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1 **Coupled survey of lithium isotopes and Li/Ca in**  
2 **biogenic and inorganic carbonates**  
3

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## 20 **Abstract**

21 Geochemists have long considered Li isotope composition of marine carbonates as one of the  
22 most straightforward oceanic archives, tracing climate regulation by continental silicate  
23 weathering. However, despite an isotopically homogenous ocean, a large range of  $\delta^7\text{Li}$  values  
24 were reported in the literature for modern biogenic carbonates. Additionally, laboratory  
25 studies highlighted variable Li isotope fractionations during foraminifera growth and during  
26 precipitation of inorganic carbonates.

27 Despite an increasing interest in this topic, there is still limited understanding of Li isotopic  
28 fractionation and of Li incorporation mechanisms in carbonates. The present review aims to  
29 filling this gap by compiling and meta-analyzing the past findings from the literature. More  
30 specifically, Li/Ca and  $\delta^7\text{Li}$  data concerning the influence of mineralogy, temperature, pH,  
31 growth rate and biological processes have been exhaustively reviewed and statistically  
32 examined, including by PCA (Principal Component Analysis). For inorganic carbonate, we  
33 demonstrate that (1) the influence of mineral type is insufficiently explored (2) the effect of  
34 temperature on Li isotopes is negligible, although temperature changes can affect calcite  
35 Li/Ca ratio, and (3) calcite  $\delta^7\text{Li}$  and Li/Ca are primarily influenced by pH and growth rate.  
36 For marine modern biogenic carbonates, our cartography highlights an uneven geographical  
37 distribution, and further studies are required in the Pacific, Indian, and Southern Oceans. Also,  
38 for both Li/Ca and  $\delta^7\text{Li}$ , there are statistically significant and systematic differences between  
39 ‘bulk carbonates’ and all studied marine biogenic groups (i.e. foraminifera, mollusks,  
40 brachiopods). A detailed examination of foraminifera data reveals that planktic species  
41 display  $\delta^7\text{Li}$  values statistically higher than benthic ones, and both anti-correlate with Li/Mg  
42 ratios. Overall, this review underlines the necessity of filling the identified gaps of knowledge  
43 and of attentively considering the impact of environmental parameters and biological  
44 processes for interpreting past  $\delta^7\text{Li}$  variations displayed by fossil shells.

45

46 **Keywords:** lithium isotopes, Li/Ca, marine carbonates, vital effects, synthesis

## 47 **1. Introduction**

48 Lithium (Li) is the least dense of all metals and naturally occurs in the environment as a free  
49  $\text{Li}^+$  ion surrounded by water molecules (Olsher et al., 1991). During the formation of  
50 carbonates in the ocean, Li can be incorporated as a trace element in their crystallographic  
51 structure and its Li isotopic composition has been used to reconstruct the ocean Li isotope  
52 variations for inferring the relationship between climate,  $p\text{CO}_2$  (partial pressure of carbon  
53 dioxide), and continental silicate weathering (Hathorne and James, 2006; Kalderon-Asael et  
54 al., 2021; Misra and Froelich, 2012). Indeed, Li is composed of two stable isotopes,  $^6\text{Li}$  and  
55  $^7\text{Li}$ , representing 7.59% and 92.41%, respectively, with a high ability to fractionate. The Li  
56 isotopic variations observed on earth display the second largest range among  
57 non-conventional isotopes, with values exceeding 40‰ (Li isotopic composition being  
58 reported as  $\delta^7\text{Li} = \left[ \frac{(^7\text{Li}/^6\text{Li})}{(^7\text{Li}/^6\text{Li})_{\text{L-SVEC}}} - 1 \right] \times 1000$ , L-SVEC being the international  
59 standard provided by the US National Institute of Standards and Technology).

60 Modern oceans contain approximately 230 billion tons of Li. Their primary sources of Li are  
61 rivers and high-temperature hydrothermal fluids, which have modern fluxes of similar  
62 magnitude, of about  $10 \times 10^9$  and  $13 \times 10^9$  mol year<sup>-1</sup>, respectively (Misra and Froelich, 2012).  
63 The average  $\delta^7\text{Li}$  value of modern river waters is 23‰, with a range from 2‰ to 43‰  
64 (Dellinger et al., 2015; Huh et al., 1998), which is higher than for marine hydrothermal fluids  
65 (8.3‰) (Chan et al., 1993; Chan et al., 1994). Owing to the large oceanic residence time of Li  
66 (~1.5 million year) (Huh et al., 1998), Li concentration and isotopic composition of seawater

67 are spatially homogeneously distributed ( $[\text{Li}]_{\text{sw}} \sim 26 \mu\text{M}$ ;  $\delta^7\text{Li}_{\text{sw}} = 31 \pm 0.3\text{‰}$ ) in the modern  
68 ocean (Millot et al., 2004), except close to hydrothermal sites (Artigue et al., 2022).  
69 During weathering of silicate rocks (e.g., incongruent continental weathering, off-axis  
70 seafloor alteration, and reverse weathering in marine sediments),  $^6\text{Li}$  is preferentially  
71 incorporated into secondary minerals, leaving residual waters enriched in  $^7\text{Li}$  (Chan et al.,  
72 1992; Huh et al., 1998; Pistiner and Henderson, 2003). As a result, past variations in seawater  
73  $\delta^7\text{Li}$  have primarily been attributed to changes in global weathering regimes in response to  
74 climate or tectonic events (Crockford et al., 2020; Hathorne and James, 2006;  
75 Kalderon-Asael et al., 2021; Lechler et al., 2015; Misra and Froelich, 2012; Pogge Von  
76 Strandmann et al., 2013; Sun et al., 2018).

77 Systematically, oceanic water  $\delta^7\text{Li}$  value is frequently assumed to be similar to the carbonate  
78 record. However, determining if the formation of biogenic carbonates in the ocean is related  
79 to significant and variable Li isotope fractionations remains challenging. Low Li  
80 concentrations in these mineral phases, effects of diagenesis, and potential contamination  
81 from Li-rich authigenic minerals may bias their pristine isotopic signatures (Bastian et al.,  
82 2018; Dellinger et al., 2020; Pogge Von Strandmann et al., 2019). It was not until the late 20<sup>th</sup>  
83 century that scientists first analyzed four samples of Pleistocene foraminifera *Pulleniatina*  
84 *obliquiloculata* as well as two marine carbonates by thermal ionization mass spectrometry  
85 (TIMS) (You and Chan, 1996). Their results showed that foraminifera have lighter Li  
86 isotopic composition (19.3‰, 23.0‰) during glacial times, compared to interglacial (26.6‰,  
87 42.2‰). Then, Hoefs and Sywall. (1997) found a large fluctuation (from 7‰ to 20‰) for

88 mixed planktic species through the Holocene, partly attributed to inadequate sample cleaning.  
89 [Kosler et al. \(2001\)](#) measured  $\delta^7\text{Li}$  in core-top *Pulleniatina obliquiloculata* by Quadrupole  
90 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and reported  $\delta^7\text{Li}$  values from  
91 27.9‰ to 31.3‰ (modern seawater value being  $31.2\text{‰} \pm 0.3\text{‰}$ ).

92 In the past, the determination of Li isotope compositions in marine carbonates was  
93 constrained by instrumentation with low precision, typically exceeded 2‰. More recently,  
94 the precision was improved ([Table S1](#)), For instance, Li isotopes have been measured in low  
95 level marine carbonates using Q-ICP-MS associated to a desolvating system, within  $\pm 1.6\text{‰}$   
96 ( $2\sigma$ ) in precision ([Misra and Froelich, 2009](#); [Seyedali et al., 2021](#), [Vigier et al., 2008](#)). The  
97 use of SIMS (Secondary Ion Mass Spectrometry / ion microprobe) also enables (*in situ*)  $\delta^7\text{Li}$   
98 analyses for carbonate minerals, while avoiding contamination from surface Fe-oxydes and  
99 clays, with a reproducibility of 1.5‰ - 2‰ ( $2\sigma$ ) (e.g. [Vigier et al., 2007](#); [Rollion-Bard et al.,](#)  
100 [2009](#)). More recently, Multicollector-Inductively Coupled Plasma Mass Spectrometer  
101 (MC-ICP-MS) have allowed to achieved the measurement of Li isotopes in multiple  
102 carbonates samples, with a precision of about 0.5‰-0.8‰ ( $2\sigma$ ) (e.g. [Dellinger et al., 2020](#);  
103 [Pogge von Strandmann et al., 2019](#)). As a result, numerous  $\delta^7\text{Li}$  values have been published  
104 for various groups (e.g. foraminifera ([Bastian et al., 2018](#); [Hathorne and James, 2006](#);  
105 [Roberts et al., 2018](#); [Vigier et al., 2015](#); [Vigier et al., 2007](#)), corals ([Bastian et al., 2018](#);  
106 [Dellinger et al., 2018](#); [Marriott et al., 2004](#); [Rollion-Bard et al., 2009](#)), mollusks ([Dellinger et](#)  
107 [al., 2018](#)), echinoderms ([Dellinger et al., 2018](#)), brachiopods ([Dellinger et al., 2018](#); [Gaspers](#)  
108 [et al., 2021](#); [Washington et al., 2020](#))), as well as for marine bulk carbonate extracted by

109 sediment leaching (e.g. Dellinger et al., 2020; Murphy et al., 2022; Pogge Von Strandmann et  
110 al., 2019).

111 Cultures of calcifying species have been performed under controlled conditions (e.g.  
112 foraminifera (Roberts et al., 2018; Vigier et al., 2015) brachiopods (Gaspers et al., 2021), and  
113 mollusks (Dellinger et al., 2018)). Also, inorganic carbonate phases have been grown at the  
114 laboratory to study inorganic Li isotope fractionations ( $\Delta^7\text{Li}_{\text{carb-sol}}$ ) and their controls, which  
115 were compared to their biogenic equivalent (Day et al., 2021; Fuger et al., 2022; Gabitov et  
116 al., 2011; Marriott et al., 2004; Marriott et al., 2004; Seyedali et al., 2021; Taylor et al.,  
117 2019).

118

119 Table 1: Summary of the Li isotopic composition of biogenic and abiogenic carbonates.

|                     | $\Delta^7\text{Li}_{\text{carb-sol}}$ Minimum | $\Delta^7\text{Li}_{\text{carb-sol}}$ Maximum | Mean   | 2sd | N   |
|---------------------|---|---|--------|-----|-----|
| Biogenic calcite    | -11.5‰  | +9.7‰   | -2.83‰ | 6.5 | 192 |
| Synthetic calcite   | -10.1‰  | +3.8‰   | -5.11‰ | 6.1 | 73  |
| Biogenic aragonite  | -16.2‰  | -5.7‰   | -11.7‰ | 4.2 | 168 |
| Synthetic aragonite | -12.0‰  | -7.7‰   | -10.9‰ | 2.9 | 8   |

120 References for biogenic calcite are from (Marriott et al., 2004a; Hall et al., 2005; Hathorne and James, 2006;  
121 Vigier et al., 2007; Misra and Froelich, 2012; Vigier et al., 2015; Dellinger et al., 2018; Roberts et al., 2018;  
122 Washington et al., 2020; Gaspers et al., 2021; Hall and Chan, 2004; Bryan and Marchitto, 2008; Yun et al., 2005;  
123 Bryan and Marchitto, 2008; Hendry et al., 2009; Delaney et al., 1989) ; synthetic calcite are from : (Day et al.,  
124 2021; Marriott et al., 2004a; Marriott et al., 2004b; Fuger et al., 2022; Seyedali et al., 2021; Gabitov et al., 2011;  
125 Fuger et al., 2022); for biogenic aragonite from: (Marriott et al., 2004b; Rollion-Bard et al., 2009; Bastian et al.,  
126 2018; Dellinger et al., 2018; Cuny-Guirriec et al., 2019; Dellinger et al., 2020), and for synthetic aragonite from:  
127 (Day et al., 2021; Gabitov et al., 2011; Marriott et al., 2004;).

128

129 In the last 5-10 years, as the study of marine carbonates intensified, researchers have  
130 gradually found that modern marine carbonates exhibit a significant range of Li isotopic  
131 compositions (Table 1 and Fig. 1). The isotopic fractionation  $\Delta^7\text{Li}_{\text{carb-sol}}$  can vary from -16.2‰

132 (Aragonite mussel (Dellinger et al., 2018)) to +9.7‰ (Calcite scallop (Dellinger et al.,  
133 2018)).

134 Theoretically, “vital effects” can be quantified when comparing the isotope signature of  
135 biogenic and inorganic phases (Dellinger et al., 2018; Pogge Von Strandmann et al., 2019).

136 However, when we compile all published data from the literature, it appears that the range of  
137  $\Delta^7\text{Li}_{\text{carb-sol}}$  values in inorganic phases is as large as that of biogenic phases (see Fig. 1).

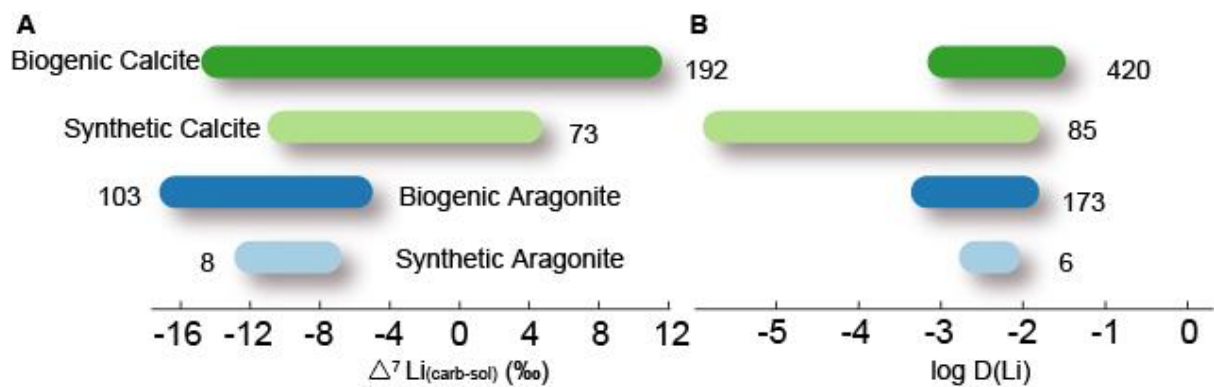
138 Consequently, it is difficult to use this method to demonstrate either the lack or the  
139 occurrence of biological Li isotope fractionations. Another key point is that the Li  
140 concentrations (or Li/Ca ratios) are rarely discussed while the environmental controls of  
141 biogenic Li concentrations may also impact Li isotopes (Thibon et al., 2021).

