



# Lithium elemental and isotope systematics of modern and cultured brachiopods: Implications for seawater evolution

Natalie Gaspers<sup>a,b</sup>, Tomáš Magna<sup>a,\*</sup>, Hana Jurikova<sup>c,d</sup>, Daniela Henkel<sup>c</sup>, Anton Eisenhauer<sup>c</sup>, Karem Azmy<sup>e</sup>, Adam Tomašových<sup>f</sup>

<sup>a</sup> Czech Geological Survey, Klárov 3, CZ-118 21 Prague 1, Czech Republic

<sup>b</sup> Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Kamýcká 129, CZ-16500 Prague-Suchdol, Czech Republic

<sup>c</sup> GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstr. 1-3, D-24148 Kiel, Germany

<sup>d</sup> School of Earth and Environmental Sciences, University of St. Andrews, Bute Building, St. Andrews KY16 9TS, United Kingdom

<sup>e</sup> Department of Earth Sciences, Memorial University of Newfoundland, St. John's, NL A1B 3X5, Canada

<sup>f</sup> Geological Institute, Slovak Academy of Sciences, Dúbravská cesta 9, SK-84005 Bratislava, Slovakia

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## ABSTRACT

Lithium has proven a powerful tracer of weathering processes and chemical evolution of seawater. Skeletal components of marine calcifying organisms, and in particular brachiopods, present promising archives of Li signatures. However, Li incorporation mechanisms and potential influence from biological processes or environmental conditions require a careful assessment. In order to constrain Li systematics in brachiopod shells, we present Li concentrations and isotope compositions for 11 calcitic brachiopod species collected from six different geographic regions, paralleled with data from culturing experiments where brachiopods were grown under varying environmental conditions and seawater chemistry (pH–pCO<sub>2</sub>, temperature, Mg/Ca ratio). The recent brachiopod specimens collected across different temperate and polar environments showed broadly consistent  $\delta^7\text{Li}$  values ranging from 25.2 to 28.1‰ (with mean  $\delta^7\text{Li}$  of  $26.9 \pm 1.5\text{‰}$ ), irrespective of taxonomic rank, indicating that incorporation of Li isotopes into brachiopod shells is not strongly affected by vital effects related to differences among species. This results in  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  values (per mil difference in  $^7\text{Li}/^6\text{Li}$  between brachiopod calcite shell and seawater) from  $-2.9\text{‰}$  to  $-5.8\text{‰}$  (with mean  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  value of  $-3.6\text{‰}$ ), which is larger than the  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  values calculated based on data from planktonic foraminifera ( $\sim 0\text{‰}$  to  $\sim -4\text{‰}$ ). This range of values is further supported by results from brachiopods cultured experimentally. Under controlled culturing conditions simulating the natural marine environment, the  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  for *Magellania venosa* was  $-2.5\text{‰}$  and not affected by an increase in temperature from 10 to 16 °C. In contrast, a decrease in Mg/Ca (or Li/Ca) ratio of seawater by addition of CaCl<sub>2</sub> as well as elevated pCO<sub>2</sub>, and hence low-pH conditions, resulted in an increased  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  up to  $-4.6\text{‰}$ . Collectively, our results indicate that brachiopods represent valuable archives and provide an envelope for robust Li-based reconstruction of seawater evolution over the Phanerozoic.

## 1. Introduction

Reconstructing the chemical evolution of seawater and its reflection of rapid and/or long-term changes in weathering plays an important role in understanding the processes that shape Earth's surface and climate. Due to the absence of direct seawater samples from the past, proxy-based approach must be applied to infer past variations in seawater chemistry. A number of isotope proxies have proven useful and versatile in providing information about different aspects of the evolution of

Earth's surface conditions over the Phanerozoic. Typical examples are  $^{87}\text{Sr}/^{86}\text{Sr}$  reflecting tectonic evolution and changes in chemical weathering (Burke et al., 1982; Veizer et al., 1999),  $\delta^{44/40}\text{Ca}$  showing changes in the global Ca cycle and ocean temperatures (Heuser et al., 2005; Farkaš et al., 2007; Blättler et al., 2012),  $^{187}\text{Os}/^{188}\text{Os}$  (e.g., Peucker-Ehrenbrink and Ravizza, 2000) providing information about short time-scale fluctuations of seawater chemistry and thus, a tool for differentiating between climatic and tectonic forcing, or  $\delta^{11}\text{B}$  used for paleo-pH reconstructions (Sanyal et al., 2000; Jurikova et al., 2020a; Müller

\* Corresponding author.

E-mail address: [tomas.magna@geology.cz](mailto:tomas.magna@geology.cz) (T. Magna).

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et al., 2020).

Lithium with its large relative mass difference between the two stable isotopes ( ${}^6\text{Li}$  and  ${}^7\text{Li}$ ) is very useful for tracing different types of weathering regimes and their intensity (e.g., Kısakürek et al., 2005; Tipper et al., 2012; Pogge von Strandmann et al., 2013; Pogge von Strandmann and Henderson, 2015). Being almost exclusively hosted in silicate minerals, Li is unlike other recorders of oceanic chemistry such as Sr or Os (Misra and Froelich, 2012). The Li isotope composition (expressed as  $\delta^7\text{Li}$ ) of silicate rocks is limited to a narrow range compared to river waters transporting Li to the ocean (e.g., Huh et al., 2001; Pogge von Strandmann et al., 2006; Liu et al., 2015). Furthermore, Li is not known to be involved in any biological processes that might influence the  $\delta^7\text{Li}$  (Lemarchand et al., 2010; Pogge von Strandmann et al., 2016). In addition, through its involvement in the formation of secondary minerals during weathering processes Li can also provide information about the nature of these processes that more traditional tracers cannot (Pogge von Strandmann et al., 2014). In short, weathering of predominantly silicate phases transports metal ions into seawater where they are removed by sea-floor alteration, recrystallization, adsorption and carbonate precipitation, for example by foraminifera and brachiopods (Burton and Vigier, 2011).

Lithium is considered a conservative element in seawater with globally homogeneous Li abundances, a residence time of  $\sim 1.2$  million years and the mixing time of  $\sim 1000$  years (Misra and Froelich, 2012). The seawater  $\delta^7\text{Li}$  value of  $\sim 31\text{‰}$  has remained uniform for the last ca. 8 Myr whereas past seawater  $\delta^7\text{Li}$  reconstructed from a foraminiferal record suggest up to 10‰ variations over the Cenozoic (Košler et al., 2001; Misra and Froelich, 2012; Vigier and Godd ris, 2015) and even larger  $\delta^7\text{Li}$  variations found for pre-Cenozoic seawater (Crockford et al., 2021; Kalderon-Asael et al., 2021). Inorganic carbonates have commonly been employed for inferring the Li isotope evolution of past seawater (e.g., Crockford et al., 2021; Kalderon-Asael et al., 2021). Skeletal remains of marine calcifying organisms, such as corals (Rollion-Bard et al., 2009), mollusks (Dellinger et al., 2018), or brachiopods (Dellinger et al., 2018; Washington et al., 2020; Kalderon-Asael et al., 2021) present an even more promising archive for deconvolving the oceanic  $\delta^7\text{Li}$  variations throughout the Phanerozoic, because they often are well-preserved

during diagenesis. However, it is unclear if Li isotope fractionation between biogenic calcite and seawater, as opposed to precipitation of inorganic calcite (Marriott et al., 2004a), is consistent for a range of natural conditions, if there are particular physico-chemical conditions (i.e. pH and carbonate system parameters, temperature and/or chemical composition of seawater including Mg/Ca or Li/Ca) potentially responsible for Li isotope fractionation (Ullmann et al., 2013; Roberts et al., 2018), and whether organisms' biological influence on biomineralization – “vital effects” – need to be considered (Dellinger et al., 2018).

In order to assess the Li elemental and isotope response in calcite to vital effects and changes in physico-chemical conditions during the growth of biogenic carbonates, we investigated the Li contents and isotope compositions of brachiopod species *Magellania venosa* cultured under controlled experimental settings. In addition, Li contents and isotope compositions were determined for a suite of recent brachiopod species (*Terebratalia transversa*, *Magasella sanguinea*, *Liothyrella neozelanica*, *Liothyrella uva*, *Liothyrella notorcadensis*, *Acrobrochus blochmanni*, *Aerothyris kerguelensis*, *Magellania fragilis*, *Magellania joubini*, *Compsothyris racovitzae*; Fig. 1) to allow a comparison between data from culture and nature and constrain inter-specific variations. Brachiopods present a well-preserved and highly abundant fossil group in the geological record having survived all mass extinctions, and this study aims to contribute to understanding the Li incorporation and fractionation mechanisms in this important archive in order to enable the reconstruction of past  $\delta^7\text{Li}$  of seawater.

