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1 **A simple biomineralization model to explain Li, Mg, and Sr incorporation into**  
2 **aragonitic foraminifera and corals**

3  
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17  
18 **Abstract**

19 In contrast to Li/Ca and Mg/Ca, Li/Mg is strongly anticorrelated with growth temperature in  
20 aragonites precipitated by the benthic foraminifer *Hoeglundina elegans* and a wide range of  
21 scleractinian coral taxa. We propose a simple conceptual model of biomineralization that  
22 explains this pattern and that is consistent with available abiotic aragonite partition coefficients.  
23 Under this model the organism actively modifies seawater within its calcification pool by raising

24 its [Ca<sup>2+</sup>], using a pump that strongly discriminates against both Li<sup>+</sup> and Mg<sup>2+</sup>. Rayleigh  
25 fractionation during calcification effectively reverses this process, removing Ca<sup>2+</sup> while leaving  
26 most Li<sup>+</sup> and Mg<sup>2+</sup> behind. The net effect of these two processes is that Li/Mg in the calcifying  
27 fluid remains very close to the seawater value, and temperature-dependent abiotic partition  
28 coefficients are expressed in the biogenic aragonite Li/Mg ratio. We further show that coral  
29 Sr/Ca is consistent with this model if the Ca<sup>2+</sup> pump barely discriminates against Sr<sup>2+</sup>. In *H.*  
30 *elegans* the covariation of Sr/Ca and Mg/Ca requires either that the pump more strongly  
31 discriminates against Sr<sup>2+</sup>, or that cation incorporation is affected by aragonite precipitation rate  
32 via the mechanism of surface entrapment. In either case Li/Mg is minimally affected by such  
33 ‘vital effects’ which plague other elemental ratio paleotemperature proxies.

34

35 **Keywords:** biomineralization; Li/Ca; Mg/Ca; Sr/Ca; paleotemperature proxies

36

## 37 **1. Introduction**

38 Dissolved Li, Mg, Sr, and Ca all behave nearly conservatively in seawater, meaning that their  
39 ratios are approximately constant throughout the oceans. The oceanic residence times of these  
40 four elements are relatively long, on the order of 1 to 10 Ma, so that oceanic metal/Ca ratios are  
41 also relatively constant through time during the late Quaternary. Hence any changes in the  
42 metal/Ca of biogenic CaCO<sub>3</sub> may potentially be attributed to variations in the environmental  
43 parameter(s) that affect metal partitioning into the mineral, such as temperature. Mg/Ca has been  
44 widely applied as a paleotemperature proxy in calcitic foraminifera (Nürnberg, 1995), while  
45 Sr/Ca has been similarly used in aragonitic corals (Beck et al., 1992). In both cases ancillary  
46 environmental parameters such as carbonate saturation state, and/or physiological parameters

47 such as growth rate, often appear to overprint the temperature signal. For the ratios that are not  
48 widely used as paleotemperature proxies, Sr/Ca in foraminifera and Mg/Ca in corals, such  
49 ancillary effects likely obscure any temperature dependence. Improved characterization of the  
50 various influences on metal partitioning is therefore a crucial goal of paleoceanographic proxy  
51 development, with an eye toward greater understanding of the biomineralization process.