142 The present study compiles, to the best of our knowledge, all the published data on modern  
143 carbonates. Due to the low Li levels in modern marine carbonate, their Li concentration and  
144 isotopic compositions are easily influenced by silicate minerals present in the same  
145 environment (clay micrograins in particular) (Pogge Von Strandmann et al., 2021; Dellinger  
146 et al., 2020; Pogge Von Strandmann et al., 2019; Bastian et al., 2018; Dellinger et al., 2018;  
147 Misra and Froelich, 2009; Vigier et al., 2007; Hall et al., 2005). As a consequence, our  
148 dataset does not include carbonates that have been affected by marine diagenesis. Since  
149 different authors may have inconsistent criteria for diagenetic imprint (e.g., Mn/Ca, Al/Ca,  
150 Sr/Fe, Li/(Mg+Ca), etc.), and there are significant differences in the criteria for assessing  
151 contamination in carbonate samples coming from different sites and sedimentary contexts,  
152 we strictly followed each authors' standards when selecting data to include.



153 Through statistical tests, we aim to clarify the potential differences in Li isotopic  
 154 compositions and in Li/Ca among the various carbonate phases, and various categories, but  
 155 also evaluate the role of environmental parameters when possible. This work also tentatively  
 156 highlights the gaps to fill for future works in paleo-environment and paleoceanography.

157



158

159 **Fig. 1:** Range of **A)** carbonate - water Li isotope fractionations ( $\Delta^7\text{Li}_{\text{carb-sol}}$ ) and **B)** Li partition  
 160 coefficients ( $D(\text{Li})$  in  $\mu\text{mol mol}^{-1} = (\text{Li}/\text{Ca})_{\text{carb}}/(\text{Li}/\text{Ca})_{\text{sol}}$ ) published for inorganic calcite (light  
 161 green), inorganic aragonite (light blue), modern biogenic calcite (dark green) and modern biogenic  
 162 aragonite (dark blue). Modern biogenic phases include core-top data and a few living organisms.  
 163 More detailed subset data can be found in the Sup. Mat. [Table S2](#). Same references as in [Table 1](#).

164 **2. Multiple controls of Li/Ca and Li isotopes during inorganic carbonate**  
 165 **growth**

166 To date, seven studies investigated the Li isotopic composition of synthetic carbonates grown  
 167 under controlled conditions ([Day et al., 2021](#); [Füger et al., 2022](#); [Gabitov et al., 2011](#);  
 168 [Marriott et al., 2004](#); [Marriott et al., 2004](#); [Seyedali et al., 2021](#); [Taylor et al., 2019](#)). While  
 169 the study conducted by [Taylor et al. \(2019\)](#) focuses on carbonate formation at high  
 170 temperatures (which is not discussed here), the remaining studies utilized a wide range of

171 experimental conditions, as summarized in [Table 2](#).

172 [Marriott et al. \(2004a\)](#) were the pioneers in investigating the effect of temperature on the Li  
173 isotopic composition of inorganic carbonates. At different temperatures (5-30°C), calcite is  
174 synthesized by mixing  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  solutions. The authors report a Li isotopic  
175 fractionation  $\Delta^7\text{Li}_{\text{carb-sol}} \sim -8\text{‰}$ , unaffected by temperature. In contrast, calcite Li/Ca ratio  
176 decreases significantly with increasing temperature (from 7.51 to 2.47  $\mu\text{mol mol}^{-1}$ ). [Marriott](#)  
177 [et al. \(2004b\)](#) further investigated the influences of minerals and salinity. Their results show  
178 that the mineral type has a decisive effect on Li isotopes. Indeed, the Li isotope fractionation  
179 during aragonite growth is relatively large (-11‰) compared to the calcite one (-3‰).  
180 Salinity variations (from 10 to 50 psu) do not affect the Li isotopic composition for both  
181 minerals. Nevertheless, an increase in solution salinity increases the Li/Ca ratio of calcite  
182 (from 14.5 to 62.9  $\mu\text{mol mol}^{-1}$ ), while aragonite Li/Ca remains essentially constant (19.3  
183  $\mu\text{mol mol}^{-1}$ ). Importantly, a comparison of the two studies ([Marriott et al., 2004a and 2004b](#))  
184 reveals a significant difference in the Li isotopic fractionation during calcite formation (of  
185 5‰). One potential explanation might be the higher solution pH used in [Marriott et al.](#)  
186 [\(2004b\)](#) compared to [Marriott et al. \(2004a\)](#) (pH= 7.7 to 8.3 vs. 6.9 to 7.1, respectively).  
187 Another factor could be that [Marriott et al. \(2004b\)](#) precipitated calcite from artificial  
188 seawater, while [Marriott et al. \(2004a\)](#) used deionized water.

189 Several years later, [Gabitov et al. \(2011\)](#) precipitated aragonite by adding  $\text{Na}_2\text{CO}_3$  to  
190 pre-concentrated seawater (1L of seawater was evaporated to half of its volume). The  
191 corresponding  $\Delta^7\text{Li}_{\text{carb-sol}}$  ranges from -10.5‰ to -7.7‰, which is smaller in magnitude

192 compared to the findings of Marriott et al. (2004b) (-11‰). In 2021, Day et al. simulated  
193 cave stalagmites precipitation by degassing. They dropped a calcite-saturated solution from a  
194 container with a high partial pressure of carbon dioxide, into a container with a lower partial  
195 pressure of carbon dioxide. The initial solution was made from dissolved calcite spiked with  
196 trace elements. The Li isotope fractionation  $\Delta^7\text{Li}_{\text{carb-sol}}$  is -6.5 to -9.9‰ for calcite,  $-7.3 \pm 0.6\text{‰}$   
197 for high-Mg calcite (HMC), and  $-10.7 \pm 0.5\text{‰}$  for aragonite. In contrast to Marriott et al.  
198 (2004b), the study indicates that carbonate minerals have a limited influence Li isotopic  
199 fractionation. Instead, they highlight a strong influence of the mineral growth rate, with  
200 higher rates leading to larger Li isotopic fractionation.

201 The same year, Seyedali et al. (2021) grew calcite under controlled conditions by mixing  
202  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  solutions at different pH. They find that the  $\Delta^7\text{Li}_{\text{carb-sol}}$  values increase  
203 from -6‰ to +2‰ as the pH increase. They suggest a key role of Li speciation inferring that  
204 Li in solution is first bound into calcite as  $\text{LiHCO}_3$  before being incorporated into the calcite  
205 structure. Thus, their  $\Delta^7\text{Li}_{\text{carb-sol}}$  values may result from kinetics processes related to surface  
206 attachment and from changes in the Li speciation in solution, depending on both dissolved  
207 carbon concentration and pH.

208 Most recently, by mixing  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  solutions to grow calcite grains, Fuger et al.  
209 (2022) find that the  $\Delta^7\text{Li}_{\text{carb-sol}}$  values range from -5.3‰ to -1.8‰, and decrease in magnitude  
210 when solution pH increases (under a growth rate of  $10^{-7.5}$  to  $10^{-7.9}$  mol m<sup>-2</sup> s<sup>-1</sup>), or when the  
211 growth rate decreases (for  $8.1 < \text{pH} < 8.4$ ).

212 Overall, most experiments led to a lighter Li isotopic composition of the synthesized  
213 carbonates relative to the growth solution, except for a few data published by [Seyedali et al.](#)  
214 [\(2021\)](#). Additionally, all experiments led to significantly low  $D(\text{Li})$  ( $< 10^{-1} - 10^{-5}$ ), essentially  
215 expressing the lack of compatibility of Li into carbonate phases. In the following, we further  
216 detail the current knowledge on major control factors investigated in the literature  
217 (mineralogy, temperature, pH, growth rate).

219 Table 2: Summary of the characteristics of all published experiments of inorganic carbonate precipitation. \*HMC indicates high magnesium calcite.

|                                 | Marriott et al. 2004a                   | Seyedali et al. 2021                                 | Day et al. 2021                    | Fuger et al. 2022                                    | Marriott et al. 2004b                                | Gabitov et al. 2019             | Day et al. 2021                    | Marriott et al. 2004b                                | Gabitov et al. 2011             | Day et al. 2021                    |
|---------------------------------|---|--|------------------------------------|--|--|---------------------------------|------------------------------------|--|---------------------------------|------------------------------------|
| <b>Mineralogy</b>               | Calcite                                 | Calcite  | Calcite                            | Calcite  | Calcite  | Calcite                         | Aragonite                          | Aragonite  | Aragonite                       | *HMC                               |
| <b>Seed crystal</b>             | Calcite                                 | Vaterite   | Calcite                            | Calcite  | Calcite  | Unseeded                        | Calcite                            | Calcite  | Unseeded                        | Calcite                            |
| <b>Media solution</b>           | Deionized water                         | Deionized water                                      | Deionized water                    | NaCl solution  | Artificial seawater                                  | Artificial seawater             | Deionized water                    | Artificial seawater                                  | Natural Seawater                | Deionized water                    |
| <b>Li source</b>                | LiCl                                    | Li <sub>2</sub> CO <sub>3</sub>                      | -                                  | LiCl   | Li <sub>2</sub> CO <sub>3</sub>                      |                                 | -                                  | Li <sub>2</sub> CO <sub>3</sub>                      | Li <sub>2</sub> CO <sub>3</sub> | -                                  |
| <b>Reactants</b>                | CaCl <sub>2</sub><br>NaHCO <sub>3</sub> | CaCl <sub>2</sub><br>Na <sub>2</sub> CO <sub>3</sub> | Ca(HCO <sub>3</sub> ) <sub>2</sub> | CaCl <sub>2</sub><br>Na <sub>2</sub> CO <sub>3</sub> | CaCl <sub>2</sub><br>Na <sub>2</sub> CO <sub>3</sub> | Na <sub>2</sub> CO <sub>3</sub> | Ca(HCO <sub>3</sub> ) <sub>2</sub> | CaCl <sub>2</sub><br>Na <sub>2</sub> CO <sub>3</sub> | Na <sub>2</sub> CO <sub>3</sub> | Ca(HCO <sub>3</sub> ) <sub>2</sub> |
| <b>Li (μmol L<sup>-1</sup>)</b> | 176 to 210                              | 90 to 570  | 25 to 71                           | 230 to 500   | 82 to 409  | 44.5 and 47.4                   | 17                                 | 82 to 409  | ~ 600                           | 28                                 |
| <b>Mg (mmol L<sup>-1</sup>)</b> | 0                                       | 0  | 0.044 to 0.14                      | 0  | 1.5 to 7.6   | 42.4 and 42.5                   | 4.7                                | 15 to 76   | 1.22                            | 2.5                                |
| <b>Ca (mmol L<sup>-1</sup>)</b> | 240 to 470                              | 0.02 to 135.93                                       | 2.0 to 4.8                         | 0.1 to 12.17   | 2.85 to 14.3   | 7.3 and 7.6                     | 1.2                                | 2.85 to 14.3   | 229.54                          | 1.9                                |
| <b>pH</b>                       | 6.9 to 7.1                              | 6.2 to 9.5   | 7.4 to 8.1                         | 6.31 to 9.59   | 7.7 to 8.3   | 8.55 and 8.54                   | 8.3                                | 7.7 to 8.3   | -                               | 8.1                                |
| <b>T (°C)</b>                   | 5 to 30                                 | 20.7±1.5   | 7 to 35                            | 25   | 25   | 24                              | 20                                 | 25   | 25                              | 20                                 |
| <b>Duration (days)</b>          | 0.21                                    | 5 to 400   | 21                                 | 1  | 0.33   | 244                             | 21                                 | 0.33   | -                               | 21                                 |

## 220 **2.1 Debated mineralogical control**

221 Synthetic inorganic carbonates include three types: calcite, aragonite, and  
222 high-magnesium calcite (HMC). As illustrated in [Fig. 1](#), most published Li/Ca and  
223  $\delta^7\text{Li}$  values concern calcite minerals ( $n = 85$  and  $73$  respectively), while there are only  
224 few experimental data for inorganic aragonite ( $n = 6$  and  $8$  respectively). Therefore, it  
225 remains difficult to compare both datasets statistically. For inorganic calcite, every  
226 additional published experiment has enlarged the range of values for  $\Delta^7\text{Li}_{\text{carb-sol}}$  and  
227  $D(\text{Li})$ , and we can suspect that it will be the same for experimental aragonite in the  
228 future.

229 Another concern arises from the lack of synthesis experiments conducted under  
230 natural seawater conditions. Although [Gabitov et al. \(2011\)](#) initially employed  
231 seawater, they diminished its volume by half through evaporation. Consequently, the  
232 concentrations of all dissolved elements were twice as high as those found in typical  
233 natural seawater. Other published experiments used simplified artificial seawater or  
234 deionized water.

235 In a seawater-like (synthetic) environment ([Gabitov et al., 2011](#); [Marriott et al., 2004](#)),  
236 the Li isotope fractionation during calcite growth ( $-3.1\text{‰}$  to  $-1.9\text{‰}$ ) is smaller  
237 compared to one obtained during aragonite growth ( $-7.7\text{‰}$  to  $-12\text{‰}$ ). A similar  
238 phenomenon can be observed when deionized water is used; however, the extent of  
239 fractionation displayed by calcite synthesized in deionized water can be greater ( $-10.1\text{‰}$   
240 to  $+0.2\text{‰}$ ) ([Day et al., 2021](#); [Füger et al., 2022](#); [Marriott et al., 2004](#)). Yet, more data

241 are required for a reliable statistical treatment and establish the role of the solution  
242 chemical composition.