## 2. Samples and methods

Approximately 20 mg aliquots of calcium carbonate powders from recent natural and cultured brachiopod shells were prepared using three different sampling strategies as detailed below and schematically plotted in Fig. 2. (i) One valve of each specimen as mentioned below in Section 2.1 was cleaned with dentist tools and bleached in  $\text{H}_2\text{O}_2$  (30% by volume) to remove any adherent contamination and the periostracum or other organic components. The volume of  $\text{H}_2\text{O}_2$  depended on the shell valve size to ensure complete immersion during the oxidation;

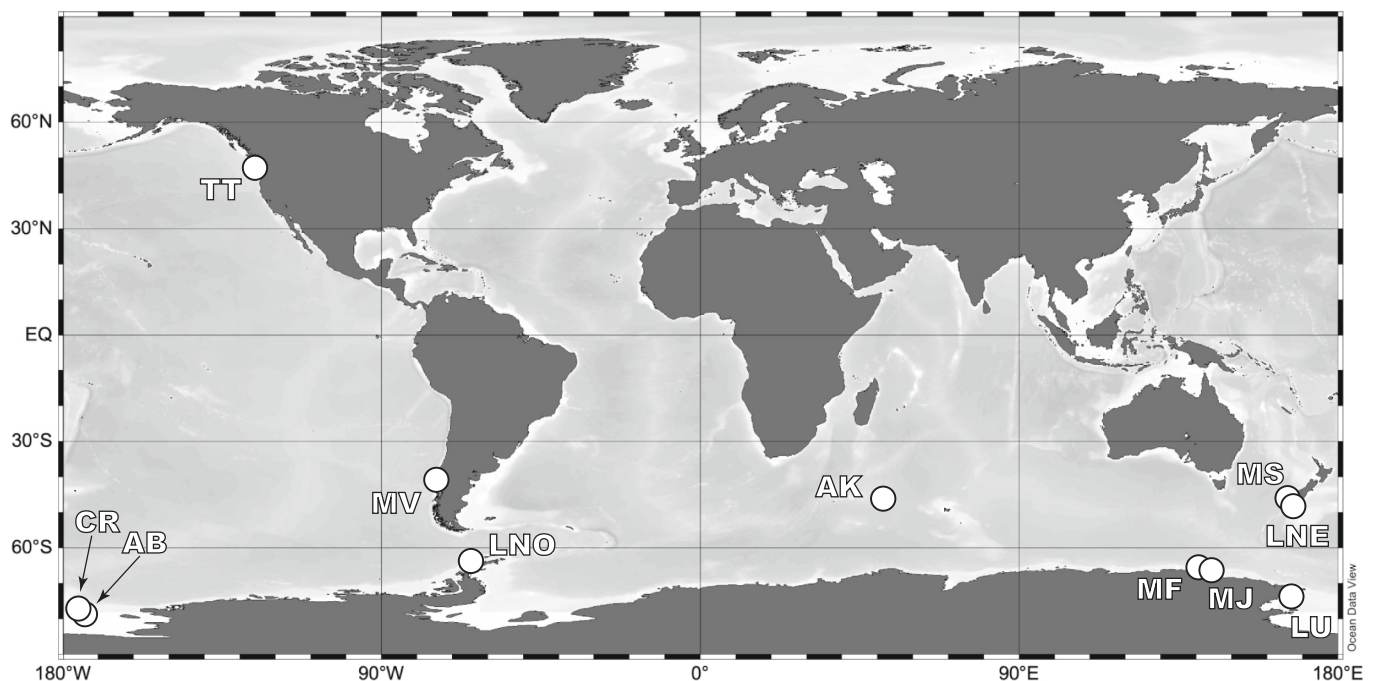


Fig. 1. Map of sampling locations of brachiopods from this study. Abbreviations are as follows: TT – *T. transversa*, MS – *M. sanguinea*, LNE – *L. neozelanica*, LU – *L. uva*, LNO – *L. notorcadensis*, LB – *L. blochmanni*, CR – *C. racovitzae*, AK – *A. kerguelensis*, MF – *M. fragilis*, MJ – *M. joubini*, MV – *M. venosa*.

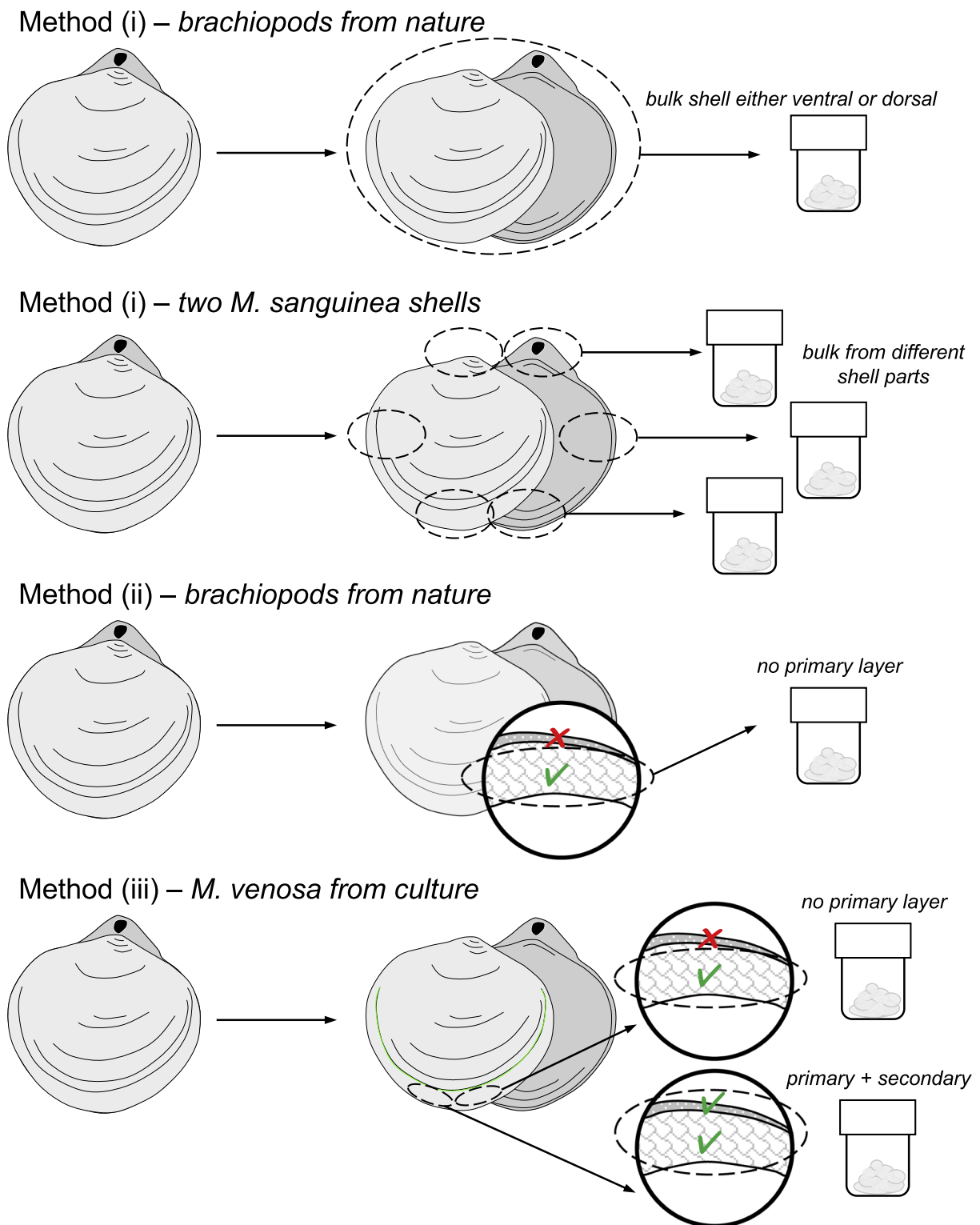


Fig. 2. Schematic drawing of individual sampling strategies applied for sampling of brachiopod shells. See Section 2 for detailed description.

approximately 100–200 ml was typically used. Carefully selected pieces of the shells were ground to powder and dissolved consecutively in high-purity 14 M HNO<sub>3</sub> and 6 M HCl. This preparation method included all shell layers (i.e. primary, secondary and where applicable tertiary layer). (ii) The other half of the shells was prepared following the protocol of Zaky et al. (2015) where solely the secondary layer was sampled. (iii) Individual specimens of *Magellania venosa* collected from both cultures and non-cultured individuals were first rinsed with MilliQ-

water and then bleached in 2.5% H<sub>2</sub>O<sub>2</sub> to remove organics. Subsequently, the shells were photographed using a Zeiss stereomicroscope Discovery.V8 mounted with a fluorescent filter to allow calcein imaging, and therewith identify growth fragments produced in cultures under specific experimental conditions (Fig. 3). The shells were then immersed in 2.5% H<sub>2</sub>O<sub>2</sub> again for 48 h and then cut in half using a slow-speed saw. Finally, the secondary layer was sampled with a precision drill (Proxon) mounted with dentist drilling tips. Using this preparation scheme,

