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## Article

# Controls on Lithium Incorporation and Isotopic Fractionation in Large Benthic Foraminifera

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**Abstract:** The lithium (Li) isotopic composition of carbonates is considered to be a reliable archive of past seawater Li isotopic compositions, which are useful as a tracer of silicate weathering. However,  $\delta^7\text{Li}$  values have been shown to be dependent on either pH or DIC in two studies using similar species of large, benthic foraminifera from the genus *Amphistegina*. To resolve this issue, we conducted culture experiments on *Amphistegina lessonii* in decoupled pH–DIC conditions, under two different light treatments, and with normal or Li-enriched seawater. The  $\delta^7\text{Li}$  values and Li/Ca ratios in the foraminifera tests were analysed by ion microprobe and LA-ICP-MS, respectively. No links between either the pH or DIC and  $\delta^7\text{Li}$  or Li/Ca values were observed for any of the treatments, and growth rates also did not seem to influence the Li incorporation or isotopic fractionation, contrary to observations from inorganic carbonate-precipitation experiments. Overall, these findings appear to support the use of Li isotopes in large benthic foraminifera to reconstruct past seawater chemistry and to infer changes in chemical weathering during carbon-cycle perturbations.

**Keywords:**  $\delta^7\text{Li}$ ; Li/Ca; lithium; large benthic foraminifera; culture experiments; pH; DIC; geochemical proxies

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## 1. Introduction

The chemical weathering of continental silicate rocks removes  $\text{CO}_2$  from the atmosphere and exerts a fundamental control on the Earth's climate over geological timescales (e.g., [1]). Characterizing and quantifying silicate weathering in the past is therefore crucial for understanding feedback in the climate system. Lithium (Li) is mainly hosted in silicate minerals and has two stable isotopes ( $^6\text{Li}$  and  $^7\text{Li}$ ). Silicate weathering and riverine transport strongly fractionate the isotopic composition of Li [2–4]. Specifically, the isotopic fractionation in soils and river systems occurs during secondary mineral formation, since clays and oxides favour the incorporation of the lighter isotope  $^6\text{Li}$  [2,3,5]. Hence, the isotopic composition of lithium ( $\delta^7\text{Li}$ ) is considered a useful proxy for tracing chemical weathering processes (e.g., [5–10]).

In the ocean, the two major sources of dissolved Li are rivers and hydrothermal fluxes (review in [11] and references therein). Lithium is a conservative element in seawater, with a modern residence time of ~1.5 million years [12], which is long compared to the ocean mixing time (~1000 years), such that Li is spatially homogenous in concentration (26  $\mu\text{M}$ ) and isotopic composition ( $\delta^7\text{Li} = -31.2\text{‰}$ ; [13,14]). Trace elements

from seawater are incorporated during both inorganic and biogenic marine-carbonate precipitation, so carbonate Li isotope measurements have been used to examine geological variations of seawater  $\delta^7\text{Li}$  values and to reconstruct long-term changes in continental weathering conditions [7,8,15–19]. However, the Li isotopic fractionation during biogenic carbonate formation is complex, and it has been suggested that biological control during biomineralization (so-called “vital effects”), species-specific effects, and local environmental parameters (i.e., carbonate system parameters), could impact  $\delta^7\text{Li}$  values in various marine calcifiers [10,20–23].

Foraminifera are ubiquitous calcifying protists that are widely used for paleoceanographic reconstructions (review in [24] and references therein). Lithium isotopes have been measured in various modern planktic species and provide values that are generally close to the seawater composition, with a small and relatively consistent offset of ~1‰ towards lower  $\delta^7\text{Li}$  values [7,25–28] that differs from the larger fractionation seen in inorganic calcite [29–33]. This small and approximately constant offset has justified the use of planktic foraminiferal  $\delta^7\text{Li}$  measurements to estimate past seawater  $\delta^7\text{Li}$  values (e.g., [7,8]). Although measurements on benthic species are scarce, one study has reported similar  $\delta^7\text{Li}$  values in small benthic foraminifera (SBF) to seawater, with no sensitivity of  $\delta^7\text{Li}$  values to temperature [30]. In contrast, Li isotopic fractionation and Li/Ca ratios in large benthic foraminifera (LBF) were observed to be significantly influenced by parameters of the carbonate system in two independent studies [21,22]. Those results are enigmatic, since both studies used similar species of the genus *Amphistegina* but reported differing controls on  $\delta^7\text{Li}$  values, with a positive correlation with dissolved inorganic carbon (DIC) but no effect of pH observed in one case [21] and a negative correlation with pH but no effect of DIC seen in the other case [22]. Large benthic foraminifera are a group of species dwelling in warm coral reef environments and hosting algal symbionts that provide them with energy through photosynthesis [34,35]. They are major carbonate producers as well as key bio-indicators in tropical carbonate platforms (review in [36]), and they are widespread through the geological record, thereby providing excellent potential for paleoclimate reconstructions of bottom water conditions. It is therefore necessary to clarify how  $\delta^7\text{Li}$  values and Li/Ca ratios in LBF tests are impacted during biomineralization, in order to determine the potential of Li isotopes in LBF as a reliable weathering archive or as a proxy of the carbonate system.

Here, to address the earlier contradictory results on the Li isotope behaviour in the hyaline and low-Mg calcite LBF species *Amphistegina lessonii*, we performed culture experiments under decoupled pH/DIC conditions and analysed the  $\delta^7\text{Li}$  values and Li/Ca ratios in the tests. In the first set of experiments, two different light treatments were implemented to investigate the potential role of the symbionts. In the second set of experiments, we explored the potential impact of the seawater-Li concentration ( $\times 1$ ,  $\times 5$ , and  $\times 10$ , compared to modern seawater concentrations) on the  $\delta^7\text{Li}$  values and Li/Ca ratios.

## 2. Materials and Methods

### 2.1. Culture Experiments

Specimens of *Amphistegina lessonii* were obtained from a coral reef aquarium at the Klimahaus (Bremerhaven, Germany). They were kept in a stock culture at the Alfred Wegener Institute (AWI) in a climatized room at 25 °C and under 12hr:12hr day/night cycles. Approximately 100 adult specimens were isolated in well plates. After ~10 days, approximately half of them had reproduced asexually. Juveniles (2–3 chambers) were selected and exposed to decoupled pH–DIC treatments until they reached adult size. Details of the culture medium preparation and carbonate system setup are described in Kaczmarek et al. (2015) [37], with the exception that in our case the boron content of the culture medium was equivalent to modern seawater. Briefly, the culture cups containing the specimens were placed in beakers filled with modified North Sea water (NSW), as

summarised in Table 1. The water was changed weekly in order to avoid drifting of the carbonate system parameters.

**Table 1.** Water chemical variables for all treatments in both experiments. Alkalinity and pH were measured every week and DIC was measured every second week; pCO<sub>2</sub> and Ω<sub>cal</sub> were calculated using the CO2SYS software. Uncertainties represent the external error (2σ).