243 Concerning carbonate Li contents, we can compare different contexts and  
244 experiments by using Li partition coefficients ( $D(\text{Li}) = (\text{Li}/\text{Ca})_{\text{calcite}} / (\text{Li}/\text{Ca})_{\text{solution}}$ ).

245 For inorganic calcite,  $D(\text{Li})$  range is wider than for inorganic aragonite ( $10^{-5.7} - 10^{-2}$   
246 and  $10^{-2.6} - 10^{-2.2}$ , respectively), but the number of data is scarce for the latter (Fig. 1).

247 For HMC there is currently only one data ( $10^{-1.9}$ ).

248 Given that Li ions are incorporated differently into the calcite and the aragonite  
249 structures, a significant discrepancy between both phases would be expected for both  
250 Li isotopes and  $D(\text{Li})$ . Indeed, Li ions substitute for the Ca ions site in aragonite,  
251 whereas in calcite, Li can be incorporated into interstitial positions in its hydrated  
252 form (Marriott et al., 2004a). This may explain why calcite  $D(\text{Li})$  increases with  
253 increasing salinity, while aragonite  $D(\text{Li})$  remains relatively stable when salinity  
254 varies (Marriott et al., 2004a). More data are however needed to better quantify these  
255 aspects, particularly for aragonite and HMC.

## 256 **2.2 Small influence of temperature**

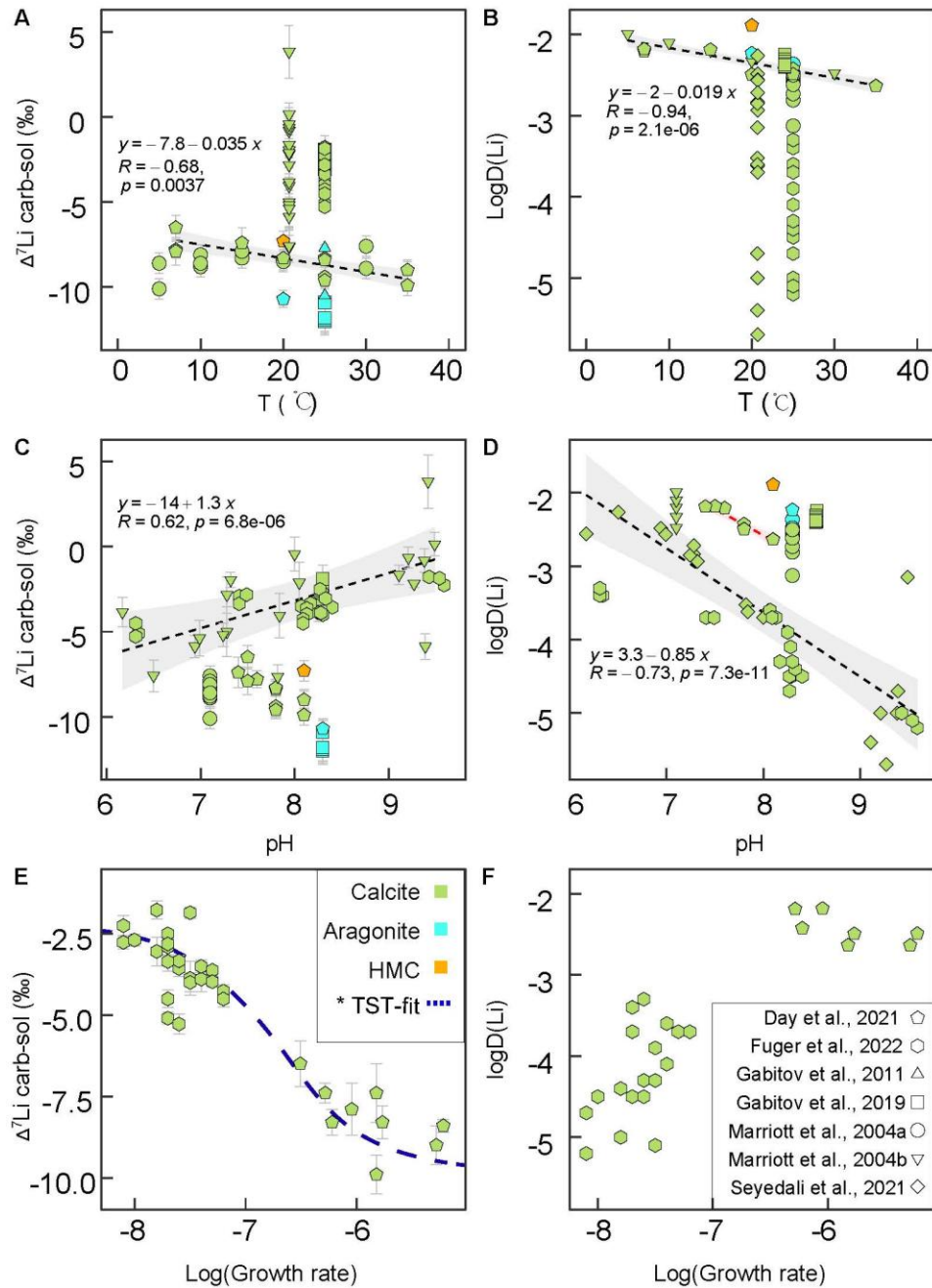
257 Two studies found that the Li isotope fractionation between calcite and growth  
258 solution ( $\Delta^7\text{Li}_{\text{carb-sol}}$ ) is negligibly affected by temperature (Day et al., 2021; Marriott  
259 et al., 2004a). Day et al. (2021) experiment led to a slight but significantly negative  
260 correlation with temperature, as shown in Fig. 2A. In their experiment, other

261 parameters such as pH and growth rate (see [Fig. 2C, 2E](#)) varied as well, and among  
262 them it appears that temperature induced the smallest effect.

263 In contrast,  $D(\text{Li})$  (expressed as  $\log D(\text{Li})$ ) corresponding to synthetic calcites show a  
264 very consistent and negative correlation with temperature ( $R = -0.94$ , [Day et al., 2021](#);  
265 [Marriott et al., 2004a](#)). Thus, calcite formed at high temperatures contains less Li than  
266 at low temperatures ([Fig. 2B](#)). Both studies give consistent results and used a Ca  
267 solution enriched in Li as the growth medium, although the technique used to reach  
268 saturation was different (see [Table 1](#)). Interestingly, two other experimental studies of  
269 inorganic calcite formation ([Füger et al., 2022](#); [Seyedali et al., 2021](#)), show that, at  
270 constant temperature, the variations in both Li isotope values and  $D(\text{Li})$  values are  
271 much larger than those caused by varying the temperature alone. It strongly suggests  
272 that temperature is not the dominant control factor and that other parameters play a  
273 crucial role in Li incorporation by calcite.

274 Finally, [Day et al. \(2021\)](#) and [Marriott et al. \(2004a\)](#) evaluate the effect of  
275 temperature for aragonite and high magnesium calcite. Their Li data are roughly  
276 consistent with the results obtained for calcite. Nevertheless, additional experiments,  
277 covering a larger temperature range, are required to precisely confirm these  
278 statements (see [Fig. 2A and 2B](#)).





279

280 **Fig. 2:** Compilation of Li isotopic fractionations and Li partition coefficients between  
 281 precipitated inorganic carbonate and growth solution. Each data point represents a value  
 282 measured for one carbonate aliquot (**A and B**) Effect of temperature. The black dashed lines  
 283 indicate linear regressions for calcite, gray shading represents confidence intervals. Data are  
 284 from [Marriott et al. \(2004a\)](#) and [Day et al. \(2021\)](#); (**C and D**) Effect of the solution (final) pH.  
 285 Black dashed lines indicate linear regressions for calcite. Data are from [Seyedali et al. \(2021\)](#)  
 286 and [Füger et al. \(2022\)](#); (**E and F**) Effect of the growth rate (in log10). The trend shown in  
 287 [Fig. 2E](#) is reported from [Füger et al. \(2022\)](#) and represents a TST model using specific  
 288 modifications (e.g. backward calcite dissolution rate), distinguishing it from the TST model  
 289 classically used for divalent ions (see text for more details).

## 290 **2.3 Significant influence of pH**

291 Fig. 2C reveals a strong linear relationship between Li isotope fractionation for calcite  
292 and the solution pH. As the pH decreases, the extent of fractionation increases.  
293 Similarly, for calcite, there is a significant linear relationship between the  $\log D(\text{Li})$   
294 and pH, where lower pH values correspond to higher  $\log D(\text{Li})$  values and (Fig. 2D).  
295 The observed similarity in the behavior of Li isotope fractionation and elemental  
296 partitioning in calcite with respect to pH suggests the involvement of a common  
297 mechanism regulating both processes.

298 There is still controversy regarding the species in which Li is incorporated into  
299 forming carbonate, and if the solution pH may play a role. Some authors argue that  
300 there is only one type of Li incorporated into calcite, while others propose that there  
301 are more than two Li species, depending on the pH. For example, Seyedali et al.  
302 (2021) suggested that over a large pH range (between 6.2 and 9.5), the most likely  
303 form of Li incorporation into calcite is as  $\text{LiHCO}_3$  (rather than as  $\text{Li}_2\text{CO}_3$  or  $\text{LiNaCO}_3$ ).  
304 The authors argue that in the absence of kinetic effects and with constant activity  
305 coefficients, the overall process of Li incorporation into calcite must maintain charge  
306 balance. Therefore, the equilibrium constants for the  $\text{LiHCO}_3$  should remain  
307 unchanged as a function of pH (for a given growth rate). Fuger et al. (2019, 2022).  
308 propose that the dominant reaction for Li incorporation into calcite is as follows:



310 which indicates that Li incorporation in calcite is not only related to the solution  
311  $\text{HCO}_3^-$ , but also controlled by the  $\text{Li}^+$  and  $\text{Ca}^{2+}$  concentration of the solution. When  
312 the dissolved concentration of  $\text{Ca}^{2+}$  and  $\text{Li}^+$  are constant (e.g.  $\text{Ca}^{2+}$ -saturated solution),  
313 a decrease in pH triggers  $\text{LiHCO}_3$  formation, and more Li can be incorporated into  
314 calcite. In contrast, when dissolved Ca concentration is not constant (the  $\text{Ca}^{2+}$   
315 concentration is usually increased at lower pH to keep an oversaturated medium), a  
316 lower pH results in less  $\text{LiHCO}_3$  formation and, therefore, in less Li in calcite. This  
317 may explain why we observe a negative correlation between  $\log D(\text{Li})$  and pH in Fig.  
318 2D. Fuger et al. (2022) therefore suggest that  $\text{LiHCO}_3$  is dominant within a specific  
319 pH range, rather than the entire range of 6.3 to 9.5.

320 Concerning Li isotopes, early precipitation experiments (Marriott et al., 2004a;  
321 Marriott et al., 2004b) did not consider pH as a potential variable because  $\text{Li}^+$  in  
322 seawater mainly remains surrounded by four water molecules, in contrast with other  
323 biogeochemical tracers such as boron, for which speciation in seawater is known to be  
324 pH dependent (e.g. Foster and Rae, 2016). Nevertheless, a positive correlation was  
325 recently found for inorganic calcite between  $\Delta^7\text{Li}_{\text{carb-sol}}$  and solution pH (Seyedali et  
326 al., 2021; Fuger et al., 2019; Marriott et al., 2004a; Marriott et al., 2004b). As the pH  
327 of the solution increases, the extent of fractionation of the calcite Li isotope decreases.  
328 As shown in Fig. 2C, this pH effect may reconcile the isotopic discrepancy observed  
329 between the two Marriott et al. studies (2004a; 2004b). In contrast, the stalactite  
330 experiments performed by Day et al. (2021) exhibit a small (negative) correlation  
331 between  $\Delta^7\text{Li}_{\text{carb-sol}}$  and solution pH, but the range of tested pH was narrow (from 7.4

332 to 8.3 [Fig. 2C](#)), and the calcite growth rate significantly higher. It cannot be excluded  
333 that variations in the Li aqueous speciation caused by changes in solution chemistry  
334 may induce changes in the equilibrium isotopic fractionation factor. Indeed, under a  
335 given growth rate and at isotopic equilibrium, if dissolved Li occurs under as a single  
336 specie only, the isotopic fractionation should remain constant.

337 Another parameter of importance is the Saturation Index (SI), which is often related to  
338 the solution pH. In our [Fig. S2](#) (Supplementary Material), we can see that at a single  
339 SI, a large variation of isotopic fractionations can be found. Also, when SI increases  
340 significantly, relatively small  $\Delta^7\text{Li}_{\text{carb-sol}}$  variations are observed. This preliminary  
341 observation suggests a weak influence of the SI on Li isotopic fractionation. However,  
342 as experimental conditions among the various studies are very distinct in salinity, in  
343 solution chemical composition and in calcium concentrations, it is difficult to directly  
344 compare their SI values. More experimental work will need to be undertaken under  
345 natural seawater conditions to better evaluate the role of this parameter. Finally, it  
346 cannot be excluded that the trends as a function of pH ([Fig. 2C](#) and [Fig. 2D](#)) may also  
347 be – at least partly - driven by growth rates.

## 348 **2.4 Strong influence of growth rate**

349 Currently, there are two articles investigating the influence of the growth rate of  
350 inorganic calcite on Li isotope fractionation ([Day et al., 2021](#); [Füger et al., 2022](#)).  
351 However, their measurement methods for growth rate differ. [Füger et al. \(2022\)](#) used  
352 mass balance equations. [Day et al. \(2021\)](#) applied image analysis to estimate the

353 surface area of calcite and conducted eight experiments to establish a relationship  
354 between surface area and growth mass. Despite these differences, the two studies  
355 display a consistent trend, as displayed in Fig. 2E and 2F and consequently we  
356 consider in the following that their comparison appears overall reasonable.

