand et al. (2003, 2013, 2015) new material collected for this study, and those of Epstein et al. (1951). In addition, it excludes all results from the umbo and other parts of the shell deemed unsuitable for producing reliable and robust temperature determinations (cf. Fig. 8; Carpenter & Lohmann 1995; Parkinson et al. 2005; Brand et al. 2013).

way was needed to assess the potential of brachiopods as robust archives of water temperature. The early results of Epstein et al. (1951) and Lowenstam (1961) were quite promising, but the question of equilibrium in brachiopods essentially remained unresolved all these decades.

Here, we present an update on this issue with Figure 5, which shows brachiopod oxygen isotope results covering the world's oceans from all latitudes, depths, salinity and temperature (Fig. 1). Considerable 'noise' is evident in the data, because it includes  $\delta^{18}\text{O}$  results from all parts of the brachiopod shell (dorsal and ventral) from the umbo (posterior) to the commissure (anterior), but with one exception. No results from the primary layer were used in the reconstruction of Figure 5, since it has been documented that this layer is definitely in isotopic disequilibrium (e.g., Carpenter & Lohmann 1995; Auclair et al. 2003; Brand et al. 2003; Parkinson et al. 2005). Another version of the same database but without results from the umbo area and other undesirable areas (e.g., muscle scars) improves the correlation (Fig. 8). However, the best oxygen isotope-temperature relationship is realized when we limit the results to this study, and select ones from the study of Brand et al. (2013; Fig. 6) with ambient seawater temperatures or oxygen isotope compositions or both. Following the principle used in formulating the first biogenic isotope-tem-

perature relationship (cf. Epstein et al., 1953), a 2<sup>nd</sup> order polynomial correlation is highly satisfactory ( $r^2 = 0.980$ ,  $p < 0.05$ ) for the brachiopod-based results after adjustment for seawater- $^{18}\text{O}$ . This newly minted relationship does not require an adjustment for Mg contents or salinity to determine 'robust' temperatures of the ambient seawater. Specimens from cold to warm settings give 'consistent' temperatures in excellent agreement with actual depositional conditions. Unfortunately, the really slow-growing brachiopod *N. anomala* could not be accommodated in this relationship, but due to its extremely slow growth, its oxygen isotope contents and those of other inarticulated brachiopods deserve further investigation.

### Oxygen Thermodynamic Equilibrium

A recent study by Watkins et al. (2013) suggested that oxygen thermodynamic equilibrium was unlikely between calcite and ambient water whether formed in natural settings or precipitated in the laboratory. This observation was affirmed by Bajnai et al. (2018) who investigated oxygen and clumped isotopes in modern brachiopods. Their conclusions confirmed the statement by Coplen (2007) about a general lack of thermodynamic equilibrium, but instead, suggests that kinetic fractionation may govern the oxygen isotope compositions of many marine carbonates.



Tab. 2 - Compilation of some select oxygen-isotope based temperature equations for various abiogenic, synthetic and biogenic carbonates. Note:  $\delta c-\delta^{18}O$  ‰ (PDB) of carbonate,  $\delta w-\delta^{18}O$  ‰ (SMOW) of seawater/water,  $\Delta Mg$  – mol % of  $MgCO_3$ ; (B) – benthic, (P) – planktonic; Art. - articulated