Treatment	Experiment 1 (Normal Seawater)					Experiment 2 (×5 Li-Enriched Seawater)				
	Alkalinity at 25 °C (μeq kg <sup>-1</sup> )	pH (pH NBS scale)	DIC (μmol·kg <sup>-1</sup> )	pCO <sub>2</sub> (μatm)	Ω <sub>cal</sub>	Alkalinity at 25 °C (μeq kg <sup>-1</sup> )	pH (pH NBS scale)	DIC (μmol·kg <sup>-1</sup> )	pCO <sub>2</sub> (μatm)	Ω <sub>cal</sub>
Control	2501 ± 9	8.16 ± 0.01	2188 ± 10	471	5.33	2468 ± 7	8.10 ± 0.01	2189 ± 18	549	4.67
High pH	2657 ± 10	8.36 ± 0.01	2194 ± 20	282	8.07	2607 ± 17	8.22 ± 0.02	2235 ± 27	415	6.14
Low pH	2368 ± 14	7.88 ± 0.03	2191 ± 10	945	2.96	2356 ± 8	7.90 ± 0.01	2167 ± 20	889	3.02
High DIC	3248 ± 8	8.18 ± 0.01	2854 ± 12	584	7.26	3009 ± 8	8.10 ± 0.01	2580 ± 42	672	5.72
Low DIC	1575 ± 11	8.15 ± 0.01	1489 ± 83	299	3.26	1658 ± 13	8.05 ± 0.03	1397 ± 42	415	2.81

The specimens were fed with the algae *Nannochloropsis* spp. after every water change. In this first set of experiments, two light treatments were applied in order to assess any potential effects of the symbionts: all the beakers went through the same day/night cycles, but half of them were wrapped in black mesh. As a result, the light intensity during the light period was ~200 μmol photons·m<sup>-2</sup>·s<sup>-1</sup> for half of the specimens (light/dark treatment) and ~20 μmol photons·m<sup>-2</sup>·s<sup>-1</sup> for the other half (dark treatment). This first set of experiments lasted for 11 weeks.

A second set of experiments was performed under similar conditions using Li-enriched seawater. The NSW was modified by adding LiCl to achieve a final Li concentration ([Li]) five times higher than normal seawater. It was then further modified in order to reach each specific carbonate system condition, summarised in Table 1. Additionally, ~50 specimens were grown in Li-enriched water with ten times higher [Li] than normal seawater and maintained under control conditions (i.e., without any modifications of the carbonate system). This second set of experiments lasted for 15 weeks.

Upon completion of the culture period, the specimens were rinsed three times with distilled water and dried for 24 h at 50 °C. Scanning electron microscope (SEM) images were taken for, on average, 18 random specimens per condition and were scrutinized for potential dissolution features. No signs of decalcification were observed on any of the specimens. The specimens added chambers under all experimental conditions. In the first experiment, they increased in size from an average of 148 ± 16 μm as juveniles to an average adult size of 511 ± 41 μm in the light/dark treatment, and to an average adult size of 465 ± 38 in the dark treatment (Table 2). In the second experiment, specimens grew from an average of 148 ± 16 μm as juveniles to an average adult size of 644 ± 48 μm in the ×5 Li-enriched seawater, and to an average adult size of 419 ± 88 μm in the ×10 Li-enriched seawater (Table 2). In both sets of experiments, the specimens grew the most under control conditions, and grew the least under the slow-DIC conditions, although the differences were small.

## 2.2. Analytical Methods

### 2.2.1. Seawater Carbonate Parameters

The pH (NBS scale) and alkalinity of the culture matrices were measured every week, and the DIC was measured every second week. The pH was measured with a multimeter Multi 340i (WTW), calibrated with a pH of 6.87 and 9.18 WTW technical buffer solutions. Alkalinity and DIC were determined as described in Kaczmarek et al. (2015) [37] (Table 1). The CO2SYS software program [38] was used to estimate the partial pressure of carbon dioxide (pCO<sub>2</sub>) and calcite saturation (Ω<sub>cal</sub>). Input parameters were alkalinity, pH, salinity,

and temperature. Equilibrium constants from Lueker et al. (2000) [39] were applied for K1 and K2, and a  $\text{HSO}_4^-$  dissociation constant from Dickson (1990) [40] and a total boron concentration from Uppström (1974) [41] were used, as recommended in Orr et al. (2015) [42].

### 2.2.2. Seawater Li Isotopes

The modified seawater samples were purified and analysed for Li isotopes as detailed in Pogge von Strandmann et al. (2019) [43]. Briefly, the samples were passed through a two-stage cation exchange chemistry using AG50W X-12 resin and 0.2 M HCl as an eluent. Analyses were performed on a Nu Plasma 3 multi-collector inductively coupled plasma mass spectrometer in the LOGIC laboratories at University College London, using a sample-standard bracketing technique normalised to the IRMM-016 standard, which has an identical isotopic composition to the LSVEC standard [43]. Seawater was analysed alongside these samples, providing  $\delta^7\text{Li}$  values of  $31.2 \pm 0.2\text{‰}$ , in agreement with a long-term value in those laboratories of  $\delta^7\text{Li} = 31.18 \pm 0.38\text{‰}$  ( $n = 43$ ). Other geological standards for this method are reported in Pogge von Strandmann (2011; 2019) [43,44]. The  $\delta^7\text{Li}$  values for normal seawater,  $\times 5$  enriched-Li seawater, and  $\times 10$  Li-enriched seawater were  $31.2 \pm 0.2$ ,  $24.8 \pm 0.2$ , and  $24.8 \pm 0.2\text{‰}$ , respectively.

### 2.2.3. Foraminifera Li Isotopes

Between one and three specimens per treatment for both sets of experiments were selected for Li-isotope analysis by ion microprobe. The specimens were embedded in epoxy sections, polished down to  $1 \mu\text{m}$ , and coated with gold. Analyses were performed using the Cameca IMS 1280 HR ion probe at the Centre de Recherches Pétrographiques et Géochimiques (CRPG, Nancy, France). The Li isotopic compositions were measured with in situ spot analysis, using a  $15\text{--}20 \mu\text{m}$   $^{16}\text{O}^-$  primary beam of about 50 nA for both the foraminifera and the in-house reference material (CAL-HTP calcite [27]). The mass-resolving power (MRP) was set to 3000, with the energy slit well-centred and opened to 30 eV. A single Li-isotope analysis consisted of 1 min of pre-sputtering and 30 cycles of peak switching on masses 6 and 7, which were successively counted on an electron multiplier for a duration of 12 s and 8 s, respectively. The background was measured at mass 5.5. Reproducibility based on repeated measurements of the CAL-HTP was between  $\pm 0.6$  and  $\pm 1.1\text{‰}$  ( $1\sigma$ ) for the analytical session. The Li-isotope analysis could not be performed on the specimens grown in the low-DIC treatment under dark conditions in experiment 1 because none of the tests were thick enough to allow for the measurements.