52 Following the pioneering work of Delaney et al. (1985), Li/Ca has received renewed  
53 attention in both foraminifera and corals, but has not yet seen widespread application as a  
54 paleoceanographic proxy. Several studies have demonstrated a negative correlation between  
55 biogenic Li/Ca and temperature, but significant ancillary influences such as calcification rate  
56 have also been suggested (e.g. Hall and Chan, 2004; Hathorne et al., 2013; Marriott et al., 2004a,  
57 2004b). Benthic foraminiferal Li/Ca from a holothermal depth transect is positively correlated  
58 with seawater saturation state with respect to calcite (Lear and Rosenthal, 2006), leading to the  
59 suggestion that Mg/Ca and Li/Ca can be used in linear combination to solve for both  
60 paleotemperature and saturation state (Lear et al., 2010). Bryan and Marchitto (2008) showed  
61 that Mg/Li in several taxa of benthic foraminifera is better correlated to temperature than either  
62 Mg/Ca or Li/Ca alone, especially for the aragonitic *Hoeglundina elegans* ( $r^2=0.49$  for Mg/Ca,  
63  $0.90$  for Mg/Li). They proposed that both Mg/Ca and Li/Ca reflect, in part, modification of the  
64 internal calcification pool, and that the ratio Mg/Li effectively corrects for physiological and/or  
65 saturation state influences, thereby isolating the temperature effect. A similar improvement using  
66 Mg/Li (or Li/Mg) has since been demonstrated in a diverse range of aragonitic corals, including  
67 deep sea taxa (Case et al., 2010; Montagna et al., 2014; Raddatz et al., 2013).

68 Here we further explore the relationship between Li/Ca and Mg/Ca in biogenic aragonites,  
69 and use it to construct a simple model of biomineralization. We then discuss the implications of  
70 that model for the coral Sr/Ca paleotemperature proxy.

71

## 72 **2. Materials and methods**

73 We present 11 new metal/Ca ratios in *H. elegans* from nine Holocene core tops (Table 1).  
74 Each sample contained ~5-10 individuals >250  $\mu\text{m}$ , which were crushed and reductively and  
75 oxidatively cleaned following the methods of Boyle and Rosenthal (1996). Samples were  
76 analyzed for a suite of trace and minor elemental ratios by high-resolution sector field ICP-MS,  
77 as described by Marchitto (2006). Long-term  $1\sigma$  precision is 0.9% for Li/Ca, 0.5% for Mg/Ca,  
78 and 0.6% for Sr/Ca. Concentrations of contaminant elements Al, Fe, and Mn were all negligible.  
79 We also report 34 previously unpublished *H. elegans* Sr/Ca ratios from the Florida Straits core  
80 tops measured for Li/Mg by Bryan and Marchitto (2008) (Table S1), analyzed using the methods  
81 described above; and 19 previously unpublished Sr/Ca ratios from a subset of the fibrous Li/Mg  
82 samples presented in Montagna et al. (2014) (Table S2), measured by laser ablation quadrupole  
83 ICP-MS following the methods of Montagna et al. (2007), with a  $1\sigma$  precision of 1.6% based on  
84 a *Porites* external standard.

85 Published core top *H. elegans* Li/Ca and Mg/Ca results are compiled from Hall and Chan  
86 (2004) and Bryan and Marchitto (2008). Hall and Chan (2004) Mg/Ca is corrected downward by  
87 the 15% laboratory offset noted by Rosenthal et al. (2006). We omit one *H. elegans*  
88 measurement from Bryan and Marchitto (2008) that has a much different Li/Mg value than its  
89 replicate; and further reject one new sample that is a  $3\sigma$  outlier from an exponential fit of Li/Mg  
90 versus temperature (Table 1). Modern coral Li/Ca and Mg/Ca data are compiled from Case et al.

91 (2010), Hathorne et al. (2013), Montagna et al. (2014), Raddatz et al. (2013), and Fowell et al.  
92 (2016). The interpolated monthly Hathorne et al. (2013) data (excluding the anomalous 1979-80  
93 interval, as in that study), and the monthly to bi-monthly Fowell et al. (2016) data, are binned  
94 into 3°C quasi-seasonal groups based on sea surface temperature at the time of formation, to  
95 prevent individual specimens from exerting undue influence on regressions. For Montagna et al.  
96 (2014) we plot all of their solution-based measurements, plus laser ablation measurements (on  
97 fibrous aragonite) from corals where solution measurements were not made; they found no  
98 significant difference between the two methods when performed on the same corals. Among the  
99 compiled coral data we omit the two samples that Case et al. (2010) flagged as ‘chalky’ and  
100 chemically anomalous; and further reject two  $3\sigma$  Li/Mg outliers as was done for *H. elegans*. *H.*  
101 *elegans* paired Mg/Ca and Sr/Ca data are compiled from Hall and Chan (2004) and Rosenthal et  
102 al. (2006). Coral paired Mg/Ca and Sr/Ca data are compiled from Allison and Finch (2010),  
103 López Correa et al. (2010), Gagnon et al. (2007), Inoue et al. (2007), Montagna et al. (2007),  
104 Reynaud et al. (2007), Shirai et al. (2005), Wei et al. (2000), and Xiao et al. (2014).