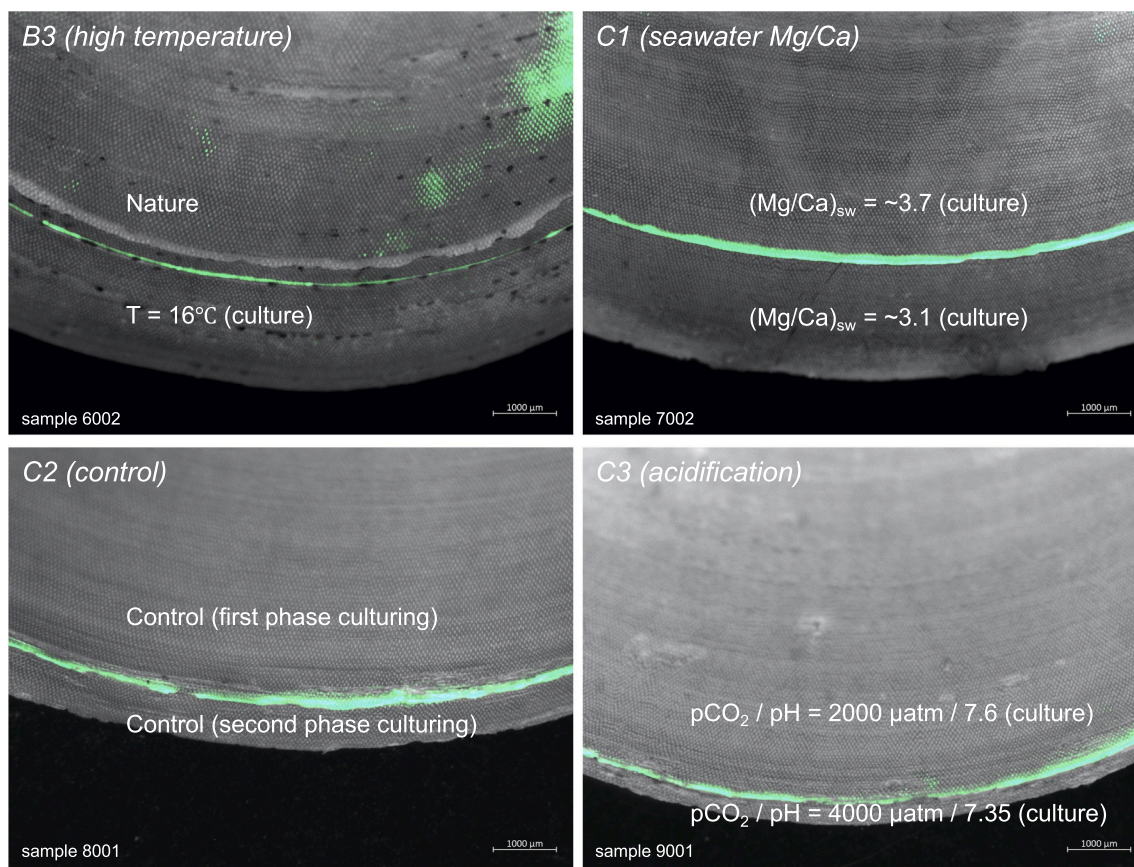


Fig. 3. Images of the cultured *M. venosa* shells taken using a Zeiss stereomicroscope Discovery.V8 mounted with fluorescent filter showing the calcein marking that was used to identify shell parts grown under specific culturing conditions.

two aliquots were prepared for selected specimens, one including the entire shell consisting of primary and secondary layer, and the other containing only the secondary layer with the primary layer removed. As explained below in Section 2.2, the acidification experiments were performed in two phases. In order to accommodate sufficient amounts of Li for analytical and instrumental procedures during the second culturing phase which was shorter and resulted in less shell growth in the pH-pCO<sub>2</sub> treatment as well as its corresponding control treatment, shells of two brachiopod specimens from the same tank were combined to a single sample, i.e. two specimens from the pH-pCO<sub>2</sub> tank and two from the control tank (Fig. 3). All other measurements represent one individual only.

### 2.1. Natural samples

Samples of natural modern brachiopods (*T. transversa*, *M. sanguinea*, *L. neozelanica*, *L. uva*, *L. notorcadensis*, *A. blochmanni*, *A. kerguelensis*, *M. fragilis*, *M. joubini*, *C. racovitzae*) were collected at San Juan Islands/US, Doubtful Sound/NZ, Paterson Inlet/NZ, Îlots des Apôtres/FR, McMurdo Sound/AQ and in the D'Urville Sea/AQ (Fig. 1). *Terebratalia transversa* was collected in San Juan Channel at 64 m water depth (annual temperature range = 7–11 °C); *M. sanguinea* and *L. neozelanica* were collected at 20 m water depth in the Doubtful Sound (annual temperature range = 12–17 °C), and one specimen of *M. sanguinea* was collected at Paterson Inlet at 17.5 m water depth (annual temperature range = 10–13 °C).

Following the collection, *T. transversa*, *M. sanguinea* and *L. neozelanica* were prepared following protocol (i) as described above. For two *M. sanguinea* shells, parts from different areas of the shell (posterior, anterior, side, dorsal and ventral valve) were dissolved to test

for vital effects as reported by Dellinger et al. (2018). The shells of *T. transversa* and *M. sanguinea* consist of a primary and secondary layer (Griesshaber et al., 2007; Goetz et al., 2009), whereas *L. neozelanica* also has a relatively thick tertiary layer (Parkinson et al., 2005; Goetz et al., 2009). Differences in the chemical and isotope composition between the layers have been reported for a wide range of elements. The secondary layer and the tertiary layer, if present, were suggested as the most optimal targets in terms of both preservation in the geological record and kinetic effects (Carpenter and Lohmann, 1995; Auclair et al., 2003; Parkinson et al., 2005; Yamamoto et al., 2010a, 2011; Cusack et al., 2012; Penman et al., 2013; Romanin et al., 2018; Jurikova et al., 2019; Rollion-Bard et al., 2019). Considering this and in order to test different sampling techniques and their effect on the Li elemental/isotope systematics, the other half of the samples was prepared following the protocol of Zaky et al. (2015) (Procedure-5) involving physical scraping, H<sub>2</sub>O<sub>2</sub> bleaching, HCl leaches and Milli-Q water rinses. *Liothyrella uva*, *L. notorcadensis*, *A. blochmanni*, *A. kerguelensis*, *M. fragilis*, *M. joubini* and *C. racovitzae* were prepared following the protocol (ii) as described above.

### 2.2. Cultured samples

Specimens of *Magellania venosa* were collected from the Comau Fjord (42°30'S, 73°50'W) in Chilean Patagonia and transported to GEOMAR Kiel in Germany for culturing. The culturing setup and experimental conditions are detailed elsewhere (Jurikova et al., 2019; Jurikova et al., 2020b) and we only reiterate the key points here. In the laboratory, the brachiopods were first kept for 5 weeks under near-natural conditions to allow them to acclimatize. Subsequently, the brachiopods were labelled with a fluorescent calcein dye (Sigma-Aldrich) to mark the timing of the

**Table 1**  
Experimental settings for culturing of *Magellania venosa*.

Aquarium No.	Treatment	Salinity [psu]	T [°C]	pCO <sub>2</sub> [μatm]	pH	Ω <sub>calcite</sub>	[Mg/Ca] <sub>seawater</sub>
		±0.05	±1	±10%	±0.05		mol/mol
B3	High temperature	30	16	600	8.20	7.5	5.6
C1	Low Mg/Ca	30	10	600	8.05	6.3	3.7/3.1
C3	pCO <sub>2</sub> /pH change	30	10	2000/4000	7.6/7.35	1.1/0.6	6.2/6.9
C2	Control	30	10	600	8.05/8.15	2.0/3.5	6.3/6.6

Experimental settings under which *Magellania venosa* specimens were cultured. Further details on the culturing conditions are available in Jurikova et al. (2020b); their Table 1 or Supplementary material).

newly growing shell parts under experimental conditions. In tanks with two-step culturing (i.e. two-step acidification and Mg/Ca lowering), the brachiopods were marked with calcein a second time, prior to the start of the second experimental phase to distinguish between shell parts grown under the different conditions. Likewise, brachiopods from the control tank were marked along to enable a close comparison to the control group (Fig. 3). Each experimental setting consisted of a separate 150 l tank filled with artificial seawater or culture medium prepared by mixing deionised water and Tropic Marin Pro-Reef commercial sea salt. To maintain water quality, ~10% of the seawater was replaced biweekly with newly prepared artificial seawater from a holding reservoir tank. Water samples were regularly collected from all culturing tanks, filtered and acidified, and stored in cool conditions until elemental and isotope analyses were performed.

For this study, nine individuals of *M. venosa* were used from four different experimental treatments (Table 1; B3, C1, C2 and C3 described elsewhere; Jurikova et al., 2019; Jurikova et al., 2020b). In the tank B3, the water temperature was elevated (from 10 °C representing usual conditions in nature) and maintained at 16 °C to assess temperature proxies and study the impact of increased temperatures on the Li elemental/isotope systematics of brachiopods. In C1 the seawater chemistry was manipulated by adding calcium chloride (CaCl<sub>2</sub>) and lowered to an Mg/Ca ratio of seawater of 3.7 ± 0.2 mol/mol. For a short

period of culturing (2–3 months) the Mg/Ca of seawater was further lowered to 3.1 mol/mol. The aim of this experiment was to evaluate the response of brachiopods to different Mg/Ca (as well as Li/Ca) of the seawater as previous studies have suggested that the geochemical composition of fossil archives requires a correction for changing Mg/Ca of the oceans in the past (e.g., Ligi et al., 2013). In C3, a two-step CO<sub>2</sub>-acidification experiment was settled. Elevated levels of CO<sub>2</sub> were maintained through bubbling of CO<sub>2</sub>-enriched air into the water in order to decrease the pH, and thereby evaluate pH-proxies in brachiopods as well as the impact of CO<sub>2</sub>-induced seawater acidification on brachiopod shell growth (Jurikova et al., 2019; Ye et al., 2019) as also observed in other marine organisms such as corals, mollusks or coccolithophores (Gazeau et al., 2007; Silverman et al., 2009). The pCO<sub>2</sub> levels were first kept at 2000 μatm for nine months, and then increased to 4000 μatm for four months, which resulted in pH of 7.60 and 7.35 ± 0.05, and calcite saturation state Ω<sub>cal</sub> of 1.1 and 0.6, respectively. In C2 typical natural conditions for *M. venosa* were mimicked that served as a control group for the other experiments, with a temperature of 10 °C, pH of 8.0 and 8.15, and Ω<sub>cal</sub> of 2 and 3.5, corresponding to the first and second phase of CO<sub>2</sub> acidification, respectively. Several specimens of *M. venosa* collected in the Comau Fjord during the 2015 sampling campaign but not further cultured were also used in this study and were processed equally to the cultured specimens for comparison.