**Table 2.** Specimen size at the end of the culture period,  $\delta^7\text{Li}$  values, and Li/Ca ratios in *Amphistegina lessonii* for all treatments in both experiments. Note that  $\delta^7\text{Li}$  values in the specimens grown under low-DIC and dark treatment in experiment 1 could not be measured (see text for details). Uncertainties represent the external error ( $2\sigma$ ).

Treatment	Experiment 1 (Normal Seawater)						Experiment 2 <sup>1</sup> ( $\times 5$ Li-Enriched Seawater)		
	Size ( $\mu\text{m}$ )		$\delta^7\text{Li}$ (‰)		Li/Ca ( $\mu\text{mol/mol}$ )		Size ( $\mu\text{m}$ )	$\delta^7\text{Li}$ (‰)	Li/Ca ( $\mu\text{mol/mol}$ )
	light/dark	dark	light/dark	dark	light/dark	dark	light/dark	light/dark	light/dark
Control	569 $\pm$ 93	568 $\pm$ 104	26.0 $\pm$ 0.8	22.8 $\pm$ 1.5	14.3 $\pm$ 3.1	14.9 $\pm$ 8.3	693 $\pm$ 75	26.3 $\pm$ 1.4	55.7 $\pm$ 1.5
High pH	485 $\pm$ 87	445 $\pm$ 104	24.5 $\pm$ 1.4	24.4 $\pm$ 1.1	13.5 $\pm$ 2.8	16.6 $\pm$ 4.3	636 $\pm$ 88	24.1 $\pm$ 0.7	61.1 $\pm$ 2.6
Low pH	504 $\pm$ 110	512 $\pm$ 82	25.4 $\pm$ 0.9	23.1 $\pm$ 1.4	15.3 $\pm$ 1.8	12.0 $\pm$ 1.2	670 $\pm$ 121	23.6 $\pm$ 0.7	66.9 $\pm$ 3.3
High DIC	521 $\pm$ 88	471 $\pm$ 65	24.3 $\pm$ 1.3	24.5 $\pm$ 1.1	15.8 $\pm$ 2.1	19.4 $\pm$ 2.0	650 $\pm$ 130	25.7 $\pm$ 0.6	61.9 $\pm$ 2.6
Low DIC	476 $\pm$ 78	328 $\pm$ 61	25.0 $\pm$ 1.2	-	16.6 $\pm$ 3.8	27.6 $\pm$ 5.9	573 $\pm$ 113	24.1 $\pm$ 0.7	61.9 $\pm$ 2.6

<sup>1</sup> For the  $\times 10$  Li-enriched seawater experiment implemented in control conditions, size was  $419 \pm 88 \mu\text{m}$ , and  $\delta^7\text{Li}$  was  $23.9 \pm 1.3\text{‰}$ .

### 2.2.4. Foraminifera Li Concentrations

Between two and three specimens per treatment were selected for [Li] analysis. A femtosecond-laser-ablation system coupled to an ICP-MS (AWI) was used, and the masses monitored included  ${}^7\text{Li}$  and  ${}^{44}\text{Ca}$ . The beam diameter was set at 50  $\mu\text{m}$ , the repetition rate was 30 Hz, and the specimens were ablated in the test central area (knob) with an energy at the surface sample of 1  $\text{J}\cdot\text{cm}^{-2}$ . Using the software program PULSE [45], the foraminifera data were blank-corrected and the element-to-Ca ratios were calculated and drift-corrected using a standard-sample-standard bracketing technique with the NIST SRM 610 glass standard [46].

For the experiments using  $\times 10$  Li-enriched seawater, we used the number of counts per second (cps) obtained with the ion probe measurements, as the cps are proportional to the abundance of the element. Since the cps for Li were almost identical between the  $\times 5$  Li and  $\times 10$  Li samples from the control-condition experiments, and assuming that the Ca concentration is the same, we considered the Li/Ca ratios between the two enriched water experiments to be the same.

### 3. Results

The  $\delta^7\text{Li}$  values in the foraminifera cultured in normal seawater ranged from  $24.3 \pm 1.3$  to  $26.0 \pm 0.8\text{‰}$  for the light/dark treatment, and from  $22.8 \pm 1.5$  to  $24.5 \pm 1.1\text{‰}$  for the dark treatment (Table 2). No significant correlation was observed with either the pH or DIC of the medium within analytical uncertainty (Figure 1A). Similarly, no correlation with the pH or DIC was observed for the  $\delta^7\text{Li}$  values in specimens cultured in  $\times 5$  Li-enriched seawater within analytical uncertainty (Figure 1B), and those values ranged from  $23.6 \pm 0.7$  to  $26.3 \pm 1.4\text{‰}$  (Table 2). The  $\delta^7\text{Li}$  value in the foraminifera cultured in control conditions and  $\times 10$  Li-enriched seawater was  $23.9 \pm 1.3\text{‰}$ . In the first set of experiments (normal seawater), the  $\delta^7\text{Li}$  values of the specimens cultured in the control and in the low-pH media were significantly lower in the dark treatment when compared to those cultured in the light/dark treatment (Figure 1A).

The Li/Ca ratios in the specimens cultured in normal seawater ranged from  $13.5 \pm 2.8$  to  $16.6 \pm 3.8 \mu\text{mol}\cdot\text{mol}^{-1}$  for the light/dark treatment and from  $12.0 \pm 1.2$  to  $27.6 \pm 5.9 \mu\text{mol}\cdot\text{mol}^{-1}$  for the dark treatment (Table 2; Figure 2A). In the specimens cultured in  $\times 5$  Li-enriched seawater, the Li/Ca ratios ranged from  $55.7 \pm 1.6$  to  $66.9 \pm 3.3 \mu\text{mol}\cdot\text{mol}^{-1}$  (Table 2; Figure 2B). There was no significant correlation between the pH or DIC of the medium and Li/Ca ratios in the foraminifera tests, for either the normal seawater or the  $\times 5$  Li-enriched water cultures, within analytical uncertainty (Figure 2). In the first set of experiments (normal seawater), the Li/Ca ratios of the specimens cultured in the low-pH and in the low-DIC media were lower and higher, respectively, in the dark when compared to in the light/dark treatment (Figure 2A).