Source material	Equation	Reference
Abiogenic Carbonate	$T^{\circ}C = 22.5280 - 4.5378(\delta c - \delta w) + 0.0942(\delta c - \delta w)^2$	Coplen 2007
Synthetic Carbonate	$T^{\circ}C = 16.0 - 5.17(\delta c - \delta w) + 0.092(\delta c - \delta w)^2$	McCrea 1950
"	$T^{\circ}C = 16.9 - 4.38((\delta c - \delta w) + 0.1((\delta c - \delta w)^2$	O'Neil et al. 1969
"	$T^{\circ}C = 13.728 - 4.5378(\delta c - \delta w) + 0.0942(\delta c - \delta w)^2$	Kim & O'Neil 1998
Molluscs	$T^{\circ}C = 16.5 - 4.3(\delta c - \delta w) + 0.14(\delta c - \delta w)^2$	Epstein et al. 1953
"	$T^{\circ}C = 15.75 - 4.30(\delta c - \delta w) + 0.14(\delta c - \delta w)^2$	Sharp 2007
Foraminifera (B)	$T^{\circ}C = 16.9 - 4.0(\delta c - \delta w) + 0.1(\delta c - \delta w)^2$	Shackleton 1974
Foraminifera (P)	$T^{\circ}C = 13.2 - 4.89(\delta c - \delta w)$	Bemis et al. 1998
Foraminifera (P)	$T^{\circ}C = 14.32 - 4.28(\delta c - \delta w) + 0.07(\delta c - \delta w)^2$	Mulitza et al. 2003
Art. Brachiopods	$T^{\circ}C = 16.192 - 3.468((\delta c - \Delta Mg) - \delta w)$	Brand et al. 2013
Art. Brachiopods	$T^{\circ}C = 17.3750 - 4.2535(\delta c - \delta w) + 0.1473(\delta c - \delta w)^2$	This Study

### Comparison of thermometers

The brachiopod-based oxygen-isotope thermometer appears to give robust temperatures that mimic the ambient water and thus represent brachiopod-based equilibrium (BBE, Fig. 6). It was this general observation of BBE (cf. Epstein et al. 1951; Lowenstam 1961) that is the impetus for the re-evaluation of brachiopod oxygen isotope compositions and their fidelity in producing reliable paleo-temperatures. Over the years, a number of oxygen-isotope thermometers have been constructed for various synthetic, abiogenic and biogenic carbonates, and a small subset is presented in Table 2. Comparison of the various thermometers shows general similarities in the slope, with few exceptions, but they differ significantly in their intercept values (Tab. 2, Fig. 7). For many years, the oxygen isotope thermometer of Kim & O'Neil (1997) was regarded as the one closest to representing equilibrium conditions and was extensively used to determine water temperatures of various marine abiogenic and biogenic carbonates. The work of Coplen (2007) clearly demonstrates that synthetically precipitated laboratory carbonates are anything but equilibrium products, and the follow-up work by Kluge et al. (2014) strongly supports thermodynamic equilibrium precipitation of the Devils Hole cave (southcentral Nevada) abiogenic carbonates (mammillary vein calcite). This further supports the observation that synthetically formed carbonates and their isotope-based thermometers are not suitable alternatives or substitutes for determining ambient seawater temperatures of biogenic marine carbonates (cf. Fig. 7); we discuss this below.

### Isotope and temperature offsets

Calculating the isotope and temperature 'offsets' relative to the abiogenic calcite presented by

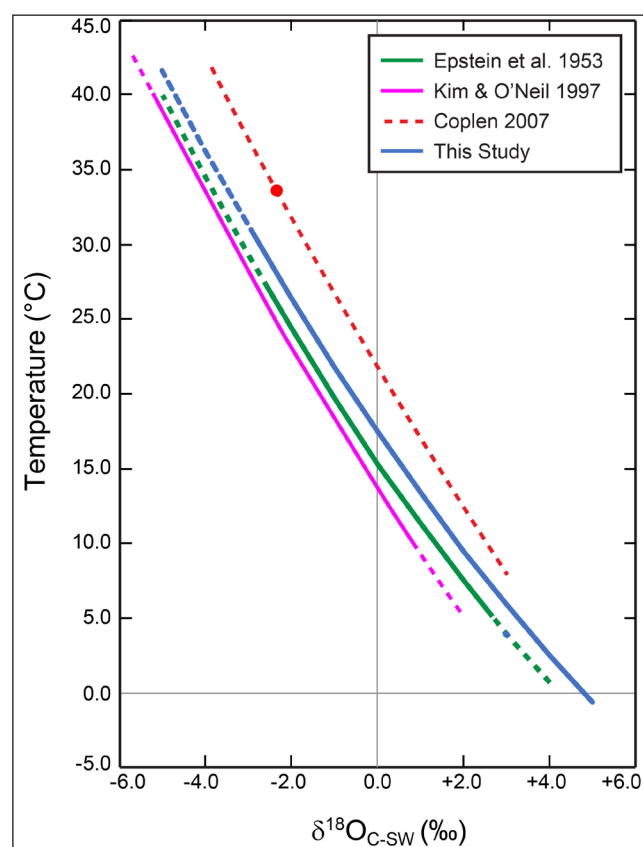


Fig. 7 - Plot of regression lines computed for a number of temperature-oxygen isotope relationships of abiogenic, synthetic and brachiopod-based data. The regression for the abiogenic carbonate of Coplen (2007) is extrapolated from its singular datum point and the similar precipitation conditions, such as no change with rate, noted for synthetic carbonates (Kim & O'Neil 1997; Coplen 2007, fig. 3). Dashed lines represent extrapolations/extensions of actual data covering the regression lines.