**Table 2**  
Lithium contents and isotope compositions in reference and other materials from this study.

Name	Type of material	Notes	Li (ppm)	δ <sup>7</sup> Li	2SD
BHVO-2	Hawaiian basalt (USGS)		4.62	4.55	0.19
			4.61	4.57	0.30
			4.63	4.57	0.27
IAPSO	Atlantic Ocean Seawater (OSIL)		0.181	30.84	0.11
			0.184	30.82	0.40
JCt-1	Carbonate (GSJ)		0.37	14.77	0.91
NIST 1d	Argillaceous carbonate (NIST)		2.01	5.47	0.28
			2.12	5.35	0.19
		1 M HCl	1.70	2.18	0.22
		0.2 M HNO <sub>3</sub>	0.98	1.23	0.18
Other materials					
Comau Fjord, Chile	Natural seawater		0.170	30.40	0.47
La Palma, Canary Islands	Natural seawater		0.295	30.75	0.01
MVS-1	Bulk <i>Magellania venosa</i>		2.51	26.87	0.23
			2.58	27.02	0.42
			2.26	26.76	0.50
		Replicate		27.02	0.42
		Replicate		26.76	0.50
			2.21	26.92	0.46
			2.65	26.90	0.48
	Replicate		27.01	0.40	

Results for reference materials are consistent with literature values (e.g., Jeffcoate et al., 2004; Magna et al., 2004; Rosner et al., 2007; Kössler et al., 2009; Huang et al., 2010; Choi et al., 2013; Liu et al., 2015; Bastian et al., 2018; Bohlin et al., 2018; Li et al., 2019; Mayfield et al., 2021). There appears to be some ambiguity regarding the δ<sup>7</sup>Li value for JCt-1 material.

Complete dissolution using a mixture of concentrated HNO<sub>3</sub>–HF and equilibration in HCl (see Magna et al., 2004, for details) was used for the argillaceous carbonate NIST 1d and the results are consistent with Li et al. (2019). Treatment with 0.2 M HNO<sub>3</sub> and 1 M HCl, respectively, to primarily dissolve the carbonate fraction of NIST 1d yielded lower Li contents and δ<sup>7</sup>Li values for leachates obtained independently by both methods, indicating that a non-negligible proportion of isotopically heavy Li is bound in silicate portion (note that NIST 1d is not a pure carbonate and has ~4.1 wt% SiO<sub>2</sub>). MVS-1 is an in-house brachiopod standard further described in Jurikova et al. (2019).

**Table 3**  
Lithium contents and isotope compositions of recent natural brachiopod species.

Sample	ID	Species	Shell part	Location	Li (ppm)	$\delta^7\text{Li}$	2SD	Sample	ID	Species	Shell part	Location	Li (ppm)	$\delta^7\text{Li}$	2SD
D540L	1	<i>Terebratalia transversa</i>	bulk	San Juan Islands/US	2.28	27.39	0.24	DS425L	15	<i>Liothyrella neozelanica</i>	bulk	Doubtful Sound/NZ	1.04	27.14	0.26
S008L	2	<i>Terebratalia transversa</i>	bulk	San Juan Islands/US	2.44	27.97	0.40	DS425L II	16	<i>Liothyrella neozelanica</i>	SL	Doubtful Sound/NZ	1.77	27.79	0.56
D567L	3	<i>Terebratalia transversa</i>	bulk	San Juan Islands/US	2.45	27.59	0.34	DS425L IIa	17a	<i>Liothyrella neozelanica</i>	SL, posterior	Doubtful Sound/NZ	1.45	27.66	0.12
D515L	4	<i>Terebratalia transversa</i>	bulk	San Juan Islands/US	2.35	27.55	0.20	DS425L IIb	17b	<i>Liothyrella neozelanica</i>	SL, ventral left	Doubtful Sound/NZ	1.81	27.44	0.18
D523L	5	<i>Terebratalia transversa</i>	bulk	San Juan Islands/US	2.43	27.54	0.12	DS425L IIc	17c	<i>Liothyrella neozelanica</i>	SL, ventral right	Doubtful Sound/NZ	1.62	27.96	0.32
D514L	6	<i>Terebratalia transversa</i>	bulk	San Juan Islands/US	2.28	27.73	0.16			<b>Average (17a–c)</b>	<b>SL</b>		<b>1.63</b>	<b>27.69</b>	<b>0.52</b>
		<b>Average (1–6)</b>			<b>2.37</b>	<b>27.63</b>	<b>0.40</b>	AA02B	18	<i>Liothyrella uva</i>	SL	McMurdo Sound/AQ	2.49	26.00	0.41
D523L II	7	<i>Terebratalia transversa</i>	SL	San Juan Islands/US	2.35	27.30	0.38	AA05	19	<i>Liothyrella notorcadensis</i>	SL	Lambda Island/AQ	2.42	26.05	0.13
DS410L	8	<i>Magasella sanguinea</i>	bulk	Doubtful Sound/NZ	2.06	26.77	0.07	AA06	20	<i>Acrobrochus blochmanni</i>	SL	McMurdo Sound/AQ	2.55	26.55	0.18
DS412L	9	<i>Magasella sanguinea</i>	bulk	Doubtful Sound/NZ	2.04	27.38	0.49	AA09	21	<i>Compsothyris racovitzae</i>	SL	McMurdo Sound/AQ	2.48	26.07	0.19
DS411L	10	<i>Magasella sanguinea</i>	bulk	Doubtful Sound/NZ	1.88	27.21	0.59	AA09B	22	<i>Compsothyris racovitzae</i>	SL	McMurdo Sound/AQ	2.34	26.48	0.11
PS5L	11	<i>Magasella sanguinea</i>	bulk	Paterson Inlet/NZ	2.25	27.18	0.78	AA12	23	<i>Aerothyris kerguelensis</i>	SL	Îlots des Apôtres/FR	1.86	26.61	0.38
DS409L	12	<i>Magasella sanguinea</i>	bulk	Doubtful Sound/NZ	1.96	27.08	0.39	AA13	24	<i>Aerothyris kerguelensis</i>	SL	Îlots des Apôtres/FR	1.88	26.45	0.34
DS409La	12a	<i>Magasella sanguinea</i>	dorsal posterior	Doubtful Sound/NZ	1.80	26.91	0.05	AA14B	25	<i>Magellania fragilis</i>	SL	D'Urville Sea/AQ	2.37	26.24	0.18
DS409Lb	12b	<i>Magasella sanguinea</i>	dorsal left	Doubtful Sound/NZ	1.94	27.09	0.27	AA16B	26	<i>Magellania joubini</i>	SL	D'Urville Sea/AQ	2.17	25.62	0.09
DS409Lc	12c	<i>Magasella sanguinea</i>	dorsal center	Doubtful Sound/NZ	1.96	27.33	0.14	MB1564	27	<i>Magellania joubini</i>	SL	D'Urville Sea/AQ	2.21	25.69	0.42
DS409Ld	12d	<i>Magasella sanguinea</i>	dorsal anterior	Doubtful Sound/NZ	2.03	27.05	0.13	MB1565	28	<i>Magellania joubini</i>	SL	D'Urville Sea/AQ	2.34	25.22	0.23
DS409Le	12e	<i>Magasella sanguinea</i>	dorsal anterior	Doubtful Sound/NZ	2.07	27.01	0.20	29a		<i>Magellania venosa</i>	bulk	Comau Fjord/CL	2.95	27.81	0.06
DS409L II	13	<i>Magasella sanguinea</i>	bulk	Doubtful Sound/NZ	1.98	27.09	0.53	29b		<i>Magellania venosa</i>	bulk	Comau Fjord/CL	2.73	27.75	0.16
DS409L IIa	13a	<i>Magasella sanguinea</i>	ventral posterior	Doubtful Sound/NZ	1.94	27.07	0.13	29c		<i>Magellania venosa</i>	complete SL	Comau Fjord/CL	3.27	27.71	0.42
DS409L IIb	13b	<i>Magasella sanguinea</i>	ventral anterior	Doubtful Sound/NZ	1.96	27.00	0.38	29d		<i>Magellania venosa</i>	complete SL	Comau Fjord/CL	2.25	27.50	0.20
DS409L IIc	13c	<i>Magasella sanguinea</i>	ventral middle	Doubtful Sound/NZ	2.03	27.19	0.35	29e		<i>Magellania venosa</i>	part of SL	Comau Fjord/CL	2.79	28.10	0.11
		<b>Average (8–13c)</b>			<b>1.99</b>	<b>27.10</b>	<b>0.32</b>	29f		<i>Magellania venosa</i>	part of SL	Comau Fjord/CL	3.48	27.96	0.20
DS410La	14a	<i>Magasella sanguinea</i>	SL, dorsal	Doubtful Sound/NZ	2.12	26.69	0.09			<b>Average (29a–f)</b>			<b>2.91</b>	<b>27.81</b>	<b>0.42</b>
DS410Lb	14b	<i>Magasella sanguinea</i>	SL, posterior	Doubtful Sound/NZ	2.12	27.09	0.15								
		<b>Average (14a–b)</b>			<b>2.12</b>	<b>26.89</b>	<b>0.57</b>								

SL – secondary layer.