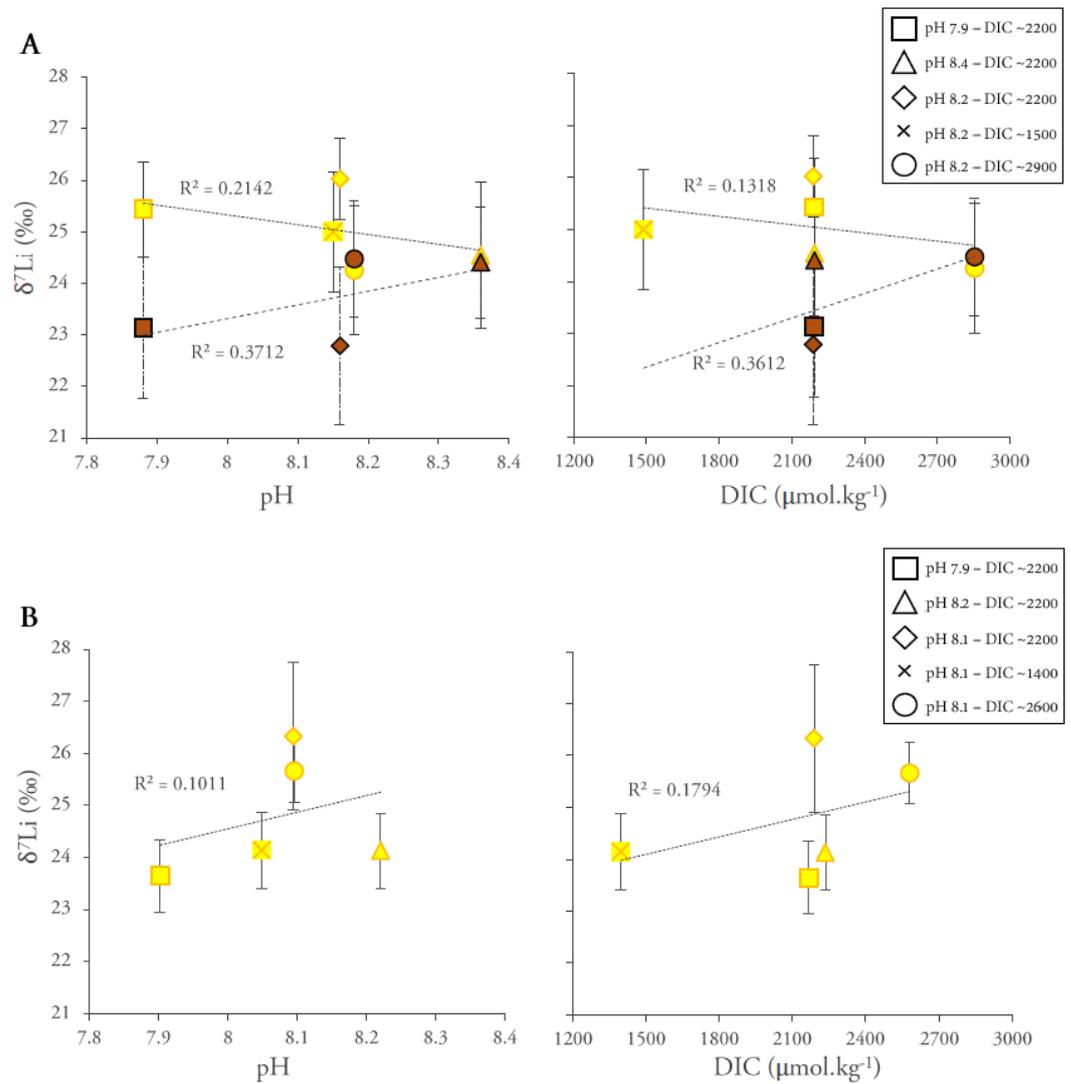
We calculate the apparent partition coefficient,  $K^*d$ , which is defined as:

$$K^*d = (\text{Li}/\text{Ca})_{\text{foram}}/(\text{Li}/\text{Ca})_{\text{w}}$$

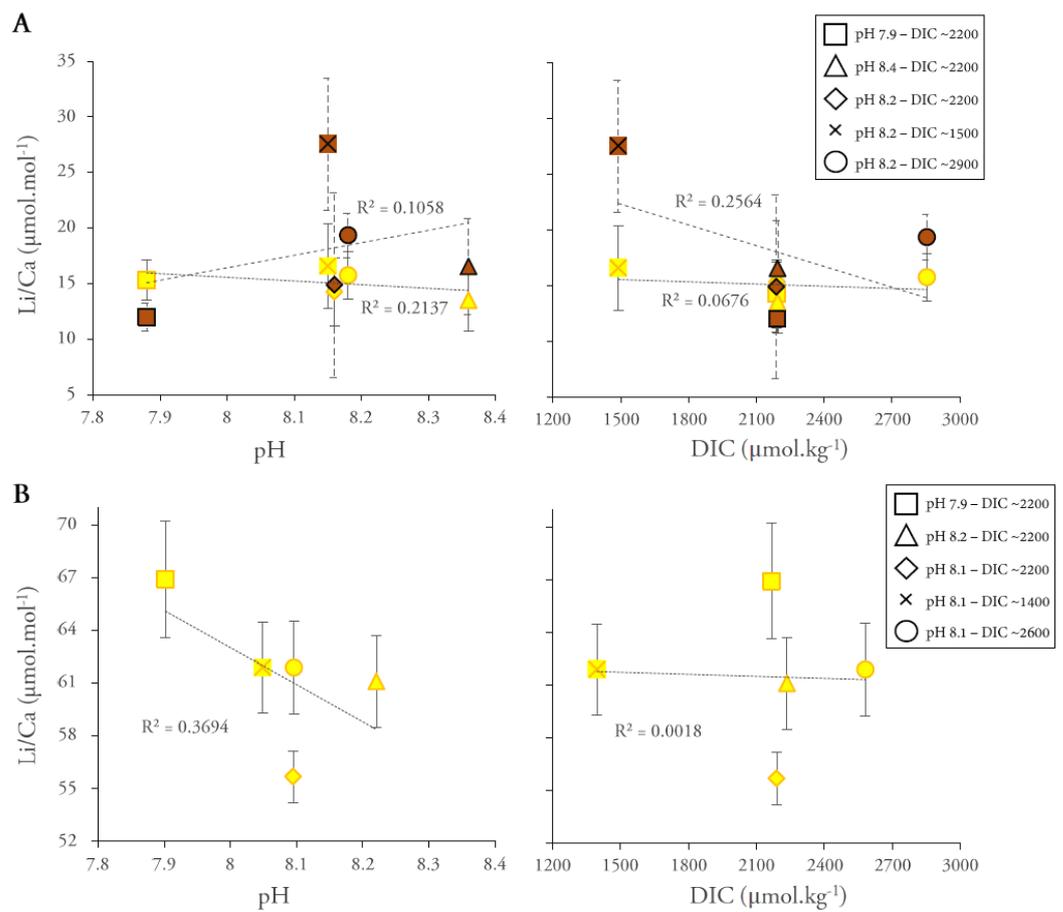
where  $(\text{Li}/\text{Ca})_{\text{w}}$  is the Li/Ca ratio in the culture medium and  $(\text{Li}/\text{Ca})_{\text{foram}}$  is the Li/Ca ratio measured in the foraminifera tests. The apparent  $K^*d$  values, calculated considering a [Li] of 26  $\mu\text{M}$  and a Ca concentration ([Ca]) of 10.28 M for the normal seawater medium, Li concentrations of 130  $\mu\text{M}$  for the  $\times 5$  Li-enriched medium, and [Li] of 260  $\mu\text{M}$  for the  $\times 10$  Li-enriched medium, are  $5.97 \times 10^{-3}$ ,  $4.86 \times 10^{-3}$ , and  $2.43 \times 10^{-3}$ , respectively (Figure 3A). The apparent  $K^*d$  seems to decrease with increasing [Li] in the culture medium (Figure 3A). This decrease in  $K^*d$  is accompanied by a change in the isotopic fractionation from  $-5.2 \pm 0.1\text{‰}$  in the normal seawater to  $-0.9 \pm 1.5$  and  $+1.6 \pm 1.6\text{‰}$  in the  $\times 10$  Li-enriched and  $\times 5$  Li-enriched seawaters, respectively (Figure 3B). This observation suggests that the manipulation of the [Li] of the culture medium has an impact on the incorporation of Li into the foraminifera test.