Source	Type	$\delta^{18}\text{O}$	$\Delta^{18}\text{O}$ offset	$\Delta\text{T}^\circ\text{C}$ offset	$\Delta\text{T}^\circ\text{C}$ (K&O, 97)		$\Delta\text{T}^\circ\text{C}$ (This study)	
		0 ‰, 33.7°C	from A	from A	0 ‰, 2°C	0 ‰, 28°C	0 ‰, 2°C	0 ‰, 28°C
Coplen 2007	A	-2.35	-	-	+8.8	+8.8	+2.9	+5.6
O'Neil et al. 1969	S	-3.55	-1.20	-6.0	+3.6	+2.7	-1.9	-0.4
Kim & O'Neil 1997	S	-4.05	-1.70	-8.8	0	0	-5.9	-3.2
Epstein et al. 1953	Molluscs	-3.85	-1.50	-7.7	+2.8	+1.1	-2.1	-2.1
Sharp 2007	Molluscs	-3.72	-1.37	-7.1	+3.0	+1.7	-2.0	-1.5
Mulitza et al. 2003	Foraminifera	-4.23	-1.88	-8.9	+1.1	-0.4	-4.6	-3.4
Brand et al. 2013*	Brachiopods	-5.05	-2.70	-9.4	+5.1	+2.3	-0.1	+0.1
This study	Brachiopods	-3.43	-1.08	-5.5	+4.8	+3.3	0.0	0.0

Tab. 3 - Isotope and temperature offsets determined for some oxygen isotope thermometers (cf. Tab 1) proposed over the years for abiogenic (A), synthetic (S) and biogenic (molluscs, foraminifera, articulated brachiopods) carbonates. Note: \*adjustment for Mg content set to 2000 and 16,000  $\mu\text{g/g}$  at 2°C and 28°C, respectively (cf. Brand et al. 2013).

Coplen (2007) from Devils Hole, Nevada, clearly shows the importance of mineralogy and taxa in temperature determinations (Tab. 3). The  $\Delta^{18}\text{O}$  offset varies from a low of -1.08 ‰ to a high of -2.70 ‰, with corresponding offsets in their temperatures ranging from a low of -5.5° to a high of -9.4°C. These offsets from thermodynamic equilibrium may be quite large when it comes to documenting real-time trends in deep-time and near-time climate change studies based on abiogenic and biogenic carbonates and using the 'wrong' oxygen isotope thermometer (Tab. 3). The situation is not much better when using the equation developed by Kim & O'Neil (1997) based on synthetic calcite precipitated under laboratory conditions and generally assumed to give temperature results to be in 'equilibrium' with seawater. At seawater temperatures of 2°C and 28°C, the calculated temperatures for brachiopods with the Kim & O'Neil (1997) thermometer would be underestimated by 4.8° and 3.3°C, respectively (Tab. 3). Similarly, with the isotope thermometer based on articulated brachiopods, calculated temperatures for molluscs and foraminifera would be overestimated by about 2° to 4.6°C at the pre-set level of 2°C, and by about 1.5° to 3.4°C at the pre-set level of 28°C (Tab. 3).