### 2.3. Analytical and instrumental techniques

Analytical procedures for ion exchange chemistry and mass spectrometry routines were performed at the Czech Geological Survey, following the established analytical protocols (Magna et al., 2004). The pre-cleaned micro-drilled carbonate powders were dissolved in 0.2 M HNO<sub>3</sub> and Li was isolated using BioRad AG50W-X8 (200–400 mesh) resin and 1 M HNO<sub>3</sub>–80% methanol mixture. For natural and artificial seawater samples, 50 µl aliquots were evaporated to dryness and re-dissolved in 0.2 M HNO<sub>3</sub>. Due to high Na/Li of seawater, these aliquots were split in two or four columns and Li cuts were re-combined for Li isotope measurements. Lithium contents and isotope compositions were determined using a Neptune MC-ICPMS (ThermoFisherScientific), connected to a CETAC Aridus II desolvating unit, with a skimmer X-cone and a PFA nebulizer (nominally 30 µl.min<sup>-1</sup>). The resulting <sup>7</sup>Li signal was typically 600–1000 V/ppm. Lithium contents were measured against 1-, 10- and 30-ppb L-SVEC solutions. For Li isotope measurements the standard–sample bracketing method was employed. Each run consisted of 30 individual readings with an integration time of 8 s per one reading. The data is reported relative to the L-SVEC standard (Flesch et al., 1973) and calculated as  $\delta^7\text{Li} (\text{‰}) = [({}^7\text{Li}/{}^6\text{Li})_{\text{sample}} / ({}^7\text{Li}/{}^6\text{Li})_{\text{L-SVEC}} - 1] \times 1000$ , with all errors reported as two standard deviations (2SD). The accuracy and precision of the entire procedure was monitored by replicate measurements of reference materials BHVO-2 (basalt; USGS), NIST 1d (carbonate; NIST), JCT-1 (carbonate; GSJ) and IAPSO (seawater; OSIL). In addition, an in-house carbonate material prepared from a natural specimen of *M. venosa* collected in the Comau fjord (MVS-1) and natural seawater samples, collected offshore Chile and close to La Palma, Canary Islands, respectively, were also analyzed. Their results are listed in Table 2.

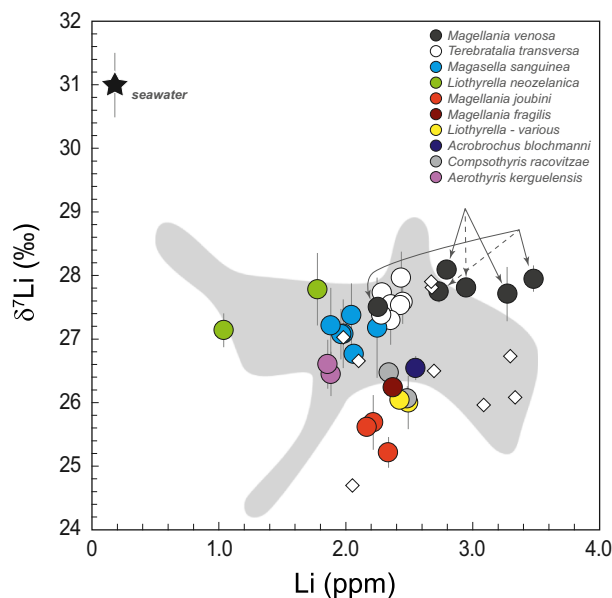


Fig. 4. The  $\delta^7\text{Li}$  values vs. Li concentrations of the analyzed brachiopod shells. To allow comparison between our data given as Li concentrations with data from Dellinger et al. (2018) and Washington et al. (2020), reported as Li/Ca ( $\mu\text{mol}/\text{mol}$ ), their data was converted to Li concentrations (assuming 40% Ca content in the brachiopod CaCO<sub>3</sub>). Open diamonds denote data for *T. transversa* and the grey field represents data from other species published by Dellinger et al. (2018) and Washington et al. (2020). Arrows connect samples from the same specimen and dashed lines point to bulk aliquots. For clarity, some samples of shell parts were omitted from the figure because their Li elemental and isotope systematics are largely indistinguishable; their results are only listed in Table 3 (DS409La–e, DS409L Ila–c, DS425L Ila–c).

Table 4

Lithium contents and isotope compositions of cultured brachiopod samples and artificial seawater from the different experimental treatments.

Sample ID	Type	Li [ppm/ppb]	$\delta^7\text{Li}$	2SD
C1 (Mg/Ca)	Bulk	2.21	-3.43	0.16
C1	Bulk	2.23	-3.10	0.07
C1	Secondary layer	2.14	-2.95	0.10
C1	Secondary layer	2.55	-2.90	0.08
<b>Average</b>		<b>2.29</b>	<b>-3.10</b>	<b>0.48</b>
C1	Bulk (conditions changed)	2.47	-3.17	0.02
C1 12/16	Culture medium/seawater	155.56	2.28	0.11
C1 02/17	Culture medium/seawater	160.34	1.47	0.39
C1 04/17	Culture medium/seawater	151.71	1.42	0.19
C1 06/17	Culture medium/seawater	150.63	1.42	0.11
<b>Average</b>		<b>155.87</b>	<b>1.44</b>	<b>0.06</b>
B3 (T)	Bulk	2.30	-1.48	0.40
B3	Bulk	2.50	-1.16	0.21
B3	Secondary layer	2.12	-1.27	0.24
B3	Secondary layer	1.87	-1.22	0.46
<b>Average</b>		<b>2.20</b>	<b>-1.28</b>	<b>0.28</b>
B3 12/16	Culture medium/seawater	159.82	4.70	0.37
B3 02/17	Culture medium/seawater	164.83	2.28	0.35
B3 04/17	Culture medium/seawater	169.19	1.53	0.34
B3 06/17	Culture medium/seawater	152.13	1.22	0.25
<b>Average</b>		<b>161.49</b>	<b>1.37</b>	<b>0.44</b>
C3 (pH, pCO <sub>2</sub> )	Bulk	2.41	-1.26	0.17
C3	Bulk	2.55	-0.99	0.23
C3	Secondary layer	2.57	-1.18	0.15
C3	Secondary layer	2.48	-0.64	0.39
<b>Average</b>		<b>2.50</b>	<b>-1.02</b>	<b>0.55</b>
C3	Bulk (conditions changed)	3.10	-1.99	0.35
C3 12/16	Culture medium/seawater	161.99	3.24	0.06
C3 02/17	Culture medium/seawater	142.65	1.48	0.15
C3 04/17	Culture medium/seawater	165.51	1.30	0.27
C3 06/17	Culture medium/seawater	147.55	1.35	0.09
<b>Average</b>		<b>154.42</b>	<b>1.37</b>	<b>0.19</b>
C2 (Control)	Bulk	2.65	-1.33	0.17
C2	Bulk	3.05	-1.30	0.16
C2	Secondary layer	2.39	-1.45	0.07
C2	Secondary layer	2.95	-1.46	0.40
<b>Average</b>		<b>2.76</b>	<b>-1.39</b>	<b>0.16</b>
C2	Bulk (conditions changed)	3.20	-2.00	0.20
C2 12/16	Culture medium/seawater	166.31	2.29	0.23
C2 02/17	Culture medium/seawater	151.00	1.25	0.26
C2 04/17	Culture medium/seawater	173.84	1.02	0.22
C2 06/17	Culture medium/seawater	151.62	1.15	0.08
<b>Average</b>		<b>163.72</b>	<b>1.14</b>	<b>0.23</b>

The sample preparation protocol (i, ii, iii) is according to description provided in Section 2.

The non-cultured samples were used to test different sampling techniques, and they thus refer to a single brachiopod shell. The Li contents are given in ppm for the brachiopod samples and in ppb for artificial seawater.

### 3. Results

The Li contents and  $\delta^7\text{Li}$  values (per mil difference of <sup>7</sup>Li/<sup>6</sup>Li from L-SVEC reference material) for various recent brachiopod species from natural conditions are listed in Table 3. The mean [Li] = 2.4 ppm ( $n = 7$ ) for bulk aliquots as well as secondary layer aliquots of *T. transversa*, [Li] = 2.0 ppm ( $n = 14$ ) for aliquots of *M. sanguinea* with both layers and [Li] = 2.1 ppm ( $n = 3$ ) for solely the secondary layer, and [Li] = 1.0 ppm ( $n = 1$ ) for *L. neozelanica* were found. For the latter species, mean [Li] = 1.7 ppm ( $n = 4$ ) through sampling of only the secondary layer was obtained, indicating that the tertiary layer is significantly depleted in Li. *Magellania venosa* showed a mean [Li] of 2.9 ppm ( $n = 6$ ) with no systematic differences between the samples of the bulk shell and aliquots consisting of only the secondary layer. For the other brachiopod species only the secondary layer was measured and for most species the [Li] was similar to *T. transversa* and *M. venosa*. Only *A. kerguelensis* showed lower [Li] of 1.87 ppm ( $n = 2$ ).