The  $\delta^7\text{Li}$  values and Li/Ca ratios showed no dependency on foraminiferal growth rates in the light/dark treatments for both normal and  $\times 5$  Li-enriched seawater (Figures

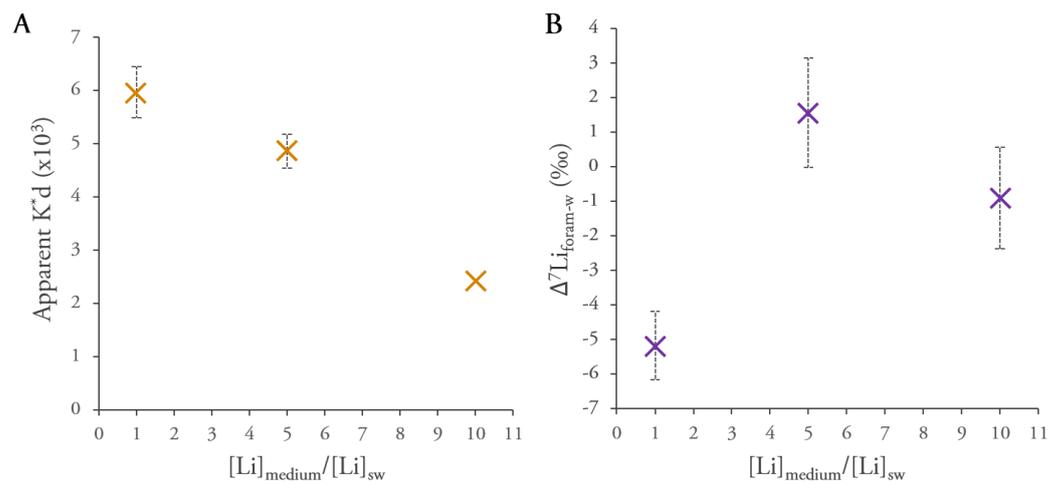
4A,B). However, an effect was observed in the dark treatment, with  $\delta^7\text{Li}$  values and Li/Ca ratios decreasing with increasing growth rates (Figure 4A).



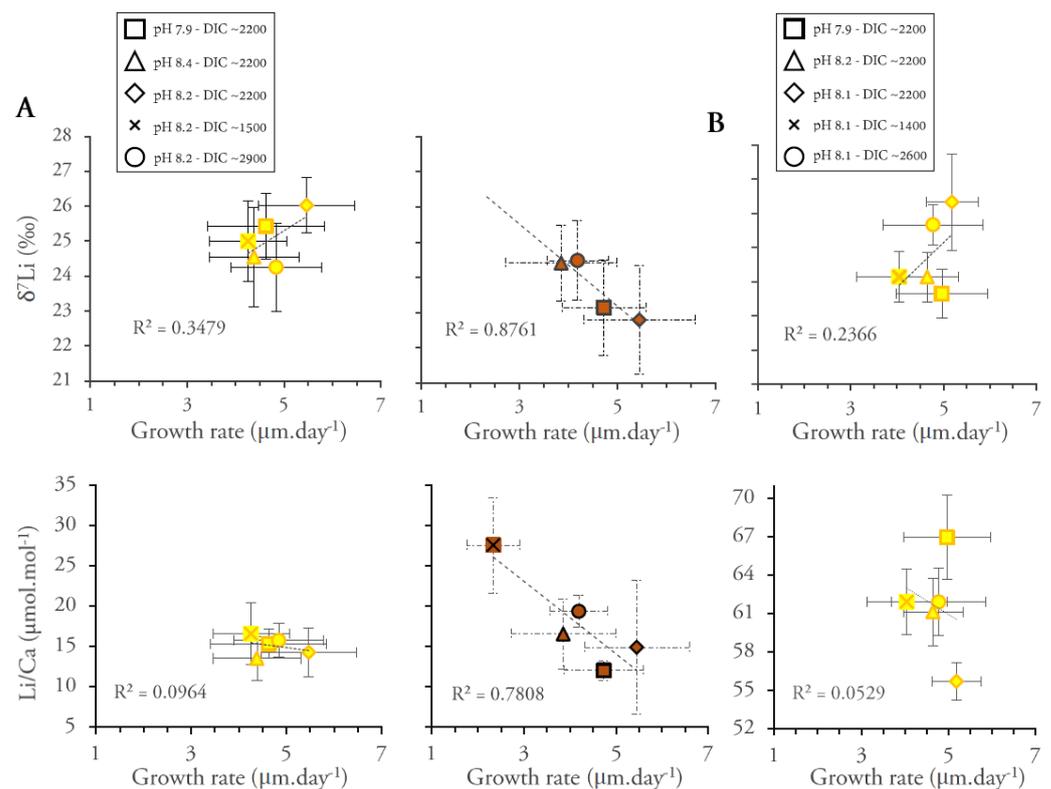
**Figure 1.**  $\delta^7\text{Li}$  values in *Amphistegina lessonii* tests as a function of pH (left panels) and DIC (right panels). (A) Normal seawater; (B)  $\times 5$  Li-enriched seawater. Yellow symbols—light/dark cycles. Brown symbols—dark only. Note that  $\delta^7\text{Li}$  values in the specimens grown under low DIC and dark treatment in experiment 1 could not be measured (see text for details). The error bars for  $\delta^7\text{Li}$  represent the external error ( $2\sigma$ ). Errors for pH and DIC are negligible (and smaller than symbol size).