These temperature offsets underscore the necessity for giving due consideration to, a) the respective mineralogy of biogenic carbonates, b) their taxonomic position (Fig. 7), and c) of using synthet-

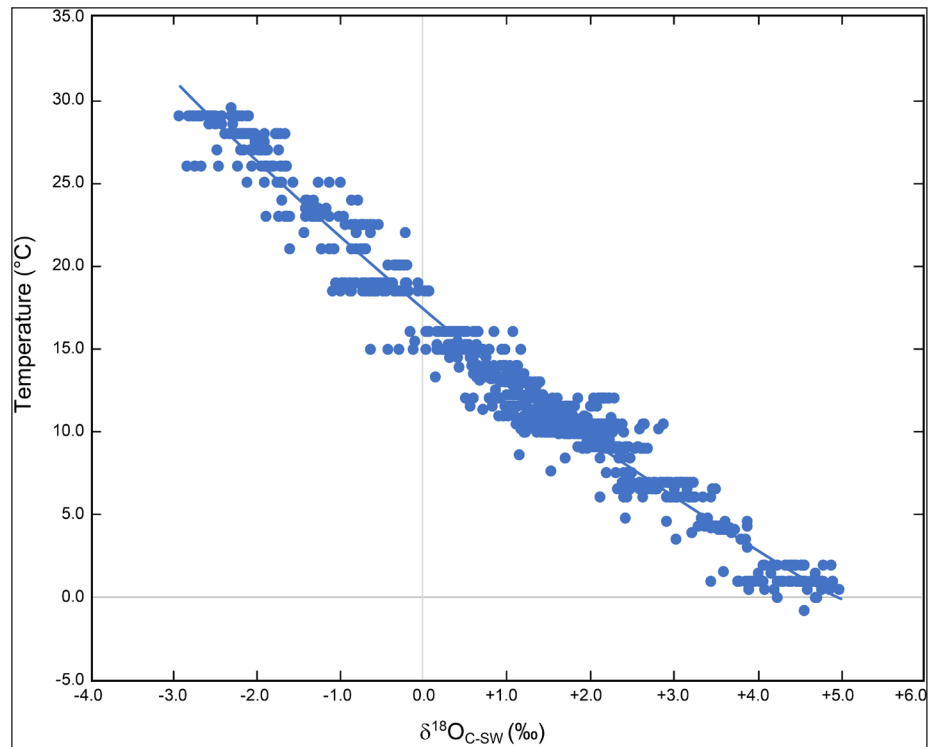
ic carbonate-based thermometers. Thus, for temperature determinations with biogenic carbonates it is inappropriate to use abiogenic and synthetic carbonate-based thermometers for paleoenvironmental reconstructions. Equally inappropriate, biogenic carbonate-based thermometers should not be used for synthetic or abiogenic carbonate paleotemperature determinations.

## CONCLUSIONS

A large database of modern brachiopods was re-evaluated for its potential to act as an archive of a reliable oxygen isotope thermometer. This review was necessitated by the observations and conclusions of Coplen (2007) and Bajnai et al. (2018) that biogenic carbonates, including articulated brachiopods, may not precipitate shell calcite in oxygen isotope thermodynamic equilibrium.

We report on an expanded database of modern brachiopod calcite and their ambient seawater temperatures and compositions from high to low, warm to cold, and shallow to deep settings. The oxygen-isotope compositions of the brachiopods are offset relative to abiogenic calcite precipitated in thermodynamic equilibrium by about 1 ‰ and relatively constant over their marine temperature range. Instead, the oxygen isotopes presented in the updated brachiopod archive and database are in apparent

Fig 8 - Plot of water-corrected oxygen isotope compositions of modern brachiopods. Database as in Figure 5 but with removal of results from the umbo, and other specialized areas giving unsuitable values (cf. Carpenter & Lohmann 1995; Parkinson et al. 2005; Brand et al. 2015).



brachiopod-based equilibrium (BBE) with ambient seawater temperatures. Thus, the brachiopod-based oxygen-isotope and water temperature relationship and thermometer is expressed as:

$$T^{\circ}\text{C} = 17.3750 - 4.2535 (\delta\text{c}-\delta\text{w}) + 0.1473 (\delta\text{c}-\delta\text{w})^2 \quad (\text{N}=578, r^2 = 0.980)$$

Since most thermometers are not based on carbonates formed in thermodynamic equilibrium with ambient fluid(s), it is imperative that a chosen thermometer must be compatible with the respective carbonate species under consideration. Thus, the newly-minted brachiopod-based thermometer should be exclusively used for brachiopod-based paleoenvironmental studies and paleotemperature determinations.

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