The  $\delta^7\text{Li}$  ranged 27.3–28.0‰ for *T. transversa*, 26.3–27.4‰ for *M. sanguinea*, 27.1–27.7‰ for *L. neozelanica* and 27.5–28.1‰ for *M. venosa* in natural specimens. The other species gave  $\delta^7\text{Li}$  similar to this with *L. uva* at  $26.00 \pm 0.41\text{‰}$ , *L. notorcadensis* at  $26.05 \pm 0.13\text{‰}$ , *A. blochmanni* at  $26.55 \pm 0.18\text{‰}$ , *C. racovitzae* at  $26.07 \pm 0.19\text{‰}$ , and  $26.48 \pm 0.11\text{‰}$ , *A. kerguelensis* at  $26.61 \pm 0.38\text{‰}$  and  $26.45 \pm 0.34\text{‰}$ , *M. fragilis* at  $26.24 \pm 0.18\text{‰}$  and *M. joubini* at  $25.51 \pm 0.49\text{‰}$  ( $n = 3$ ). The new data match the values reported by Washington et al. (2020) and Dellinger et al. (2018) with their reported mean  $\delta^7\text{Li}$  values of  $26.8 \pm 0.5\text{‰}$  ( $1\sigma$ ) and  $26.6 \pm 1.0\text{‰}$ , respectively (Fig. 4).

Three out of four specimens (three *M. sanguinea* and one *L. neozelanica*) tested for ontogenetic/vital effects by measuring different parts of a shell specified in Table 3 (posterior, anterior, sides) did not reveal any within-shell Li elemental/isotope variation. All  $\delta^7\text{Li}$  values obtained from different parts of the individual shells were essentially overlapping, ranging 26.9–27.3‰ (dorsal *M. sanguinea*), 27.0–27.2‰ (ventral *M. sanguinea*) and 27.4–27.8‰ (*L. neozelanica*), respectively. The mean [Li] of 2.1 ppm ( $n = 2$ ) for *M. sanguinea* is consistent with the data for bulk specimens of the same species prepared following the preparation protocol (ii) as described in Section 2.

The Li contents and  $\delta^7\text{Li}$  values for specimens of cultured *M. venosa* and artificial seawater are given in Table 4. There are no systematic differences in Li contents (2.3–3.5 ppm), nor do Li isotope compositions ( $\delta^7\text{Li} = 27.5\text{--}28.1\text{‰}$ ) vary for *M. venosa* samples that were prepared using the different sampling strategies (i, ii, iii). In summary, the analyzed samples of different modern brachiopod species show a mean fractionation between brachiopod calcite and seawater of  $\Delta^7\text{Li}_{\text{calcite-seawater}} = \sim -3\text{‰}$  (defined as  $\delta^7\text{Li}_{\text{calcite}} - \delta^7\text{Li}_{\text{seawater}}$ ), with modern seawater at  $\sim 31\text{‰}$  (e.g., Jeffcoate et al., 2004; Millot et al., 2004). The  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  is approximately equal to  $\ln(\alpha) \times 1000$ , and the fractionation factor  $\alpha_{\text{calcite-seawater}}$  is 0.997.

The absolute  $\delta^7\text{Li}$  values of the cultured *M. venosa* are different when compared to samples from nature due to the use of artificial seawater as a culturing medium. The  $\delta^7\text{Li}$  of the artificial seawater in the control tank (C2, control) averaged at  $1.14 \pm 0.23\text{‰}$  and the corresponding brachiopod shells showed a mean  $\delta^7\text{Li} = -1.39 \pm 0.16\text{‰}$  ( $\Delta^7\text{Li}_{\text{calcite-seawater}} = -2.5\text{‰}$ ), in agreement with fractionations observed in natural specimens. In the high temperature treatment (B3), the average  $\delta^7\text{Li}$  for brachiopod and seawater was  $-1.28 \pm 0.28\text{‰}$  and  $1.37 \pm 0.44\text{‰}$ , respectively ( $\Delta^7\text{Li}_{\text{calcite-seawater}} = -2.7\text{‰}$ ), i.e. without an observable effect of temperature on  $\Delta^7\text{Li}_{\text{calcite-seawater}}$ . In the acidification treatment (C3), at pH = 7.60 the average brachiopod  $\delta^7\text{Li}$  was  $-1.02 \pm 0.55\text{‰}$  with the artificial seawater  $\delta^7\text{Li}$  of  $1.37 \pm 0.19\text{‰}$  ( $\Delta^7\text{Li}_{\text{calcite-seawater}} = -2.4\text{‰}$ ); at pH = 7.35 the brachiopod yielded a  $\delta^7\text{Li}$  of  $-1.99 \pm 0.35\text{‰}$ , thereby increasing the  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  to  $-3.4\text{‰}$ . The largest fractionation was observed in C1 (change in Mg/Ca) where the mean brachiopod  $\delta^7\text{Li}$  of  $-3.10 \pm 0.48\text{‰}$  and seawater  $\delta^7\text{Li}$  of  $1.44 \pm 0.06\text{‰}$  amounted to a  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  of  $-4.5\text{‰}$  for Mg/Ca = 3.7; for Mg/Ca = 3.1, the resulting  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  was  $-4.6\text{‰}$ . The results show that under most conditions the fractionation of Li isotopes between brachiopod calcite and seawater is relatively constant ( $\sim -2.8 \pm 0.8\text{‰}$ ). However, both the more pronounced change in seawater carbonate chemistry (decrease in  $\text{pCO}_2/\text{pH}$  during the second acidification phase) as well as the chemical composition of the seawater (lower Mg/Ca or Li/Ca) may further shift the  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  by approximately  $-2\text{‰}$  (up to  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  of  $-4.6\text{‰}$ ).

## 4. Discussion

### 4.1. Intra-shell variations and vital effects

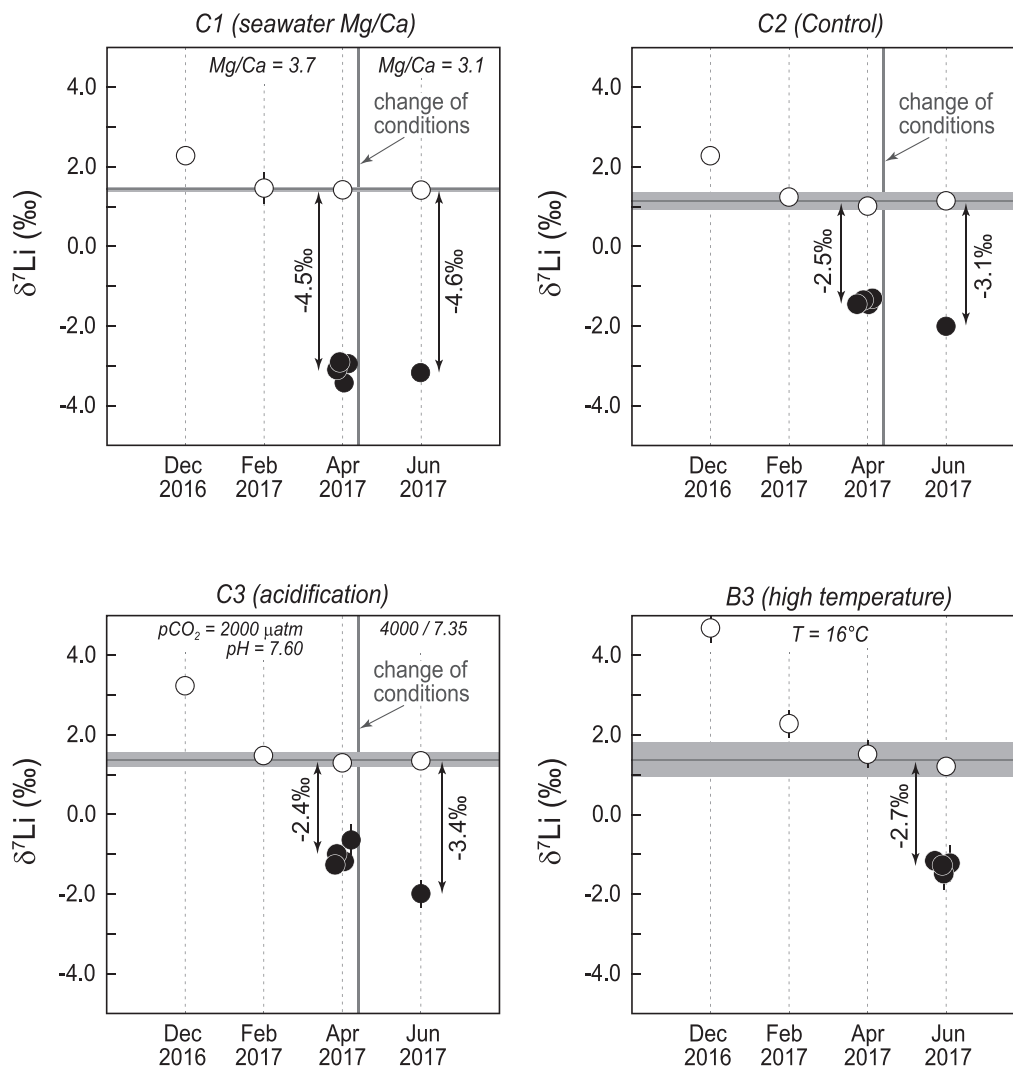
Intra-shell chemical variations in brachiopods have been observed along the ontogenetic gradient (posterior to anterior) as well as the different shell layers (primary vs. secondary or tertiary) (e.g., Buening and Spero, 1996; Auclair et al., 2003; Pérez-Huerta et al., 2008; Yamamoto et al., 2010b; Rollion-Bard et al., 2019). While the former is