**Figure 2.** Li/Ca ratios in *Amphistegina lessonii* tests as a function of pH (left panel) and DIC (right panel). (A) Normal seawater; (B)  $\times 5$  Li-enriched seawater; note the different vertical scales. Yellow symbols—light/dark cycles. Brown symbols—dark only. The error bars for Li/Ca represent the external error ( $2\sigma$ ). Errors for pH and DIC are negligible (and smaller than symbol size).



**Figure 3.** Effect of 1, 5, and 10 $\times$  Li-enriched seawater on (A) apparent partition coefficient  $K^*d$  and (B) the Li isotopic fractionation factor between foraminiferal calcite and seawater ( $\Delta^7\text{Li}_{\text{foram-w}}$ ). Values from the control treatments were used. The error bars represent the external error ( $2\sigma$ ).



**Figure 4.**  $\delta^7\text{Li}$  values and Li/Ca ratios as a function of *Amphistegina lessonii* growth rates. (A) Normal seawater and (B)  $\times 5$  Li-enriched seawater. Yellow symbols—light/dark cycles. Brown symbols—dark only. Note the different vertical scales for Li/Ca between panels. The error bars represent the external error ( $2\sigma$ ).

## 4. Discussion

### 4.1. Comparison with Inorganic Calcite

In inorganic calcite precipitation experiments,  $\delta^7\text{Li}$  values and Li/Ca ratios were shown to be affected by both growth rate and pH over a pH range from 6.3 to 9.5 [31,32]. In those studies, the authors observed a decrease in the apparent partition coefficient with pH, together with an increase in the isotopic fractionation. They suggested that this behaviour could be explained by the presence of two or more Li-bearing species, whose abundances in the solid could control the Li isotopic fractionation and the Li/Ca ratio. In comparison, the data from LBF in our study, together with those from Vigier et al. (2015) [21], do not show any relationship between pH and either the apparent partition coefficient or the isotopic fractionation. Meanwhile, Roberts et al. (2018) [22] found an inverse relationship for the isotopic fractionation with the pH. This apparently contradictory behaviour was explained by Fügler et al. (2022) [32] as an effect of the growth rate, which they suggested increased with the increasing pH. No growth rate data were available in Roberts et al. (2018) [22], and in our study there is no clear relationship between pH and the final size of the foraminifera tests ( $504 \pm 110 \mu\text{m}$  at a low pH vs  $485 \pm 87 \mu\text{m}$  at a high pH in experiment 1; Table 2). Although the precipitation rate itself is not readily obtained in foraminifera-culturing experiments, we could assume that there would be a link between the precipitation rate and the final test size. However, it is important to emphasise that the pH range in our experiments (from 7.88 to 8.36) was small compared to the range in Fügler et al. (2022) [32], and that they observed only a small difference in isotopic fractionation over our pH range ( $\Delta^7\text{Li} \approx -3\text{‰}$  at pH 7.4 and  $\Delta^7\text{Li} \approx -2.75\text{‰}$  at pH 8.3). Hence, the expected difference in  $\delta^7\text{Li}$  values of less than  $0.2\text{‰}$  between our low pH and high pH experiments would be too small to be detected by ion microprobe measurements (with a

typical reproducibility of  $\pm 1\%$ ), or even in MC-ICP-MS data (with a typical reproducibility of  $\pm 0.4\%$ ).

Another factor to consider when comparing the Li-isotope behaviour between the inorganic experiments of Fuger et al. (2019; 2022) [31,32] and foraminifera culture experiments such as ours is the chemistry of the solutions, because their precipitation experiments were conducted by mixing  $\text{CaCl}_2$ ,  $\text{LiCl}$ , and  $\text{Na}_2\text{CO}_3$  instead of using seawater.

#### 4.2. Comparison with Biogenic Carbonates

##### 4.2.1. Li/Ca Ratios

Since [Li] are homogeneous in the ocean, the large range of Li/Ca ratios observed in marine organisms may indicate the effects of different biomineralization processes [23]. Whereas the Li/Ca ratios of planktic and benthic foraminifera are found to be in a relatively small range (between 3.6 and 24.8  $\mu\text{mol}\cdot\text{mol}^{-1}$ , Figure 5A), there is a much wider range for modern brachiopods (between 5.7 and 122.1  $\mu\text{mol}\cdot\text{mol}^{-1}$ , Figure 5A). While the low values could be explained by the presence of an element-depleted tertiary layer [47], the highest values correspond to the primary layer and could reflect kinetic effects (e.g., [48]) or precipitation via an amorphous precursor [47]. The range measured in core-top foraminifera is even smaller than in LBF culture studies, with Li/Ca ratios between 13.8 and 16.9  $\mu\text{mol}\cdot\text{mol}^{-1}$  in planktic foraminifera and between 10.4 and 15.8  $\mu\text{mol}\cdot\text{mol}^{-1}$  in SBF (Figure 5A).

The Li/Ca ratios observed in our study are in the range of the previous study using the genus *Amphistegina* by Vigier et al. (2015) [21] (3.6 to 19.7  $\mu\text{mol}\cdot\text{mol}^{-1}$ ), but lower than those reported in Roberts et al. (2018) [22] (18.4 to 24.8  $\mu\text{mol}\cdot\text{mol}^{-1}$ ) (Figure 6). These Li/Ca ratios are also comparable with previous data on SBF [30]. We observed a positive correlation between the Li/Ca ratios of the culture medium and Li/Ca ratios in the foraminiferal test (Table 2), which was also previously reported in *A. lessonii* grown in a seawater-like fluid when the [Li] but not the [Ca] of the fluid was changed [49]. In that study, the apparent partition coefficient decreased with increasing Li/Ca ratios of the culture medium [49]; this was also observed in the planktic species *Globigerinoides sacculifer* and *Orbulina universa* [50], in the LBF *Operculina ammonoides* [51], and is also seen here (Figure 3). These observations are also equivalent to findings in *Operculina ammonoides* for  $\text{K}^*\text{d}(\text{Na})$  and  $\text{K}^*\text{d}(\text{Mg})$  [52].

While we observed a positive correlation between the Li/Ca ratios of the fluid and the foraminifera for seawater and the  $\times 5$  Li-enriched medium (Table 2), the foraminifera from the  $10\times$  Li-enriched medium have similar Li/Ca ratios to those from the  $5\times$  Li-enriched medium, so there appears to be a plateau in this relationship. This plateau could indicate that there is a threshold in the amount of Li that can be incorporated into the foraminifera test, although we note that, at present, this finding is based on a single control run for the  $10\times$  Li-enriched medium. Such an effect has not previously been proposed, but we note that none of the previous experiments manipulated the Li/Ca ratio of the culture medium to values more than five times the normal [Li] in seawater. The presence of such a threshold seems to suggest that foraminifera may be able to partly control the incorporation of Li into their tests. To our knowledge, Li is not considered as an essential element in biology, so this possible upper limit in the incorporation of Li should be investigated further. If this threshold is also present in other foraminifera species, it would mean that foraminifera could not be applied as a proxy for the Li/Ca ratios of past seawater if the Li content of seawater increased to more than five times the present level. However, such a large increase seems not to have occurred over at least the last 400 Ma [53].