357 Füger et al. (2022) show that  $\log D(\text{Li})$  values of inorganic calcite increase with the  
358 calcite growth rate (usually expressed in  $\text{mol m}^{-2} \text{s}^{-1}$ ) (Fig. 2F). As growth rates  
359 increase from  $10^{-8.1}$  to  $10^{-7.1} \text{ mol m}^{-2} \text{ s}^{-1}$ ,  $D(\text{Li})$  values rise strongly from  $10^{-4.8}$  to  $10^{-2.9}$ ,  
360 indicating that at a higher growth rate it is easier for Li to enter calcite grains. This  
361 was previously reported for divalent ions in calcite, i.e.,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Mg}^{2+}$  (Gabitov and  
362 Watson, 2006; Mavromatis et al., 2018; Mavromatis et al., 2013). A growth  
363 entrapment model (GEM) was developed to explain this process (Watson, 2004). The  
364 GEM suggests that the surface composition of a crystal in equilibrium with a solution  
365 is usually different from that of a bulk crystal (as divalent ions are enriched at the  
366 crystal surface). If the crystal grows excessively fast, this equilibrium is broken, and  
367 the slower diffusing divalent ions become trapped and eventually form a solid by  
368 direct substitution of Ca ions.

369 However,  $\text{Li}^+$  ions do not usually directly replace  $\text{Ca}^{2+}$ , due to a large difference in  
370 ionic radii, and to charge imbalance (Füger et al., 2019). This behavior is expected to  
371 be close to that of Na and other alkali elements. Notably, it has been shown that  $\text{Na}^+$   
372 concentration of calcite depends on the number of calcite defects (Busenberg and Niel  
373 Plummer, 1985). These crystal defects are controlled by the growth rate, i.e., the  
374 faster the growth rate, the more defects are observed at the surface of the newly

375 formed crystals, and the more Na<sup>+</sup> ions can enter the crystals. Okumura and Kitano.  
376 (1986) reached the same conclusion for other alkali elements (K<sup>+</sup> and Rb<sup>+</sup>). A recent  
377 study further supported that D(Li) and D(Na) display a similar linear relationship with  
378 growth rate (Füger et al., 2019). Overall, these studies indicate that growth rate plays  
379 an essential role in the Li - and other alkali - content of calcite.

380 It is however noteworthy that no correlation between growth rate and logD(Li) was  
381 observed in the slowly growing calcite from a doubly concentrated seawater solution  
382 (Gabitov et al., 2019). It may be explained by the fact that natural seawater contains a  
383 large amount of Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>, which can readily incorporate the calcite and  
384 potentially change its crystal structure. This discrepancy suggests that a direct  
385 comparison of synthetic calcite with marine authigenic calcite is not always  
386 appropriate, at least for D(Li).

387 Considering Li isotopes, the recent study of (Füger et al., 2022) revealed that calcite  
388  $\Delta^7\text{Li}_{\text{carb-sol}}$  value remains essentially constant ( $\Delta^7\text{Li}_{\text{carb-sol}} = -2.76 \pm 0.22\%$ ) when the  
389 calcite growth rate remains at a low level ( $< 10^{-7.7}$  mol m<sup>-2</sup> s<sup>-1</sup>). However, as the  
390 growth rate increases ( $> 10^{-7.7}$  mol m<sup>-2</sup> s<sup>-1</sup>), the  $\Delta^7\text{Li}_{\text{carb-sol}}$  increases rapidly in  
391 magnitude. This indicates that more <sup>6</sup>Li is incorporated into calcite at higher growth  
392 rates (Fig. 2E). Day et al. (2021) also observed a negative correlation between  
393  $\Delta^7\text{Li}_{\text{carb-sol}}$  and growth rate (Fig. 2E). By comparing the data from Marriott et al.  
394 (2004a) and Marriott et al., (2004b), although the surface area is not specified we note  
395 that calcite with faster growth rates (0.2 g h<sup>-1</sup> vs 0.09 g h<sup>-1</sup>) leads to a larger isotopic

396 fractionation (-8‰ versus -3‰), , as initially suggested by (Day et al., 2021), and this  
397 is fully consistent with the above findings

398 Füger et al. (2022) suggested that, when the growth rate is slow, isotopic fractionation  
399 operates near equilibrium, the net reaction rates of precipitation and dissolution are  
400 essentially equal,  $\Delta^7\text{Li}_{\text{carb-sol}}$  is small and constant. When the growth rate increases and  
401 gradually separates from equilibrium conditions, desolvation of the inner hydration  
402 sphere of aqueous  $\text{Li}^+$  ion increases the kinetic isotopic fractionation.

403 Note that the relationship between isotopes of divalent cations and growth rate can be  
404 expressed by the transition state theory (TST), assuming the generation of a  
405  $\text{Ca}_{1-x}\text{Me}_x\text{CO}_3$ -composed diluted solid solution, whose rate of precipitation under  
406 steady-state chemical conditions is equivalent to that of the  $\text{CaCO}_3$  phase. In fact, as  
407 shown in Fig. 2E, Fuger et al. (2022) managed to fit both published datasets using an  
408 adapted TST model, with specific backward calcite dissolution rate, distinguishing it  
409 from the one classically used for divalent ions. However, assuming that Li is a priori  
410 not present in calcite under a solid solution form, the same authors still consider  
411 desolvation as the most reasonable process explaining the observed negative trend.

## 412 **2.5 Principal component analysis (PCA) of the combined effects**

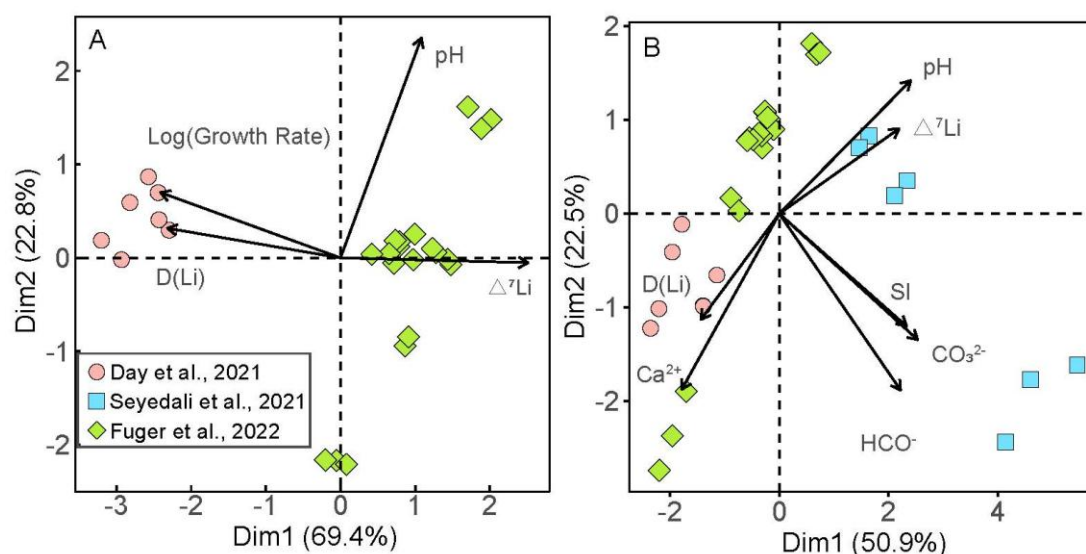
413 Overall, previous studies have shown that the inorganic calcite-solution Li isotopic  
414 fractionation appears little affected by temperature, salinity, and Li concentration of  
415 the growth solution, and display a higher influence of solution pH and kinetic effects  
416 related to the growth rate (see Fig. 2).

417 As the synergy of several parameters may control Li isotope fractionation and D(Li),  
418 we applied a principal component analysis (PCA) to the published inorganic calcite  
419 data in order to further identify the most influent parameters. In Fig. 3A, our principal  
420 component analysis was applied to the two experiments reporting growth rate data  
421 (Day et al., 2021; Fügler et al., 2022). It indicates that the  $\Delta^7\text{Li}_{\text{carb-sol}}$  and Log (Growth  
422 rate) anti-vary with each other on the principal component 1 (Dim 1), representing  
423 69.4% of the whole dataset variability (other graphs and details on all Dimensions can  
424 be seen in the Supplementary Material). It overall shows that the variability between  
425 the two studies is discriminated primarily by  $\Delta^7\text{Li}_{\text{carb-sol}}$  and Log(Growth rate), which  
426 is also consistent with Fig. 2E. Fig. 3A also highlights a strong relationship between  
427 D(Li) and Log(Growth rate) on Dim1. However, Day et al. data are grouped on this  
428 Dimension and therefore the growth rate does not participate much to their variance.  
429 On the other hand, the larger “intragroup” variability of the Fuger et al. data is mainly  
430 associated to pH variations following the principal component 2 (Dim 2), in  
431 agreement with Fig. 2D. Thus, this analysis shows that - based on the currently  
432 available data - the growth rate of calcite appears to be a major parameter for calcite  
433 Li isotope compositions.

434 Due the lack of growth rate data in Seyedali et al. (2021), we conducted another PCA,  
435 including other potentially relevant parameters that are available and also variable for  
436 the three considered experiments (e.g. bicarbonate ion concentration ( $\text{HCO}_3^-$ ),  
437 carbonate ion concentration ( $\text{CO}_3^{2-}$ ), calcium ion concentration ( $\text{Ca}^{2+}$ ), solution pH,  
438 and the Saturation Index (SI)). Similarly, all details on all Dimensions are given in the



439 Sup. Mat. Even if there does not seem to be a dominant parameter in Dim1  
 440 explaining most of the variance, Fig. 3B shows that both  $\Delta^7\text{Li}_{\text{carb-sol}}$  and D(Li)  
 441 variability are mostly related to changes in solution pH and in dissolved  $\text{Ca}^{2+}$   
 442 concentrations. Since both parameters may influence the calcite growth rate, this  
 443 result appears consistent with Fig. 2 CDEF.



444  
 445 **Fig. 3:** Principal component analysis (PCA) for inorganically precipitated calcite. Dim 1 and  
 446 Dim 2 are principal components 1 and 2. Arrow length is proportional to the percentage  
 447 contribution of these first three principal components to the observed variation of each  
 448 variable. **A)** the relationship between D(Li),  $\Delta^7\text{Li}_{\text{carb-sol}}$ , pH, and the Log(Growth rate) is  
 449 depicted. Dim 1, Dim 2 and Dim 3 represent 98.9% of the variability in the dataset. **B)**  
 450 illustrates the relationship between  $\Delta^7\text{Li}_{\text{carb-sol}}$ , solution ions ( $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ), SI, and pH.  
 451 Dim1, Dim2, and Dim3 explain 83.2% of the variability in the dataset. See Sup Mat for  
 452 complementary PCA results (Fig. S1-1; S1-2).

453  
 454 The differences observed between the Seyedali et al, (2021) and the other two  
 455 experiments can be distinguished in principal component 1, with  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and SI  
 456 contributing to the observed variations, which is consistent with experimental  
 457 conditions (Table 2). On the other hand, the disparities within the Day et al., (2021)  
 458 and the Fuger et al. (2022) datasets are mostly related to principal component 2, and

459 can be associated to differences in aqueous  $\text{Ca}^{2+}$  concentrations and pH. To some  
460 extent, this may also be related to growth rates, at least for the Fuger et al. study,  
461 which used Ca-based mass balance equations to determine them (see section 2.4).

### 462 **3. Li/Ca and Li isotopes in biogenic carbonates**

463 Several studies have been conducted to determine the role of environmental  
464 parameters on Li/Ca ratios measured in biogenic carbonates. Field samples and  
465 laboratory cultures demonstrate that the incorporation of Li is affected by a variety of  
466 factors such as temperature, dissolved inorganic carbon (DIC), pH and biology ("vital  
467 effects") (Dellinger et al., 2018; Hall and Chan, 2004; Hathorne et al., 2013; Lear and  
468 Rosenthal, 2006; Roberts et al., 2018; Vigier et al., 2015). According to Delaney et al.  
469 (1989), temperature initially appeared to significantly influence the Li/Ca ratio of  
470 brachiopod shells, similar to that observed in synthetic calcite (Marriott et al., 2004).  
471 However, no systematic relationship between Li/Ca and temperature has been found  
472 for other types of biogenic carbonates. Instead, culture experiments and core top  
473 studies have shown that the Li/Ca ratio of foraminifera is mostly influenced by  
474 growth rate, solution Li/Ca ratio and DIC (Hall et al., 2005; Hathorne and James,  
475 2006; Lear and Rosenthal, 2006; Vigier et al., 2015). Also for mollusks, Li/Ca ratios  
476 have recently been inferred to result from a combination of biological processes,  
477 growth rate, and planktic productivity (Dellinger et al., 2020; Thébault and Chauvaud,  
478 2013; Thébault et al., 2009).