understood to result largely from faster growth rates during earlier life stages and/or variations in the ambient conditions over the individual's lifetime, the latter has been linked to kinetic effects during the precipitation of the specific layers and associated textures as well as biological modulation of the conditions at the calcification site. These predominantly vital effects may present a significant source of stable isotope fractionation in living specimens and thus, impose measurable uncertainties on proxy-based reconstructions. For example, at a high resolution ( $\mu\text{m}$ -scale), carbon and oxygen isotopes as well as several trace element indicators, have been shown to vary in the different shell layers of individual brachiopods due to the layer ultrastructure and secretion rate (Penman et al., 2013; Takizawa et al., 2017; Romanin et al., 2018; Rollion-Bard et al., 2019). Boron isotopes have also been reported to vary to a high resolution across the shell following a physiological gradient with the innermost shell areas being influenced by the organism's pH-regulation processes during calcification (Jurikova et al., 2019).

Inorganic calcite shows a  $\Delta^7\text{Li}_{\text{calcite-solution}}$  of  $\sim -3\text{‰}$  compared to the growth solution (Marriott et al., 2004b), at least under seawater conditions, because inorganic calcite precipitated at pH  $\sim 7$  (Marriott et al., 2004a) and cave-analogue experiments (Day et al., 2021) yielded more depleted  $\Delta^7\text{Li}_{\text{calcite-solution}}$  values of  $\sim -8\text{‰}$  and  $\sim -9\text{‰}$ , respectively. This greater difference between solution and carbonate is also consistent with that reported for aragonite from Bahamas (Pogge von Strandmann et al., 2019), indicating that mineralogy of carbonates used to infer  $\delta^7\text{Li}$  of seawater plays a critical role (Marriott et al., 2004b). Brachiopod shells show very similar  $\delta^7\text{Li}$  values to the inorganic calcite of Marriott et al. (2004b) suggesting that vital effects are of minor importance in this regard. However, the different shell layers have shown different fractionation factors for other stable isotopes suggesting that this uneven distribution might also play a role when looking at Li isotope compositions. Washington et al. (2020) analyzed material from the primary layer of modern brachiopods. The primary layer yielded consistently but not systematically lower values than the secondary layer and the primary layer was not recommended for future studies. In this study, however, selected specimens of *M. venosa*, *M. sanguinea* and *L. neozelanica* with and without the primary layer returned mutually consistent  $\delta^7\text{Li}$  values (Fig. 4; Table 3). This indicates that for Li, bulk specimens may potentially be utilized following careful examination and thorough surface cleaning. It also follows from the new results in this study that the presence of a thick tertiary layer does not impart any measurable shift in  $\delta^7\text{Li}$  (although the tertiary layer is indeed more depleted in Li) and, therefore, the sampling strategies may be simplified for Li isotope analyses.

The intra-shell distribution of Li (dorsal, ventral shell, anterior/posterior part) which could potentially cause fractionation of Li isotopes during growth of a new shell is minimal or not existent in the examined brachiopods. Two different investigated specimens of *M. sanguinea* returned mean  $\delta^7\text{Li} = 27.08 \pm 0.31\text{‰}$  (sub-samples 12a–e) and  $27.09 \pm 0.10\text{‰}$  (sub-samples 13a–c), respectively, which are in both cases identical to the corresponding bulk aliquots ( $27.08 \pm 0.39\text{‰}$  and  $27.09 \pm 0.53\text{‰}$ , respectively). This clearly indicates that vital effects for Li in brachiopods are negligible, or at least cannot be resolved with current analytical tools, and may be considered marginal. Sub-per mil effects, if existing at all, will thus unlikely impart any measurable effects on Li inventory of brachiopods and, by inference, ocean water Li budget. The lack of Li isotope variations within a single shell was also recently observed by Dellinger et al. (2018) for a specimen of *T. transversa* from Puget Sound, USA, which is in a close agreement with the new results from this study. The data also suggests that the absence of vital effects is also valid for other brachiopod species, such as *L. neozelanica*, because the combined mean  $\delta^7\text{Li} = 27.69 \pm 0.52\text{‰}$  for the three sub-aliquots (samples 17a–c) is identical with the corresponding bulk aliquot (sample 16;  $27.79 \pm 0.56\text{‰}$ ). Therefore, the cumulative results for the three different species indicate a robust behaviour of Li in brachiopods and their relevance for reconstruction of Li isotope evolution of seawater.





**Fig. 5.** Lithium isotope compositions in experimentally grown brachiopods and samples of artificial seawater collected over a period of ~8 months. For treatments C1, C2 and C3, the last three measurements were used to calculate the mean  $\delta^7\text{Li}$  value of seawater in the respective tank. For experiment B3, only the last two measurements were used for the calculation. It is apparent that several months are required for the seawater solution to equilibrate under the experimental conditions. The calculated  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  values are given for brachiopod samples collected immediately before the change in conditions and for specimens grown for further ~2 months under different conditions.

#### 4.2. Effects of physico-chemical factors

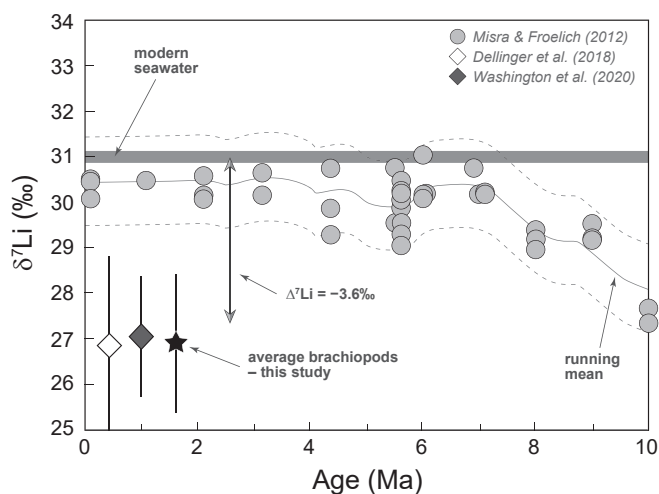
A range of physical (temperature) and chemical (pH/pCO<sub>2</sub>, carbonate chemistry, elemental composition of seawater, salinity) factors can control elemental partitioning and, by inference, isotope fractionation during growth of calcite, aragonite and other Ca-dominated phases in the oceans. Examples for this are the Mg/Ca ratio in foraminiferal calcite that is related to temperature (e.g., Dissard et al., 2010) or  $\delta^{11}\text{B}$  in brachiopods, which is dependent on the pH of the solution from which it precipitated (Penman et al., 2013; Jurikova et al., 2019). The influence of salinity and temperature on Li incorporation into calcite and aragonite has proven to be negligible (Marriott et al., 2004a; Marriott et al., 2004b). In contrast, growth rate and pH have been shown to significantly affect the Li incorporation into experimentally grown calcite. However, these findings cannot be directly applied to marine-grown carbonates because the experiments were performed with reactive fluids that did not include important ions in seawater such as Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> (Füger et al., 2019).

In biogenic carbonates such as foraminiferal species *Amphistegina lessonii* and *A. lobifera* a lack of sensitivity of  $\delta^7\text{Li}$  to varying temperature and pH was experimentally verified whereas  $\delta^7\text{Li}$  versus DIC showed a strong positive covariation (Vigier et al., 2015). In contrast to this, Roberts et al. (2018) have shown a pH dependence of  $\delta^7\text{Li}$  in cultured *A. lessonii*, hypothesized to be due to the varying strength of the hydration sphere of Li<sup>+</sup> in the solution. This pH-dependent relationship of

$\delta^7\text{Li}$  was further underscored with natural samples of epi-benthic foraminifera *Cibicoides mundulus* and *C. wuellerstorfi*.