##### 4.2.2. Li Isotopic Compositions

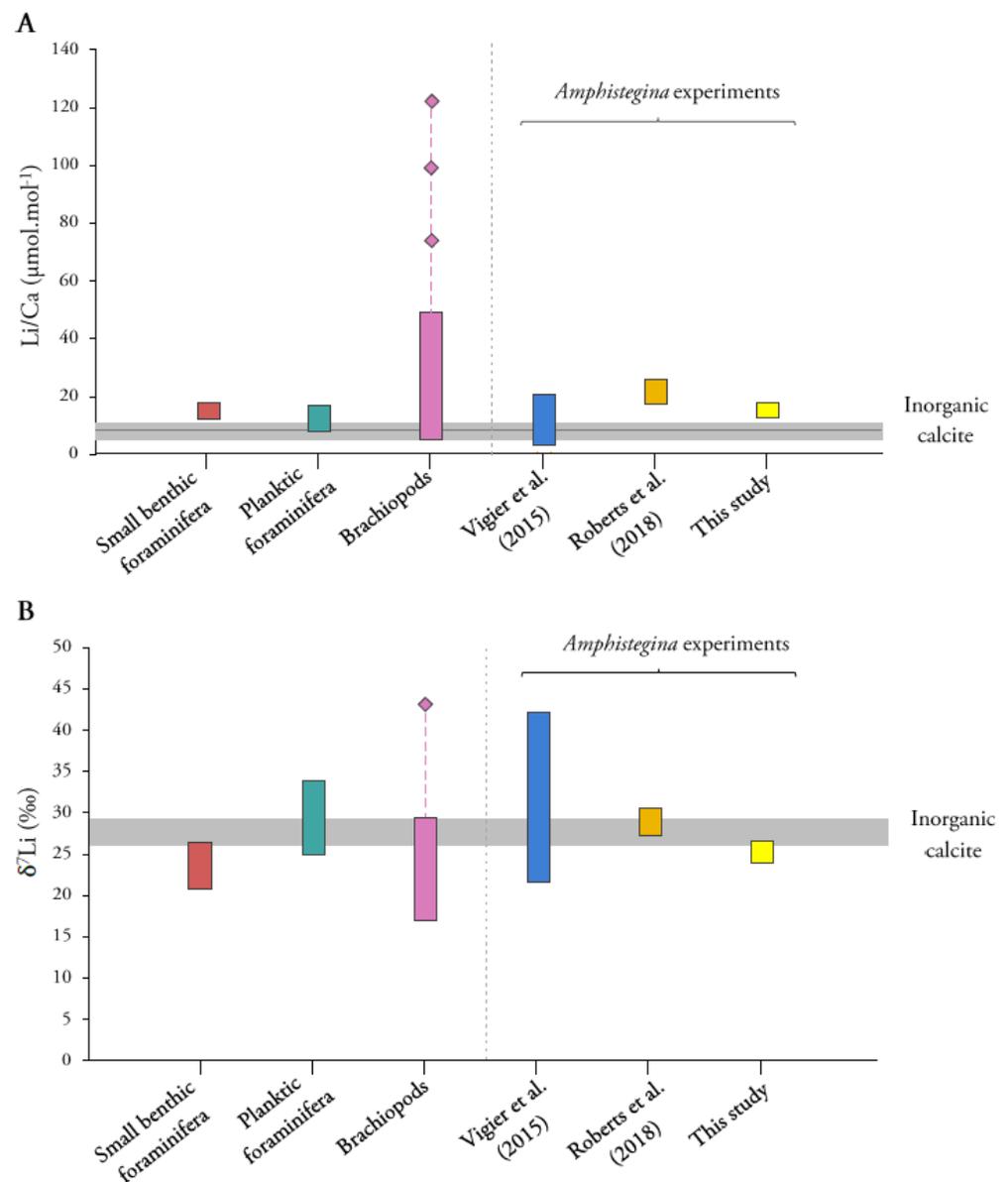
The  $\delta^7\text{Li}$  values in our specimens from normal seawater,  $\times 5$  Li-enriched seawater, and  $\times 10$  Li-enriched seawater (22.8 to 26.3‰) are in the range of previously measured values in LBF from the genus *Amphistegina* (20 to 40‰, [21] and 27.5 to 30.5‰, [22]; Figure 5B),

and in SBF from the genus *Uvigerina* (24.7 to 27.5‰ [30]). In contrast, regarding correlations with carbonate chemistry parameters, the lack of correlation of both  $\delta^7\text{Li}$  values and Li/Ca ratios with the pH or DIC of the culture medium (Figures 1 and 2) differs from previous studies on LBF. In the existing studies,  $\delta^7\text{Li}$  values were observed to be positively correlated with DIC [21] and negatively correlated with pH [22], while Li/Ca ratios were reported to be negatively or positively correlated with DIC ([21,22] respectively). Considering the study by Vigier et al. (2015) [21], some reservations about the methods were underlined by Roberts et al. (2018) [22], which could potentially explain some bias in the results. In addition, in the study by Roberts et al. (2018) [22], the use of B-enriched water may have modified the foraminifera physiology, since increased B concentrations would also change the alkalinity of seawater, particularly at a high pH. To the extent that our results are more widely applicable to LBF, the lack of control exerted by carbonate system parameters on the  $\delta^7\text{Li}$  values of LBF would appear to support their potential as an archive of past seawater Li isotopic compositions during the Phanerozoic era, including during significant perturbations of the carbon cycle.