479 Concerning Li isotopes, it has been first considered that inorganic carbonate

480 precipitation experiments could provide a theoretical basis for the study of Li isotopic  
481 fractionation mechanism during carbonates growth. However, natural processes  
482 related to the organism biology may cause additional isotopic effects (Roberts et al.,  
483 2018; Dellinger et al., 2018; Vigier et al., 2015, Thibon et al., 2021). In particular, Li  
484 isotopes may be, at the cellular level, strongly fractionated during transmembrane  
485 active and passive transport (Poet, Vigier, Bouret et al., 2023). Some of these  
486 transporters (Na-H Exchangers: NHE) are ubiquitous – present in all living species - and  
487 involved in intracellular pH regulation at play during the growth of calcifying species.  
488 In addition, different carbonate-producing organisms may form shells or skeletons  
489 with entirely different structures, growth rates, and mineralogy (Dellinger et al., 2018;  
490 Rollion-Bard et al., 2009). Besides, the calcifying fluid may be chemically and  
491 isotopically distinct from the seawater in which the organisms live. Another  
492 complication is that the environment in which organisms live may change over time  
493 (e.g., seawater pH, saturation state, nutrients). Finally, after the organism's death,  
494 sedimentary processes may bias the original carbonate isotopic signature, such as  
495 contamination by silicate minerals or Fe-Mn oxides, structure modification, isotope  
496 exchange, and fluid circulations during early diagenesis. In the following, we review  
497 the literature data (1) separating results from laboratory cultures and modern  
498 carbonates collected in the ocean and (2) providing a detailed focus on foraminifera  
499 data, since this group represents most of the published data, allowing statistical  
500 treatments. For this analysis, we took into account only the values validated by the  
501 authors as free from diagenetic effects, based on various geochemical tracers and/or

502 optical observations. Note that several methods have recently been developed for  
503 ensuring reliable and precise Li isotopic analyses of natural - low level - carbonate  
504 phases (e.g. Bastian et al., 2018; Pogge Von Strandmann et al., 2019; Van Hoecke et  
505 al., 2015).

506

### 507 **3.1 Laboratory cultures of calcifying organisms: a means to study** 508 **fractionating mechanisms**

509 Several studies investigated “vital effects” on Li/Ca and Li isotopes through aquarium  
510 cultures of calcifying organisms, i.e. foraminifera (Roberts et al., 2018; Vigier et al.,  
511 2015), mollusks (Dellinger et al., 2018) and brachiopods (Gaspers et al., 2021). So far,  
512 all foraminifera cultured at the laboratory are calcitic and epi-benthic species  
513 (*Amphistegina lessonii* and *A. lobifera*), meaning that they operate photosynthesis and  
514 can thus be studied as a biological analogue to planktic species (Erez, 1978).

515 While inorganic carbonates  $\Delta^7\text{Li}_{\text{carb-sol}}$  exhibit a positive correlation with pH (see Fig.  
516 2C), this trend is not observed in foraminifera calcite grown in laboratory (Vigier et al.  
517 2015) (*A. lobifera*). However, measurements were performed *in situ* by ion probe and  
518 the 0.7‰ variation expected for the studied pH range is challenging to reach with this  
519 method (Vigier et al. 2007). Roberts et al. (2018) cultivated *A. lessonii* and  
520 highlighted an opposite trend compared to the inorganic calcite, as for a pH increase  
521 from 7.9 to 8.6, a slight decrease in foraminifera  $\delta^7\text{Li}$  was observed from 31.6‰ to  
522 30.8‰ (measured using MC-ICP-MS, with a precision of  $\pm 0.4\%$ ). Roberts et al.

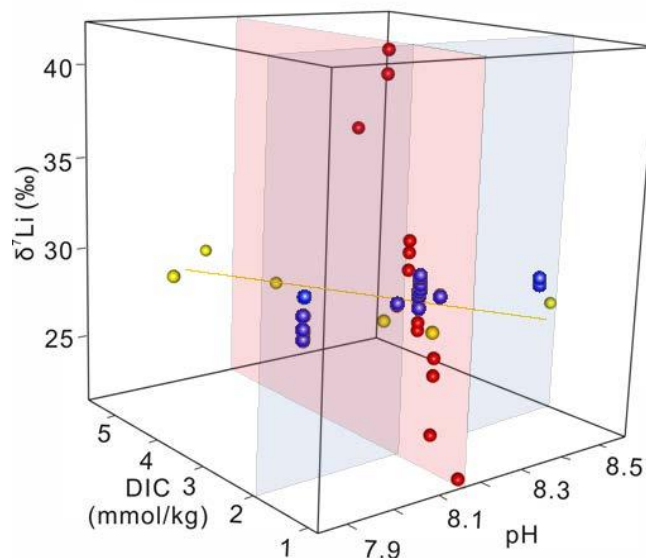
523 (2018) suggested that a pH change induces the formation of another Li hydration  
524 sphere (LiOH) in solution, which may increase the rates of  $^6\text{Li}$  desolvation. However,  
525 ion desolvation is usually related to the first hydration sphere and the formation of  
526 LiOH is unlikely at this pH (Füger et al., 2022). The pH effect on calcifying  
527 organisms and their Li isotopic composition therefore requires additional  
528 investigations.

529 Vigier et al. (2015) showed that the  $\delta^7\text{Li}$  values of cultured *A. lessonii* strongly depend  
530 upon the seawater DIC concentrations, with foraminifera  $\delta^7\text{Li}$  value ranging from  
531 21.6‰ to 41.9‰ (measured by SIMS with a  $2\sigma$  precision of  $\pm 2\%$ ) for a DIC range of  
532 1.0 to 3.0 mmol/kg. They suggested that  $\text{Li}^+$ , entering the cytoplasm through  $\text{Na}^+/\text{H}^+$   
533 exchanger (NHE), may fractionate Li isotopes in favor of the light  $^6\text{Li}$ , as expected by  
534 kinetic isotopic fractionation. A recent experimental study confirms the potential of  
535 NHEs to strongly fractionate Li isotopes (Poet, Vigier, Bouret et al., 2023). Thus, a  
536 low seawater DIC may lead to an increase in NHE activity in order to increase the pH  
537 and the alkalinity of the calcifying fluid, promoting carbonate precipitation. This  
538 process favours preferential  $^6\text{Li}$  transfer. Unfortunately, Roberts et al. (2018) and  
539 Vigier et al. (2015) did not report foraminifera growth rates, which is likely an  
540 important factor influencing Li isotope composition (Roberts et al., 2018; Vigier et al.,  
541 2015). For instance, an increase in seawater DIC may decrease the pH at the  
542 foraminiferal surface (Glas et al., 2012), which may slow down the shell growth.

543 At high DIC ( $> 2 \text{ mmol kg}^{-1}$ ), Vigier et al. (2015) reported strong isotopic  
544 fractionations in favor of the heavy  $^7\text{Li}$  in *A. lessonii* tests ( $\delta^7\text{Li}$  as high as 41.9‰).

545 Bivalve cultures also show positive biological Li isotopic fractionation in both their  
546 shells and their soft tissues (see [Dellinger et al., 2018](#); [Thibon et al., 2021](#)). A key role  
547 of Li homeostasis has been inferred. When the internal balance of Li input and output  
548 is disturbed by external conditions (e.g. high pH, high DIC, high Li contents), it is  
549 expected that the isotope composition varies, because of NHE activity in particular.  
550 The net internal Li budget can therefore be affected and may favor either the light or  
551 the heavy isotope, depending on the ratio of input *versus* output fluxes ([Thibon et al.,](#)  
552 [2021](#)).

553 The 3D graph shown in [Fig. 4](#), may reconcile all foraminifera cultures data published  
554 thus far. Indeed, there is a relationship between foraminifera  $\delta^7\text{Li}$  and DIC when  
555 foraminifera are cultured at a given and constant pH (red plane). At variable pH, when  
556 the DIC is maintained constant, the foraminifera  $\delta^7\text{Li}$  values remain constant (blue  
557 plane, [Vigier et al., 2015](#)). In contrast, when both pH and DIC vary ([Roberts et al.,](#)  
558 [2018](#)), Li isotopes follow a trend that cuts the previous datasets, indicating a  
559 combination of both effects with a dominance of the pH effect (yellow line). Perhaps  
560 compensating effects, related to intracellular  $\text{H}^+$  and DIC homeostasis, may play a  
561 major role in the Li transfer and resulting isotope compositions. Additional  
562 experiments with variable pH at a much higher DIC could be useful to better  
563 understand the Li isotope fractionation mechanisms at play in foraminifera cells.



564

565 **Fig. 4:** Three-dimensional scatter plots of  $\delta^7\text{Li}$  versus DIC and pH for cultured epi-benthic  
 566 foraminifera. Blue plane indicates groups experiments performed at constant DIC. Red plane  
 567 is for constant pH experiments (Vigier et al., 2015). The yellow dots show results obtained by  
 568 Roberts et al. (2018) during an experiment where both DIC and pH varied.

569

570 Mollusks have also been cultured in laboratory-controlled conditions for investigating  
 571 their shells Li compositions. Mollusk shells display Li/Ca ratios ranging from 7.1 to  
 572  $25.3 \mu\text{mol mol}^{-1}$  and their  $\delta^7\text{Li}$  values range from 17.2‰ to 39.6‰. Mollusk shell  $\delta^7\text{Li}$   
 573 values are controlled by the mineral composition (aragonite vs calcite) and are only  
 574 weakly related to the temperature (Dellinger et al., 2018). A significant amount of  
 575  $\delta^7\text{Li}$  data for calcitic shells (*Mytilus edulis* and *Pecten maximus*) lie above the  
 576 seawater isotopic composition, i.e. enriched in the heavy  $^7\text{Li}$  (Dellinger et al., 2018),  
 577 and cannot be explained by the sole effect of the growth rate. Dellinger et al. (2018)  
 578 suggested that Li is actively removed from the calcification site, with an isotope  
 579 fractionation in favour of the preferential removal of  $^6\text{Li}$ . This hypothesis is supported  
 580 by the negative correlation between  $\delta^7\text{Li}$  and Li/Ca, as well as between  $\delta^7\text{Li}$  and  
 581 Mg/Ca, and are consistent with the key role of Li cell transporters (NHE) recently

582 highlighted at the cellular level (Poet, Vigier, Bouret et al., 2023).  
583 Brachiopod culture experiments revealed that the Li concentration of calcitic  
584 brachiopods (*Magellania venosa*) ranges from 2.3 to 3.5 ppm and their  $\delta^7\text{Li}$  values  
585 range from 27.5‰ to 28.1‰, with no significant effect of temperature (Gaspers et al.,  
586 2021). In contrast, when pH decreases (from 7.6 to 7.35), there is a slight increase of  
587 the Li isotopic fractionation, from -2.7‰ to -3.4‰, consistent with the trend  
588 displayed by inorganic calcite. A higher solution  $\text{CaCl}_2$  concentration (lower Mg/Ca  
589 or Li/Ca ratios) also leads to a small increase in the Li isotope fractionation (from -2.7‰  
590 to -4.6‰).

591 Overall, all laboratory cultures published thus far reveal that “vital effects” may  
592 impact both Li concentrations and Li isotopic compositions of soft and calcified  
593 tissues of foraminifera and mollusks.

### 594 **3.2 Modern carbonates collected in the ocean**

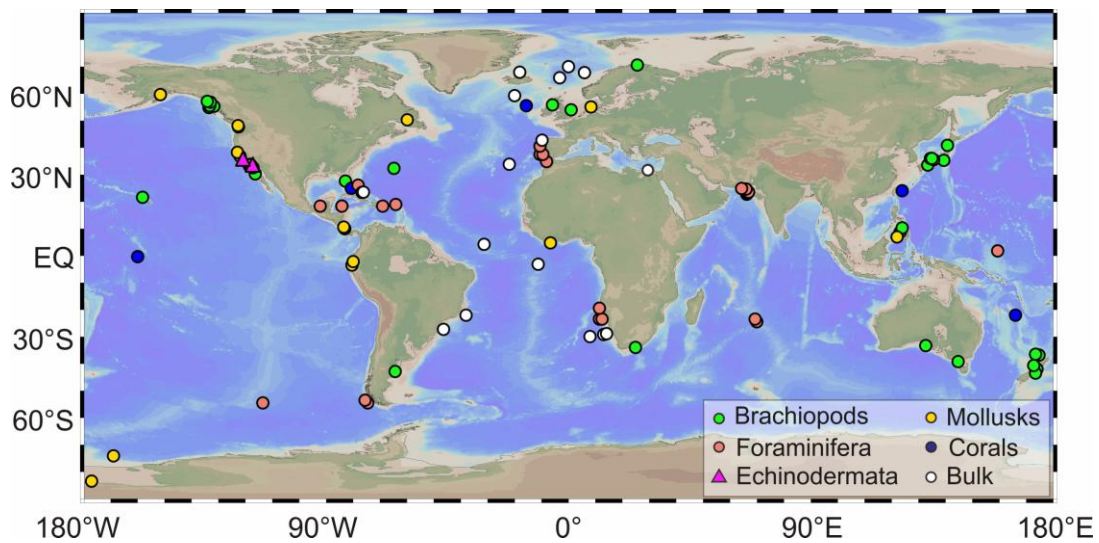
595 The environment of marine carbonates is more complex than that of in-lab synthesis  
596 and aquarium cultures because it is more susceptible to disturbances by other  
597 materials, such as contamination by marine particles (e.g., clays or Fe-Mn oxides), or  
598 by processes occurring during early diagenesis or in the water column. However, the  
599 study of modern marine shells is interesting because the Li isotopic composition of  
600 the modern ocean is homogeneous, as well as its Li/Ca ratio, so the study of  
601 contrasted isotopic signatures given by modern marine samples can give essential  
602 clues. This however requires a good representative nature of the considered dataset.



603 According to the characteristics of the samples, published Li data can be divided into  
604 two major categories. Several publications have sampled by picking various  
605 organisms from the same species or from the same trophic group. This was performed  
606 for foraminifera (Hall et al., 2005; Hathorne and James, 2006; Marriott et al., 2004;  
607 Misra and Froelich, 2012; Roberts et al., 2018; Vigier et al., 2015), corals (Bastian et  
608 al., 2018; Dellinger et al., 2020; Marriott et al., 2004; Misra and Froelich, 2009),  
609 mollusks (Bastian et al., 2018; Dellinger et al., 2018), brachiopods (Washington et al.,  
610 2020; Gaspers et al., 2021), and echinoderms (Dellinger et al., 2018). In most of these  
611 studies, shells and tests are pre-cleaned in order to remove potential contamination  
612 from oxides, silicate minerals or organic matter. In the second category of  
613 publications, the whole carbonate fraction of a marine sediment sample was extracted  
614 using a preferential dissolution by a weak acid generally (for modern carbonates:  
615 Dellinger et al., 2020; Pogge Von Strandmann et al., 2019; for past reconstructions:  
616 (Hall et al., 2005; Hathorne and James, 2006; Kalderon-Asael et al., 2021; Lechler et  
617 al., 2015; Misra and Froelich, 2012; Murphy et al., 2022; Pogge Von Strandmann et  
618 al., 2017; Pogge Von Strandmann et al., 2021; Pogge Von Strandmann et al., 2013;  
619 Washington et al., 2020). In the following, the present study will refer to the  
620 corresponding data as “bulk carbonates” (bulk). A couple of studies have compared  
621 both methods (Bastian et al., 2018; Misra and Froelich, 2012; Pogge Von Strandmann  
622 et al., 2019).