The present study aimed to evaluate the effect of seawater chemistry, namely carbonate chemistry (pCO<sub>2</sub>/pH), seawater chemical composition (Mg/Ca, Li/Ca), and temperature (Table 2; Fig. 3) on the incorporation and isotope fractionation of Li in the cultured brachiopod species of *M. venosa* (Fig. 5). Our results from the culturing experiments show comparable  $\delta^7\text{Li}$  values in individuals grown at the elevated temperature of 16 °C (B3;  $\Delta^7\text{Li}_{\text{calcite-seawater}} = -2.7\text{‰}$ ) and in the control treatment at T = 10 °C (C2; average at  $\Delta^7\text{Li}_{\text{calcite-seawater}} = -2.5\text{‰}$ ). This implies that  $\delta^7\text{Li}$  is not affected by temperature as well as growth rate since the new shell growth in individuals from the high temperature treatment was overall strongly reduced (Fig. 3; see also Jurikova et al., 2020b, for further details) in comparison to all other treatments. The lack of the effect of growth rate on  $\delta^7\text{Li}$  is largely expected since we also did not observe any variations in  $\delta^7\text{Li}$  between different brachiopod shell layers (secondary vs. tertiary), which are understood to precipitate at different rates. The lack of temperature effects on  $\delta^7\text{Li}$  in our cultured *M. venosa* specimens is also in agreement with the findings of Dellinger et al. (2018), who did not observe any relationship between temperature and  $\delta^7\text{Li}$  in their field-collected brachiopod specimens. Similarly, for inorganic calcite and coralline aragonite Marriott et al. (2004b) showed that temperature does not significantly influence  $\delta^7\text{Li}$ , although Li/Ca inversely correlated with temperature.

In two culturing treatments, the high pCO<sub>2</sub>-low pH (C3) and low



**Fig. 6.** Lithium isotope evolution of seawater reconstructed from a foraminiferal record reported by Misra and Froelich (2012). Mean  $\delta^7\text{Li}$  value for natural brachiopod specimens (bulk or secondary layer) from this study at  $26.9 \pm 1.5\text{‰}$  is consistent with earlier values reported for brachiopods ( $26.9 \pm 2.0\text{‰}$ , Dellinger et al., 2018;  $27.1 \pm 1.3\text{‰}$ , Washington et al., 2020). The  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  of  $\sim -3.6\text{‰}$  from mean ocean water can thus be applied for reconstructing the evolution of past Li isotope composition of ocean water using selected brachiopod species, following a careful treatment of samples.

Mg/Ca (C1), we found that the  $\delta^7\text{Li}$  of *M. venosa* was more fractionated compared to nature, control and/or high temperature treatments. In the acidification treatment (C3), during the first phase with  $p\text{CO}_2$  of 2000  $\mu\text{atm}$  and pH of 7.60 the  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  was  $-2.4\text{‰}$  and hence within the range of values obtained from the control tank. The  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  increased to  $-3.4\text{‰}$  during the second, more extreme acidification phase under  $p\text{CO}_2$  of 4000  $\mu\text{atm}$  and pH of 7.35. Even more pronounced  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  values were found in C1, where the  $\Delta^7\text{Li}_{\text{calcite-seawater}} = -4.5\text{‰}$  for Mg/Ca = 3.7 and  $\Delta^7\text{Li}_{\text{calcite-seawater}} = -4.6\text{‰}$  for Mg/Ca = 3.1. These results suggest that carbonate and major ion chemistry may, to a considerable extent, influence the Li isotope fractionation in biogenic calcite, at least in the brachiopod species *M. venosa*. It remains unclear whether a single underlying parameter could be responsible for the observed changes in  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  from both experiments or if this is a mutual influence of several independent parameters. The C1 treatment was manipulated through regular addition of  $\text{CaCl}_2$  which also affected the carbonate chemistry (e.g., through increased  $\Omega_{\text{cal}}$ ). However, we were unable to find a systematic link to the acidification experiments through a common carbonate system parameter. The addition of  $\text{CaCl}_2$  lowers Mg/Ca but also other elemental ratios, importantly also Li/Ca. Thus, it appears that a change in Li isotope fractionation could be affected by the Li/Ca of seawater, if not alone by the increased  $\text{Ca}^{2+}$  content in the culture seawater. Clearly, targeted studies are needed to investigate this hypothesis.

In contrast to the findings from foraminifera (Roberts et al., 2018), our results suggest a positive relationship between  $\delta^7\text{Li}$  and pH. Considering that the carbonate chemistry in our experiments was coupled, unlike in the cultures of Roberts et al. (2018), the observed  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  variation could be equally linked to both pH and  $\Omega_{\text{cal}}$ . The different nature of the carbonate system could explain the contrary relationships and might point towards  $\Omega_{\text{cal}}$ , rather than pH, as the variable affecting  $\Delta^7\text{Li}_{\text{calcite-seawater}}$ . We note, however, that only one measurement could be performed on *M. venosa* from the high  $p\text{CO}_2$ -low pH conditions (4000  $\mu\text{atm}$  and 7.35, respectively) due to the shorter duration of this experimental phase and, hence, less material available. Further calibration studies in brachiopods, but also other calcifiers would be desirable to corroborate the  $\delta^7\text{Li}$  link with carbonate chemistry, and these should also take into account the  $\Omega_{\text{cal}}$  (not only pH).

#### 4.3. Implications for reconstructions of Li isotope composition of seawater

Modern seawater shows a constant Li abundance of ca. 180 ppb (Seyfried et al., 1984), paralleled by homogeneous  $\delta^7\text{Li} = 31\text{‰}$  (Misra and Froelich, 2012). A foraminiferal record confirms this  $\delta^7\text{Li}$  homogeneity of the ocean water back to ca. 8 Ma (Hathorne and James, 2006; Misra and Froelich, 2012), although it is apparent that some variations exist even for foraminiferal species younger than ca. 1 Ma (Košler et al., 2001). The Cenozoic foraminifera record a gradual increase from  $\delta^7\text{Li}$  of  $\sim 22\text{‰}$  in the Paleocene towards the modern values attained in the Pliocene, and the Cretaceous–Paleogene boundary is associated with an abrupt decline from  $\delta^7\text{Li}$  at ca. 26–27‰ to  $\sim 22\text{‰}$  (Misra and Froelich, 2012). In fact, Li, Sr and Os isotope records display similar temporal profiles and significant variations, in particular at the Cretaceous–Paleogene boundary, due to massive continental denudation and acid rain weathering of continental soils (Misra and Froelich, 2012, and references therein). In this regard, a reliable record of Li isotope evolution of ocean water on time scales extending beyond the Cenozoic would be of great importance for past weathering histories and climatic changes (e.g., Pogge von Strandmann et al., 2013).

The experimentally obtained  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  value of  $\sim -2.8 \pm 0.8\text{‰}$  based on cultured brachiopods is consistent with laboratory data for inorganic calcite reported by Marriott et al. (2004b). This  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  value also agrees well with data from natural specimens of *M. venosa* ( $\Delta^7\text{Li}_{\text{calcite-seawater}} = -3.2\text{‰}$ ; this study) and all species ( $\Delta^7\text{Li}_{\text{calcite-seawater}} = -3.6\text{‰}$ ) analyzed in this study, and compares well with other natural data for *Campages mariae*, *Laqueus rubellus*, *T. transversa* and *Frenulina sanguinolenta*, reported by Dellinger et al. (2018) and Washington et al. (2020). Our newly determined  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  value thus appears rather robust over a range of modern latitudinal settings, taxonomies and temperature conditions. Pronounced changes in seawater composition (specifically in terms of lowering Mg/Ca and Li/Ca) and carbonate chemistry (specifically lowering of  $p\text{CO}_2/p\text{H}/\Omega_{\text{cal}}$ ) may, however, result in an increased  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  of up to  $\sim -4.6\text{‰}$ , which should be considered when reconstructing Phanerozoic ocean chemistry. Because modern seawater has  $\delta^7\text{Li} = 31\text{‰}$  (Millot et al., 2004; Misra and Froelich, 2012) and considering the near-constant Li isotope fractionation between seawater and brachiopods obtained from experimental approach for certain parameters (Marriott et al., 2004b; this study), we posit that brachiopods may provide a reliable record of  $\delta^7\text{Li}$  of modern and plausibly also past ocean water (Fig. 6). The latter would be particularly important when considering massive continental weathering in the past (Tipper et al., 2012; Pogge von Strandmann and Henderson, 2015), where Li could be particularly relevant for deciphering the extent of such climate-related effects.

## 5. Conclusions

The  $\delta^7\text{Li}$  values of different natural brachiopod species provided in this study combined with data from cultured specimens leads us to postulate that brachiopods are well-suited as tracers of ocean water  $\delta^7\text{Li}$  and the results suggest that:

- (i) the secondary layer is most suitable for determining  $\delta^7\text{Li}$  of a specimen although the difference from the signatures of the primary and tertiary layer is insignificant and sampling protocol for Li in brachiopods can thus be simplified;
- (ii) the lithium isotope fractionation between brachiopod shells and seawater is similar to that determined for inorganic calcite, thus suggesting insignificant influence of vital effects;
- (iii) the cultured brachiopod species give broadly consistent  $\Delta^7\text{Li}$  values relative to the solution (i.e. seawater) from which they have grown;
- (iv) the modification of water temperature for cultured *Magellania venosa* does not impart any measurable effect to  $\delta^7\text{Li}$  of the cultured specimens;

(v) the change in Mg/Ca of seawater and pCO<sub>2</sub>/pH is paralleled by an increase in  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  between seawater and brachiopod specimens of approximately 1–2‰, based on  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  of –3.6‰ for brachiopods in nature and –2.5‰ for cultured *M. venosa*, and results in  $\Delta^7\text{Li}_{\text{calcite-seawater}}$  of –4.5‰/–4.6‰ and –2.4‰/–3.4‰ for *M. venosa* grown under lowered Mg/Ca and pCO<sub>2</sub>/pH conditions, respectively.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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