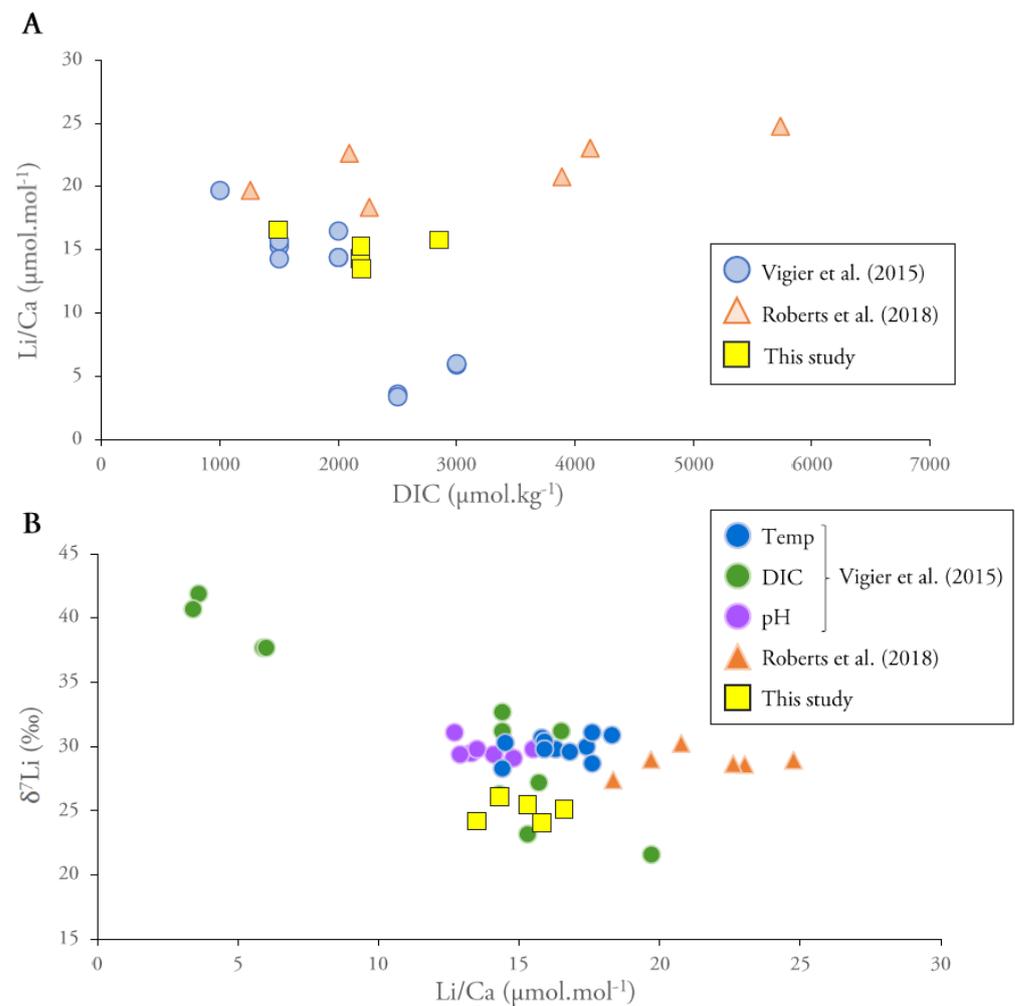
#### 4.2.3. Effect of Light Intensity

Lithium is not considered an essential element for microalgae [54,55], so an impact of the light intensity was not expected. However, small but significant differences in the  $\delta^7\text{Li}$  values and Li/Ca ratios were observed in the dark treatment in the low pH and low DIC treatments (Figures 1 and 2). In addition, growth rate had an effect on  $\delta^7\text{Li}$  values and Li/Ca ratios only in the dark treatments (Figure 4). Photosynthesis of the symbionts is known to locally increase the pH around the foraminifera, thereby reducing or even overriding the impact of a lower ambient pH [56,57]. In the dark treatments, this photosynthetic activity cannot counter low pH or low DIC conditions, which could therefore have affected the  $\delta^7\text{Li}$  values and Li/Ca ratios in the low pH and low DIC treatments. This finding is consistent with a culture study using the LBF *Peneroplis spp.*, in which three days under lower pH and darker conditions were sufficient to affect the geochemical signatures of their tests [58].

At present, it is difficult to explain the different results observed in the three culturing studies conducted on *Amphistegina*. The Li/Ca ratios do not reflect the composition expected for an inorganic calcite precipitating from seawater (Figure 5A), with the values being generally higher in the tests of LBF. This finding could be explained by a mechanism that increases the [Li] in the calcification fluid, and one possibility could be the presence of Na-ATPase. The Na-ATPase can be used to increase the pH of the calcification fluid, as previously observed by microelectrodes [59], fluorescence [60,61], and  $\delta^{11}\text{B}$  measurements [62], by exchanging one proton with one  $\text{Na}^+$  ion. Since  $\text{Li}^+$  and  $\text{Na}^+$  ions have relatively similar chemical properties, this exchange could also promote an increase of Li in the calcification fluid and thus in the foraminifera tests. If this scenario is correct, then it would be interesting to establish whether the behaviour of this  $\text{Na}^+/\text{H}^+$  exchanger is the same under both light and dark conditions. It would also be interesting to study the impact of Na-ATPase inhibitors on the calcification of foraminifera and on the elemental ratios and isotopic compositions of the tests. The impacts of elevated [Li] and/or [B] in the culture medium could also be further explored to better understand the behaviour of Li partitioning and isotopic fractionation in LBF.



**Figure 5.** Comparison with previous studies on a diverse range of calcifying organisms and inorganic experiments. **(A)** Li/Ca ratios and **(B)**  $\delta^7\text{Li}$  values. Data for the inorganic calcite are from Marriott et al. (2004) [30] for Li/Ca ratios, and Marriott et al. (2004) [30] and Füger et al. (2022) [32] for  $\delta^7\text{Li}$  values. For Li/Ca ratios in inorganic calcite, the grey field takes into account the range of temperatures for the *Amphistegina* experiments (between 18 and 33 °C), and the black line represents the Li/Ca ratio for a temperature of 25 °C, as most commonly used in LBF experiments. Data for planktic foraminifera are from Hall et al. (2005) [26], Hathorne and James (2006) [7], and Misra and Froelich (2012) [8]. Data for SBF are from Marriott et al. (2004) [30]. Data for brachiopods are from Delaney et al. (1989) [53], Dellinger et al. (2018) [23], Rollion-Bard et al. (2019) [47], Washington et al. (2020) [18], and Gaspers et al. (2021) [63]. The pink diamonds are outliers.



**Figure 6.** Comparison with previous studies on species from the *Amphistegina* genus [21,22]. (A) Li/Ca ratios versus DIC and (B)  $\delta^7\text{Li}$  values versus Li/Ca ratios. The three sets of experiments from Vigier et al. (2015) with varying temperature, DIC, and pH are presented.

## 5. Conclusions

Culture experiments performed on the coral reef-dwelling benthic foraminifera species *Amphistegina lessonii* under decoupled pH–DIC conditions show no effect of these carbonate system parameters on either  $\delta^7\text{Li}$  values or Li/Ca ratios in the tests under light/dark conditions, contrary to two previous studies conducted on similar species. In addition, no effect of growth rate was observed on either  $\delta^7\text{Li}$  values or Li/Ca ratios. However, the partition coefficient and isotopic fractionation were sensitive to the [Li] of the fluid. Moreover, an effect of different light treatments was observed, probably due to different physiological processes of the symbionts occurring in dark conditions. Overall, these findings suggest that Li isotopes in LBF can be used as a reliable archive for past bottom water Li isotopic compositions, with the potential to trace chemical weathering changes through major carbon cycle perturbations over the last several hundred million years of Earth history.

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B., D.J.W., P.A.E.P.v.S., and J.B. All authors have read and agreed to the published version of the manuscript.

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