623 The current geographical distribution of all  $\delta^7\text{Li}$  data published for marine carbonates  
624 is shown in Fig. 5. This compilation includes biogenic carbonate samples primarily

625 from marine surface sediments (burial depths less than 2 cm), and for a small number,  
 626 these data concern living organisms from the water column (e.g., foraminifera).  
 627 First of all, Fig 5 highlights significant gaps. Indeed, most studies (*viz.* 44% of the  
 628 data) focus on the Atlantic Ocean, with a relatively small amount of data available for  
 629 the Pacific Ocean, and only a few foraminifera data for the Indian Ocean. Another  
 630 observation is that most studies concern the middle and low latitudes, and littoral  
 631 environments. In the objective to use modern species as equivalent to reconstruct past  
 632 variations of the open ocean Li isotopic composition - and its links with climate -  
 633 these gaps appear essential to fill.  
 634

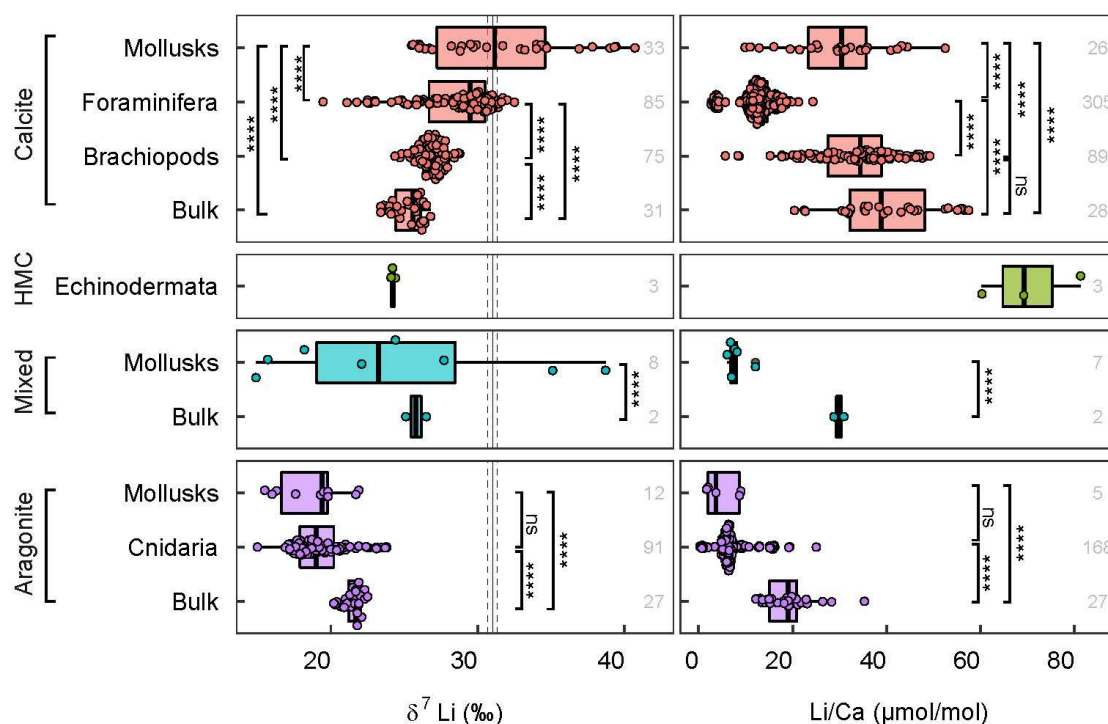


635  
 636 **Fig. 5:** Worldwide distribution of modern marine carbonates with published Li isotopic  
 637 compositions.  $\delta^7\text{Li}$  values concern corals (Bastian et al., 2018; Dellinger et al., 2020; Marriott  
 638 et al., 2004; Misra and Froelich, 2009), foraminifera (Hall et al., 2005; Hathorne and James,  
 639 2006; Marriott et al., 2004; Misra and Froelich, 2012; Roberts et al., 2018; Vigier et al., 2015)  
 640 mollusks (Bastian et al., 2018; Dellinger et al., 2018) brachiopods (Washington et al., 2020),  
 641 echinoderms (Dellinger et al., 2018) and “bulk” carbonates (obtained by preferential  
 642 dissolution, see text) (Bastian et al., 2018; Dellinger et al., 2020; Pogge Von Strandmann et  
 643 al., 2019; Murphy et al., 2022).

644 It is possible to compare data among the different studied biological groups, keeping  
645 in mind that all environmental conditions have not been explored similarly. This  
646 allows us to highlight where the knowledge is the strongest and to evaluate the  
647 representative nature of the average value that can be calculated for each one. As  
648 shown in Fig. 6 and in Fig. S3, modern marine carbonates display a wide range of  
649  $\delta^7\text{Li}$  values, from 14.9‰ (aragonitic mollusks, Dellinger et al. (2018)) to 40.7‰  
650 (calcitic mollusks from Dellinger et al. (2018)). Marine calcite  $\delta^7\text{Li}$  range from 19.5 ‰  
651 to 40.7‰, high Mg calcite from 24.1‰ to 24.4‰ and aragonite from 14.9‰ to  
652 23.8‰. There is a significant difference (Wilcoxon test: p-val. < 0.0001) between  
653 aragonite ( $19.27 \pm 3.7\%$  n = 103) and calcite ( $28.14 \pm 6.5\%$  n = 192) or high Mg  
654 calcite ( $24.2 \pm 0.3\%$  n = 3). In contrast with laboratory precipitated inorganic  
655 carbonates, which result in contrasting results, biogenic minerals highlight a more  
656 systematic distinction between calcite and aragonite. Of note that there is a relatively  
657 small statistical difference between calcite and high Mg calcite (Wilcoxon test: p-val.  
658 < 0.01).

659 Among calcitic organisms, there are also significant differences (Wilcoxon test: p-val.  
660 < 0.0001) between foraminifera ( $28.3 \pm 5.9\%$  n = 84), mollusks ( $30.9 \pm 10.7\%$  n =  
661 33), and brachiopods ( $26.8 \pm 1.8\%$ , n = 75), and they are all statistically higher than  
662 bulk carbonates (i.e. extracted by preferential dissolution) ( $23.9 \pm 2.1\%$ , n = 31). This  
663 suggests that vital – biological - effects are able to influence the Li isotopic  
664 composition of carbonates and that the Li isotopic fractionation can vary between  
665 species and between individuals. Also, bulk - calcite - carbonate  $\delta^7\text{Li}$  values are lower

666 than the data displayed by picked foraminifera, mollusks or brachiopods, indicating  
 667 that there are still calcitic phases of importance (Foram ooze, Sponge spicules etc.),  
 668 which have not been investigated yet, despite playing key role in the bulk fractions  
 669  $\delta^7\text{Li}$  values.



670  
 671 **Fig. 6:** Compilation of all existing data for  $\delta^7\text{Li}$  and Li/Ca (in  $\mu\text{mol mol}^{-1}$ ) for modern (core  
 672 top as circles, living as triangles) biogenic carbonates (Delaney et al., 1989; Hall and Chan,  
 673 2004; Marriott et al., 2004a; Marriott et al., 2004b; Hall et al., 2005; Yun et al., 2005;  
 674 Hathorne and James, 2006; Vigier et al., 2007; Bryan and Marchitto, 2008; Hendry et al.,  
 675 2009; Rollion-Bard et al., 2009; Misra and Froelich, 2012; Bastian et al., 2018; Roberts et al.,  
 676 2018; Cuny-Guirriec et al., 2019; Pogge von Strandmann et al., 2019; Delinger et al., 2020;  
 677 Washington et al., 2020; Gaspers et al., 2021; Dellinger et al., 2018). “HMC” denotes high  
 678 magnesium calcite. “Mixed” denotes a mixture of calcite and aragonite. “Bulk” denotes  
 679 sedimentary carbonate fraction extracted by preferential leaching (see text). The vertical solid  
 680 and dashed line is for the seawater  $\delta^7\text{Li}$  value ( $31 \pm 0.3\text{‰}$ ) (Millot et al., 2004). The seawater  
 681 Li/Ca ratio is  $2505 \mu\text{mol mol}^{-1}$ . Each data point represents a value for a carbonate sample. The  
 682 grey numbers on the right denote the number of published data. Asterisks show the  
 683 significance of the difference inferred through a Mann-Whitney-Wilcoxon tests: ns (not  
 684 significant) for  $p > 0.05$ , \* for  $p < 0.05$ , \*\* for  $p < 0.01$ , \*\*\* for  $p < 0.001$ , \*\*\*\* for  $p <$   
 685  $0.0001$  (highly significant difference).

686

687 Among the aragonitic species, there is no significant difference in  $\delta^7\text{Li}$  between corals  
688 ( $19.4 \pm 3.6\text{‰}$ ,  $n = 91$ ) and mollusks ( $18.2 \pm 5.9\text{‰}$ ,  $n = 12$ ) ( $p > 0.05$ ), but they are  
689 both statistically different ( $p < 0.0001$ ) from bulk carbonates ( $21.6 \pm 1.3\text{‰}$ ,  $n = 27$ ).  
690 In contrast with calcitic environments, the aragonitic bulk carbonate fractions display  
691 higher  $\delta^7\text{Li}$  values than all other groups studied thus far.

692 Most of the modern biogenic carbonates display lower  $\delta^7\text{Li}$  values than seawater, such  
693 as all brachiopods, echinodermata, and all aragonitic carbonates. However, some  $\delta^7\text{Li}$   
694 values are higher than seawater, such as the calcitic shells of mollusks, and a small  
695 fraction of foraminifera data. This indicates that they can be enriched in the heavier Li  
696 isotope  $^7\text{Li}$  relative to seawater, as observed in culture experiments (Vigier et al.,  
697 2015). More recently, Thibon et al. (2021) showed that it is possible to have an  
698 enrichment in  $^7\text{Li}$  in marine soft tissues, depending on the Li input/output (excretion)  
699 flux and of the magnitude of kinetic isotope fractionation related to the Li transport.

700 Concerning our compilation of Li/Ca ratios, it is striking that all modern marine  
701 biogenic carbonates are significantly (by several orders of magnitude) depleted in Li  
702 ( $<90 \mu\text{mol mol}^{-1}$ ) compared to the present-day seawater value ( $2505 \mu\text{mol mol}^{-1}$ ). On  
703 average, calcite groups contain more Li than aragonite ones. By calculating the  
704  $\text{LogD}(\text{Li})$  for these groups, we can compare their data to the ones found  
705 experimentally for inorganic equivalents. In biogenic carbonates,  $\text{LogD}(\text{Li})$  range  
706 from  $-3.17$  to  $-1.68$ , while they cover a wider range in inorganic phases, between  
707  $-5.70$  and  $-1.99$ . Interestingly, for Li isotopes, the opposite is observed: the  $\Delta^7\text{Li}_{\text{carb-sol}}$

708 distribution range for biogenic carbonates is larger than that for inorganic phases,  
709 independently of mineral types (see Fig. 1).

710 In biogenic calcite, Li/Ca ratios for mollusks, foraminifera, brachiopods, and bulk  
711 range from 9.9 to 52.5  $\mu\text{mol mol}^{-1}$ , from 2.69 to 24.33  $\mu\text{mol mol}^{-1}$ , from 5.7 to 49.2  
712  $\mu\text{mol mol}^{-1}$  and from 20.4 to 57.5  $\mu\text{mol mol}^{-1}$ , respectively. Except for mollusks, there  
713 is a reverse trend between the average  $\delta^7\text{Li}$  and the average Li/Ca ratio. In particular,  
714 foraminifera display the highest average isotopic composition and also the lowest  
715 Li/Ca ratio ( $12.48 \pm 7.9 \mu\text{mol mol}^{-1}$ ,  $n=305$ ) (Fig. 6). Their range in Li/Ca ratios also  
716 appears restricted compared to the variations observed within each of the other groups.

717 This may be due to the fact that Li/Ca ratios have been mostly measured in similar  
718 samples for which Li isotopes could be measured too. When no isotopic  
719 measurements were performed due to low Li levels, no Li concentration was  
720 measured neither and this limitation may induce a significant bias.

721 In contrast to biogenic calcite, biogenic aragonite appears to display a positive  
722 relationship between  $\delta^7\text{Li}$  and Li/Ca, when comparing average values for mollusks,  
723 cnidarian, and bulk carbonates. Aragonitic mollusks are particularly depleted in Li  
724 compared to calcitic mollusks, although the number of data is small (Li/Ca =  $5.02 \pm$   
725  $7.2 \mu\text{mol mol}^{-1}$ ,  $n = 5$ ). Cnidarians display relatively low Li/Ca ratios ( $7.33 \pm 6.3 \mu\text{mol}$   
726  $\text{mol}^{-1}$ ,  $n = 168$ ), while bulk aragonite extracted from sedimentary fractions display the  
727 highest average Li/Ca ratio.

728 Finally, high-Mg calcite echinoderm specimens display the highest Li/Ca values of  
729 the whole carbonate dataset, although only 3 data are reported in the literature ( $70.27$

730  $\pm 21.08 \mu\text{mol mol}^{-1}$ , n = 3) (Dellinger et al., 2018).

### 731 **3.3 Focus on foraminifera species**

732 Foraminifera are single-celled eukaryotic organisms belonging to the Phylum  
733 *Granuloreticulosa* (Pearson, 2012), and many secrete a test (or shell) made of calcium  
734 carbonate, generally low-Mg calcite, but possibly high-Mg calcite in porcelaneous  
735 species, and aragonite in some groups. Some species may include sedimentary  
736 particles (Pearson, 2012; Vigier et al., 2007). “Benthic” marine foraminifera majority  
737 live on or within the seafloor sediment, while a number float in the water column at  
738 various depths (known as “planktic”) (Hemleben et al., 2012). Currently, studies of Li  
739 isotopes in modern marine foraminifera are mainly focused on planktic species, while  
740 relatively few studies have been conducted on natural benthic foraminifera species  
741 (Table 3).

742 Planktic and benthic foraminifera do not exhibit significant differences in Li/Ca ratios,  
743 except for the Antarctic Ocean where the Li/Ca ratio of planktic foraminifera is  
744 statistically higher than that of benthic species (Table 3). In contrast, differences can  
745 be observed for Li isotopes. At first, the Li isotopic compositions of living  
746 foraminifera from the Pacific Ocean water column appear consistent with that of  
747 foraminifera picked from surface sediments. This suggests that the Li isotopic signal  
748 is not rapidly affected by early diagenesis (although specific chemical treatment  
749 targeted the removal of contaminant phases and only data validated by authors as free  
750 from diagenetic effects were considered).

751 Consequently, we included both living and sediments top-layer foraminifera in our  
752 compilation.  $\delta^7\text{Li}$  values vary from 24.9‰ to 32.5‰ for planktic foraminifera, and  
753 from 19.4‰ to 27.3‰ for benthic ones ([Fig. 7](#)). There are significant differences  
754 between planktic ( $29.7 \pm 2.9\text{‰}$  n=70) and benthic foraminifera ( $24 \pm 4.1\text{‰}$  n=23) (see  
755 [Table 4](#) and also [Fig. S3](#)).

756



757 Table 3 Compilation of  $\delta^7\text{Li}$  and Li/Ca ratios measured for modern foraminifera (uncertainties are given at the standard deviation  $\sigma$  level)

| Species                              | Source  | Habits   | n  | $\delta^7\text{Li}$ (‰) | n  | Li/Ca ( $\mu\text{mol mol}^{-1}$ ) | Reference   |
|--------------------------------------|---------|----------|----|-------------------------|----|------------------------------------|---|
| <i>Orbulina universa</i>             | Living  | Planktic | 5  | $30.5 \pm 0.3$          | 5  | $11.32 \pm 0.75$                   | Misra and Froelich, 2012  |
| <i>Globigerina ruber</i>             | Coretop | Planktic | 2  | $30.6 \pm 0.1$          | 2  | $13.51 \pm 0.78$                   | Misra and Froelich, 2012  |
| <i>Globigerina triloba</i>           | Coretop | Planktic | 6  | $30.1 \pm 0.6$          | 6  | $12.88 \pm 1.32$                   | Misra and Froelich, 2012  |
| <i>Globigerinoides conglobatus</i>   | Coretop | Planktic | 3  | $29.1 \pm 0.8$          | 3  | $10.92 \pm 0.69$                   | Misra and Froelich, 2012; Hathorne et al., 2006   |
| <i>Globigerinoides sacculifer</i>    | Coretop | Planktic | 5  | $29.0 \pm 0.6$          | 14 | $12.34 \pm 0.54$                   | Hall et al., 2005; Misra and Froelich, 2012; Hathorne et al., 2006; Hall and Chan, 2004 |
| <i>Globorotalia cultrata</i>         | Coretop | Planktic | 2  | $29.7 \pm 0.2$          | 2  | $11.90 \pm 0.28$                   | Hathorne et al., 2006   |
| <i>Globorotalia menardiib</i>        | Coretop | Planktic | 1  | 29.1                    | 1  | 12.50                              | Hall et al., 2005   |
| <i>Globorotalia merdii</i>           | Coretop | Planktic | 4  | $30.2 \pm 0.2$          | 4  | $10.94 \pm 1.14$                   | Misra and Froelich, 2012  |
| <i>Globorotalia truncatulinoides</i> | Coretop | Planktic | 5  | $28.7 \pm 1.5$          | 3  | $12.97 \pm 0.9$                    | Hall et al., 2005; Hathorne et al., 2006 Vigier et al., 2007 Misra and Froelich, 2012   |
| <i>Globorotalia tumida</i>           | Coretop | Planktic | 3  | $28.1 \pm 1.5$          | 3  | $11.56 \pm 0.46$                   | Hathorne et al., 2006 Misra and Froelich, 2012  |
| <i>Neogloboquadrina dutertrei</i>    | Coretop | Planktic | 4  | $29.1 \pm 0.8$          | 4  | $12.73 \pm 0.6$                    | Hathorne et al., 2006 Misra and Froelich, 2012  |
| <i>Neogloboquadrina pachyderma</i>   | Coretop | Planktic |    |                         | 13 | $18.28 \pm 0.70$                   | Hendry et al., 2009   |
| <i>Orbulina universa</i>             | Coretop | Planktic | 17 | $30.4 \pm 0.8$          | 32 | $11.9 \pm 1.43$                    | Hall et al., 2005; Hathorne et al., 2006 Misra and Froelich, 2012; Hall and Chan, 2004  |
| <i>Cibicidoides cicatricosus</i>     | Coretop | Benthic  |    |                         | 5  | $15.36 \pm 0.86$                   | Hall and Chan, 2004   |
| <i>Cibicidoides incrassatus</i>      | Coretop | Benthic  |    |                         | 7  | $14.47 \pm 0.53$                   | Hall and Chan, 2004   |
| <i>Cibicidoides mundulus</i>         | Coretop | Benthic  | 11 | $23.9 \pm 1.8$          | 11 | $13.08 \pm 0.88$                   | Roberts et al., 2018  |
| <i>Cibicidoides pachyderma</i>       | Coretop | Benthic  |    |                         | 56 | $12.76 \pm 1.44$                   | Hall and Chan, 2004 ; Bryan and Marchitto, 2008   |
| <i>Cibicidoides robertsonianus</i>   | Coretop | Benthic  |    |                         | 5  | $13.63 \pm 0.81$                   | Hall and Chan, 2004   |
| <i>Cibicidoides wuellerstorfi</i>    | Coretop | Benthic  | 7  | $23.6 \pm 2.4$          | 14 | $14.96 \pm 2.23$                   | Roberts et al., 2018; Hall and Chan, 2004 2005 Yun                                      |
| <i>Cibicidoides rugosus</i>          | Coretop | Benthic  |    |                         | 5  | $14.22 \pm 0.49$                   | Hall and Chan, 2004   |
| <i>Euvigerina sp.</i>                | Coretop | Benthic  | 1  | 21.1                    | 1  | 14.4                               | Marriott et al., 2004a  |
| <i>Hoeglundina elegans</i>           | Coretop | Benthic  |    |                         | 37 | $3.78 \pm 0.50$                    | Bryan and Marchitto, 2008   |
| <i>Planulina ariminensis</i>         | Coretop | Benthic  |    |                         | 17 | $13.76 \pm 1.45$                   | Bryan and Marchitto, 2008   |
| <i>Planulina foveolata</i>           | Coretop | Benthic  |    |                         | 13 | $12.31 \pm 1.41$                   | Bryan and Marchitto, 2008   |
| <i>Uvigerina peregrina</i>           | Coretop | Benthic  |    |                         | 36 | $16.70 \pm 1.90$                   | Bryan and Marchitto, 2008   |

*Uvigerina* sp.

Coretop

Benthic

3

$25.8 \pm 0.8$

3

$17.53 \pm 1.34$

[Marriott et al., 2004a](#)

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758

759 In contrast, we detect no significant difference between the different oceans for either  
760 planktic or benthic foraminifera, but the number of data is small and the test power  
761 would deserve to be reinforced with additional data for Pacific and Indian oceans.

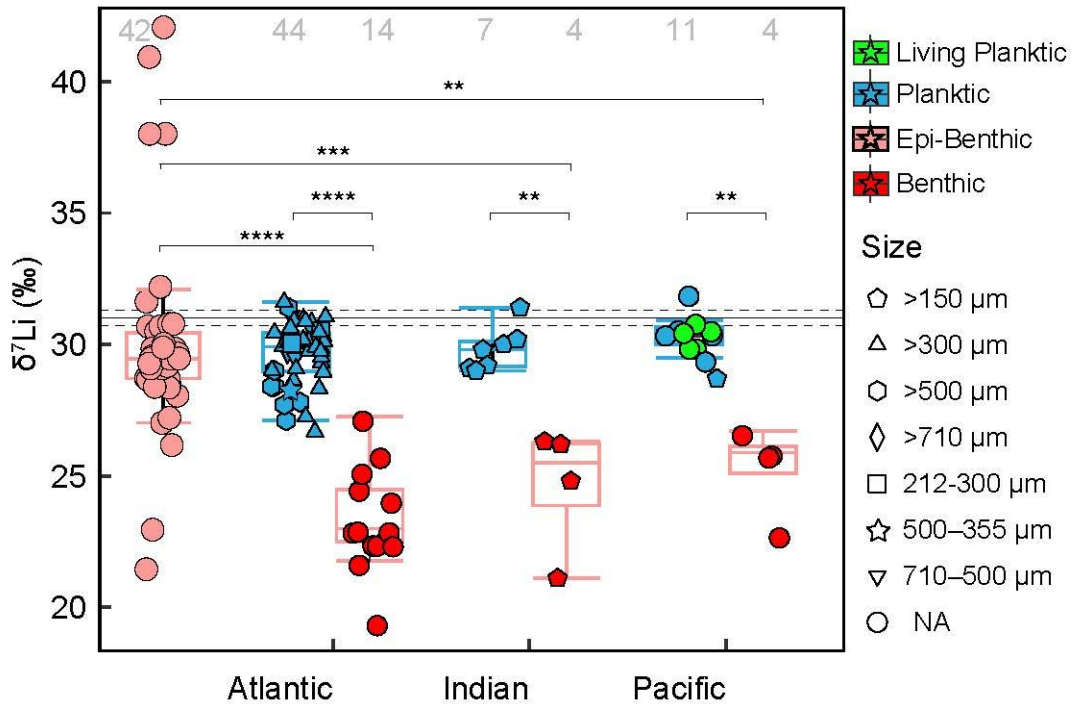
762 Table 4. Average  $\delta^7\text{Li}$  and Li/Ca values for modern foraminifera from different oceans and habitats  
763 (uncertainties are standard deviation (SD))

|                 | n         | $\delta^7\text{Li}$ (‰) | n          | Li/Ca ( $\mu\text{mol mol}^{-1}$ ) |
|-----------------|-----------|-------------------------|------------|------------------------------------|
| <b>Living</b>   | <b>5</b>  | <b>30.5</b> $\pm$ 0.3   | <b>5</b>   | <b>11.32</b> $\pm$ 0.75            |
| <b>Planktic</b> | <b>5</b>  | <b>30.5</b> $\pm$ 0.3   | <b>5</b>   | <b>11.32</b> $\pm$ 0.75            |
| Pacific ocean   | 5         | 30.5 $\pm$ 0.3          | 5          | 11.32 $\pm$ 0.75                   |
| <b>Coretop</b>  | <b>78</b> | <b>28.1</b> $\pm$ 3.0   | <b>299</b> | <b>12.48</b> $\pm$ 3.98            |
| <b>Planktic</b> | <b>56</b> | <b>29.7</b> $\pm$ 1.1   | <b>89</b>  | <b>12.86</b> $\pm$ 2.57            |
| Antarctic       |           |                         | 13         | 18.28 $\pm$ 0.70                   |
| Atlantic        | 44        | 29.6 $\pm$ 1.2          | 75         | 11.94 $\pm$ 1.30                   |
| Indian ocean    | 7         | 29.8 $\pm$ 0.8          |            |                                    |
| Pacific ocean   | 5         | 30.1 $\pm$ 1.2          | 1          | 11.50                              |
| <b>Benthic</b>  | <b>22</b> | <b>24.0</b> $\pm$ 2.0   | <b>210</b> | <b>12.32</b> $\pm$ 4.44            |
| Atlantic        | 14        | 23.4 $\pm$ 1.9          | 203        | 12.24 $\pm$ 4.46                   |
| Indian ocean    | 4         | 24.6 $\pm$ 2.4          | 4          | 16.75 $\pm$ 1.91                   |
| Pacific ocean   | 4         | 25.3 $\pm$ 1.7          | 3          | 12.07 $\pm$ 0.90                   |

764

765 If representative, the published dataset would indicate that foraminifera  $\delta^7\text{Li}$  values do  
766 not differ significantly among the different oceans, in the horizontal direction, while  
767 in the vertical direction, planktic and benthic habitats play a more decisive role in the  
768 foraminifera Li isotopic composition. The higher  $\delta^7\text{Li}$  values measured systematically  
769 in planktic species (compared to the benthic ones collected in the same ocean) are  
770 consistent with a pH control. Indeed, in modern oceans, the pH of surface seawater  
771 (up to  $8.33 \pm 0.1$ ) is usually higher than that of the bottom seawater (down to  $7.52 \pm$   
772  $0.05$ ) (Lauvset et al., 2020), except close to hydrothermal sites. Indeed, there is a

773 positive correlation between pH and  $\Delta^7\text{Li}_{\text{carb-sol}}$  observed in inorganic calcite (Fig. 2C)  
774 (Füger et al., 2022; Seyedali et al., 2021), i.e. with no influence of biology. However,  
775 the large difference observed between the two marine habitats (benthic and planktic)  
776 cannot be explained by the slope shown in Fig. 2C. Indeed, the published sampling  
777 depth of benthic foraminifera is considerable, ranging from 96 to 3729 m (Marriott et  
778 al., 2004; Roberts et al., 2018), which corresponds to a pH range as large as for the  
779 whole seawater one. Thus, substituting the highest (8.33) and lowest (7.52) seawater  
780 pH into the equation in Fig. 2C, yields isotopic fractionations ( $\Delta^7\text{Li}_{\text{carb-sol}}$ ) of -3.2‰  
781 and -4.2‰, respectively, so the theoretical maximum isotopic difference that can be  
782 produced between planktic and benthic (using the regression shown in Fig. 2C) is 1‰.  
783 In contrast, benthic foraminifera  $\delta^7\text{Li}$  values are lower by -6 or -7‰ from the seawater  
784 value while planktic  $\delta^7\text{Li}$  are lower by -1 to -3‰. Consequently, other factors such as  
785 biological processes, growth rates and temperature would deserve to be investigated  
786 in the future.



787

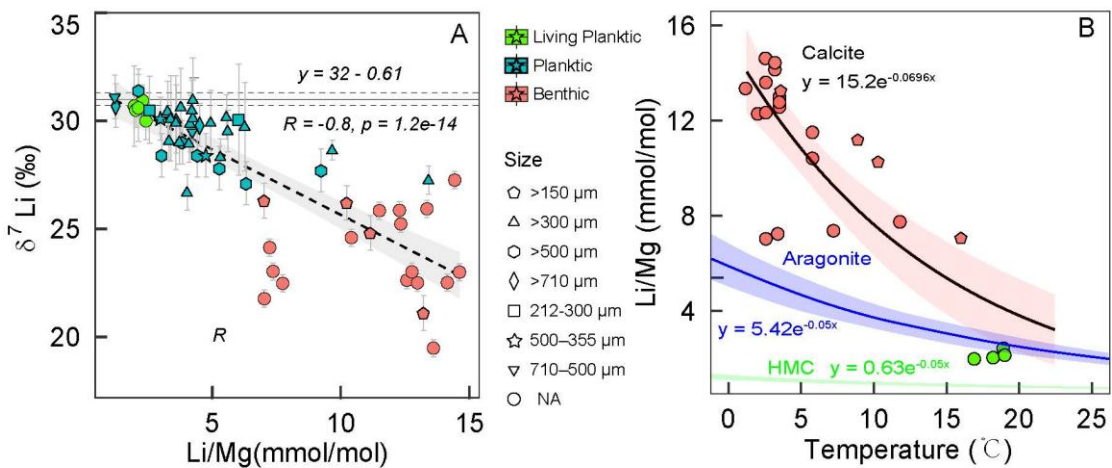
788 **Fig. 7:** The Li isotopic composition of modern oceanic foraminifera of different habitats  
 789 distinguished by oceans, except epi-benthic foraminifera, coming from laboratory-cultured (in  
 790 pink). The horizontal bars represent the seawater line. Asterisks show the significance of the  
 791 Mann-Whitney-Wilcoxon tests used to observe differences between pairs of groups: ns (not  
 792 significant) for  $p > 0.05$ , \* for  $p < 0.05$ , \*\* for  $p < 0.01$ , \*\*\* for  $p < 0.001$ , \*\*\*\* for  $p <$   
 793  $0.0001$  (highly significant difference).

794 Interestingly, we found a negative linear correlation between the  $\delta^7\text{Li}$  and Li/Mg ratio  
 795 for benthic and planktic foraminifera (Fig. 9). Li/Mg ratio of corals and foraminifera  
 796 is more strongly related to temperature than Li/Ca, and has been recently proposed as  
 797 a proxy for reconstructing global ocean temperature (Rollion-Bard and Blamart, 2015;  
 798 Stewart et al., 2020; Zhu et al., 2021). Although this temperature indicator is mostly  
 799 applied to aragonitic carbonates and high-Mg calcite thus far, a similar correlation can  
 800 be observed for the calcitic foraminifera dataset (Fig. 9). Therefore, we cannot  
 801 completely rule out that differences in seawater surface and bottom temperatures may

802 lead to the formation of different Li/Mg ratios in planktic and benthic foraminifera,  
 803 which in turn result in differences in their Li isotopic compositions.

804 The growth rate may also be an additional factor affecting the Li isotopic composition  
 805 of calcite, as shown in Fig. 2E for inorganic phases, where low growth rate  
 806 corresponds to higher calcite  $\delta^7\text{Li}$  (within the range of ocean pH). However, it is more  
 807 complicated for foraminifera, as their growth rate may also be a function of  
 808 metabolism, nutrient availability and environmental conditions. Due to the lack of  
 809 published data of foraminifera growth rates coupled with Li measurements, we cannot  
 810 further explore the influence of this factor to explain the observed difference between  
 811 planktic and benthic species.

812



813 **Fig. 8:** A) Li isotopic composition of modern foraminifera versus Li/Mg ratio measured in  
 814 their shells; and B) Li/Mg versus seawater temperature. Each data point represents a  
 815 carbonate sample. The black line with pink shade is the regression of compilation data for  
 816 foraminifera. The blue solid lines report previous aragonitic phases data regression (Stewart et  
 817 al., 2020), and bright green solid lines reports HMC data regression (Stewart et al., 2020).  
 818 Shadings show 95% confidence intervals.

820

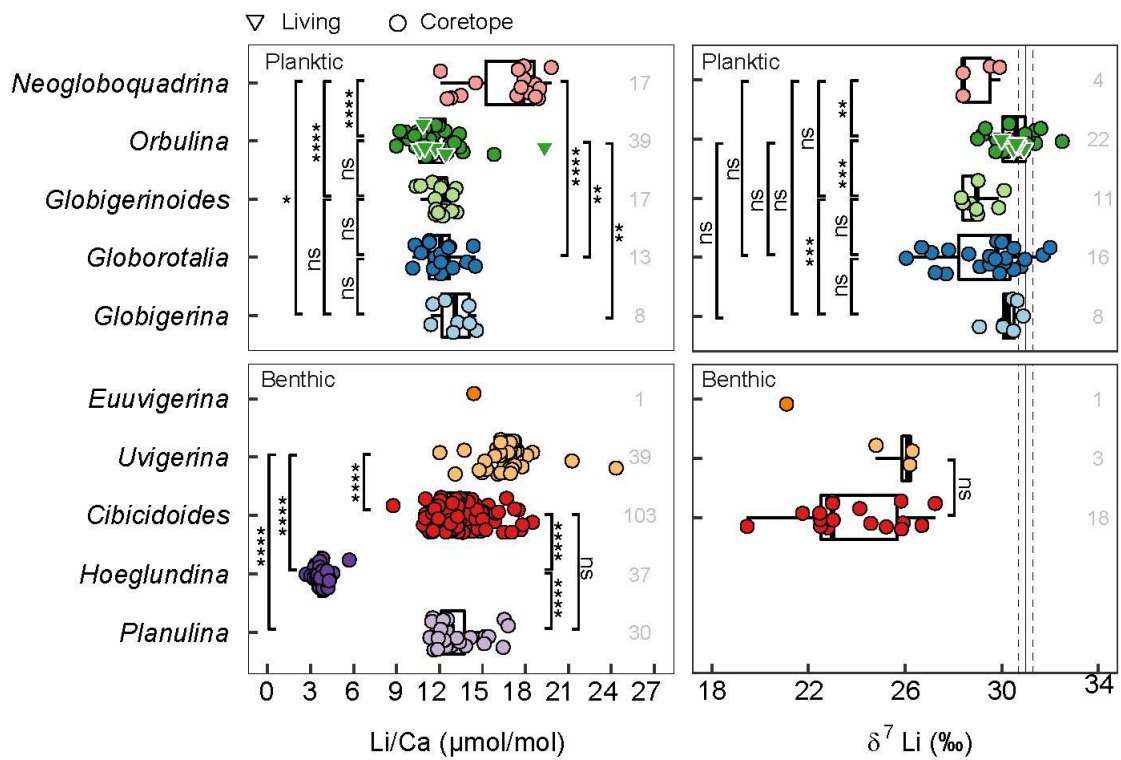
821 Due to the lack of published data of foraminifera growth rates coupled with Li  
822 measurements, we cannot further explore the influence of this factor to explain the  
823 observed difference between planktic and benthic species.

824 Based on our compilation (Table 3), it is however possible to evaluate the “species  
825 effect”, by quantifying the significance of isotopic differences between various genera  
826 of planktic foraminifera (Fig. 9). The  $\delta^7\text{Li}$  values of *Globigerinoides* ( $28.8 \pm 1.9\text{‰}$ , n  
827 = 9) are statistically lower ( $p < 0.001$ ) than those of *Globigerina* ( $30.2 \pm 1.1\text{‰}$  n = 8)  
828 and *Orbulina* ( $30.5 \pm 1.6\text{‰}$  n = 25). Statistical differences ( $p < 0.01$ ) are also  
829 observed between *Orbulina* ( $30.5 \pm 1.6\text{‰}$  n = 25) and *Neogloboquadrina* ( $28.2 \pm 2.9\text{‰}$   
830 n=5). It should be noted that the number of *Globigerinoides* (9), *Globigerina* (8) and  
831 *Neogloboquadrina* (5) samples is relatively small. No significant difference are  
832 revealed between living *Orbulina universa* ( $30.6 \pm 0.62\text{‰}$  n=6) and core-top  
833 *Orbulina universa* ( $30.5 \pm 1.8\text{‰}$ , n=19), confirming the lack of impact of rapid  
834 diagenesis, at least for this species (or correct pre-cleaning conditions as inferred  
835 previously).

836 Concerning Li/Ca ratio, Fig. 9 shows no “species effect” for planktic foraminifera,  
837 while this ratio is much more variable among benthic species. However, as described  
838 in section 2, this observation may be biased by the lack of Li concentrations  
839 measurements made in foraminifera tests not providing enough material for Li isotope  
840 measurements. This may concern low Li level species, low density (e.g. porous, thin)  
841 tests, or species with a weak abundance in the sediment.



842 We investigated the role of the size fractions in the isotopic and chemical differences  
 843 observed between foraminifera species or habitats. However, in many publications,  
 844 the precise determination of this parameter is not provided, with access often limited  
 845 to either a broad range of sizes or only the minimum size. As depicted in Fig. S4 and  
 846 Fig. S5, no significant relationship with size can be observed at this stage. It is  
 847 noteworthy that the 2D size fraction of foraminifera may not be directly linked to the  
 848 growth rate, as it is influenced by factors such as the carbonate structure and density,  
 849 lifespan, and other biological processes involved in the biomineralization process.



850

851 **Fig. 9:** Box plots exhibiting Li/Ca ratios and Li isotope compositions of modern foraminifera,  
 852 organized by phylum. Seawater  $\delta^7\text{Li}$  are added as a grey bar for comparison. The numbers at  
 853 the right of each box indicate the number of samples. Asterisks show the significance of the  
 854 Mann-Whitney-Wilcoxon tests used to observe differences between pairs of groups: ns (not  
 855 significant) for  $p > 0.05$ , \* for  $p < 0.05$ , \*\* for  $p < 0.01$ , \*\*\* for  $p < 0.001$ , \*\*\*\* for  $p <$   
 856  $0.0001$  (highly significant difference). For a representation with size fractions included, see

857 Fig. S4.

## 858 **4. Conclusions**

859 This review compiled and investigated major studies of Li/Ca and Li isotopes in  
860 inorganic and biogenic carbonates, providing an overview of the actual state of  
861 knowledge in the field. It primarily shows that it is extremely difficult to highlight  
862 “vital effects” - or the lack of “vital effects” – simply by using a direct comparison  
863 between biogenic and inorganic carbonates. Indeed, both types of carbonates vary  
864 significantly - and generally differently - as a function of specific parameters. Another  
865 point of attention is the various gaps in the knowledge concerning the influence of  
866 mineral types, growth rates, environmental conditions outside the Atlantic Ocean, and  
867 calcifying species with low Li/Ca ratios. Finally, we highlighted that the combination  
868 of Li/Ca and Li isotopes appear to be useful for interpreting the influence of  
869 environmental or biological parameters. In more detail, we observed the following  
870 main points:

### 871 **For inorganic carbonates:**

- 872 ● Current experimental studies mainly focused on calcite, while relatively little data  
873 are available for aragonite and high-Mg calcite. It is therefore too early to  
874 determine the role of the carbonate structure and mineralogy on Li isotopes.
- 875 ● The temperature has little to no effect on the Li isotopic composition of inorganic  
876 calcite, but changes in temperature can affect calcite Li/Ca ratios.
- 877 ● The extent of Li isotope fractionation between calcite and solution can be

878 significantly affected by solution pH. More  $^6\text{Li}$  is incorporated into calcite at low  
879 pH. The recently inferred explanation is that there is a Li speciation effect at the  
880 mineral surface.

881 ● A similar situation arises for growth rate: an increase in calcite growth rate leads  
882 to an increase in  $D(\text{Li})$  values and in the Li isotope fractionation. The  
883 interpretation is still debated.

884 **For biogenic carbonates:**

885 ● Marine biogenic carbonate studies mainly concern the Atlantic Ocean (44% of  
886 the data), so more effort should be put into other oceanic conditions in order to  
887 cover a broader range of environmental conditions.

888 ●  $\delta^7\text{Li}$  values are statistically different between foraminifera, mollusks, and  
889 brachiopods, and they are all statistically higher than the values measured in bulk  
890 carbonates. This strongly suggests that vital - biological - effects can influence  
891 the Li isotopic composition of biogenic carbonates and that the isotopic  
892 fractionation of Li isotopes can vary between species and between individuals.

893 ● The  $\delta^7\text{Li}$  values of planktic foraminifera are statistically higher than those of  
894 benthic foraminifera. Statistical differences are also evidenced between different  
895 species of planktic foraminifera. This supports a key role of genetics and  
896 metabolic effects that may be explored for future paleo reconstructions. In  
897 particular, the relationship between foraminiferal Li/Mg ratio and temperature  
898 suggests a new potential for reconstructing paleo-temperature that would deserve  
899 to be reinforced.

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902

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