105

### 106 **3. Results and discussion**

#### 107 **3.1. Li/Ca, Mg/Ca, and Li/Mg versus temperature**

108 With the addition of new measurements from the deep sea, the weak negative correlation  
109 between Li/Ca and temperature reported for *H. elegans* (Bryan and Marchitto, 2008; Hall and  
110 Chan, 2004) becomes even weaker ( $r^2=0.01$ , Fig 1a). Aragonitic coral Li/Ca exhibits a  
111 considerably stronger negative correlation to temperature ( $r^2=0.52$  across multiple taxa, Fig. 1a),  
112 as has been noted previously (Case et al., 2010; Montagna et al., 2014). For Mg/Ca in *H. elegans*  
113 the correlation to temperature (positive) is much better than for Li/Ca ( $r^2=0.69$ ), but across coral

114 taxa Mg/Ca is slightly worse than Li/Ca ( $r^2=0.36$ ). Li/Mg ratios are not only much better  
115 correlated to temperature than either Li/Ca or Mg/Ca, but the relationship across coral taxa is  
116 remarkably similar to that for *H. elegans* (Hathorne et al., 2013) (Fig. 1c). The best fits are  
117 exponential decay functions:

118  $H. elegans$ :  $\text{Li/Mg} = 5.43 \pm 0.11 e^{-0.0551 \pm 0.0024 T}$  ( $r^2 = 0.91$ ) (1)

119 corals:  $\text{Li/Mg} = 5.29 \pm 0.06 e^{-0.0475 \pm 0.0013 T}$  ( $r^2 = 0.96$ ) (2)

120  $H. elegans$  and corals:  $\text{Li/Mg} = 5.34 \pm 0.06 e^{-0.0502 \pm 0.0012 T}$  ( $r^2 = 0.94$ ) (3)

121 where temperature (T) is in °C. The exponents on these equations indicate a decrease in Li/Mg of  
122 roughly 5% per °C, similar to the values reported by Hathorne et al. (2013) (4.92%), Montagna  
123 et al. (2014) (4.9%), and Fowell et al. (2016) (5%), each based on subsets of the data compiled  
124 here. That the Li/Mg chemistry of aragonite produced by cnidarians behaves so similarly to that  
125 precipitated by protozoa suggests that this ratio is controlled predominantly by temperature  
126 dependent thermodynamic processes, rather than the taxon-specific physiological ‘vital effects’  
127 that appear to impact Li/Ca and Mg/Ca. Note that different genera of calcitic benthic  
128 foraminifera do not exhibit such uniformity (Bryan and Marchitto, 2008), nor do planktonic  
129 foraminifera (Allen et al., 2016), so our model does not apply directly to them (see Section 3.6).

130 Additional insight into this aragonite Li/Mg behavior may be gained by plotting Li/Ca  
131 against Mg/Ca (Fig. 2). Within a given temperature bin (color-coded in Fig. 2), *H. elegans*  
132 exhibits a range of Li/Ca and Mg/Ca values, but they plot as an array along a line that, if forced  
133 through the origin, represents constant Li/Mg (Fig. 2a). The slopes of those lines decrease as  
134 temperature increases, reflecting the decrease of Li/Mg with temperature discussed above. The  
135 various coral taxa behave in the same way, with generally higher Li/Ca and Mg/Ca ratios but  
136 similar Li/Mg compared to *H. elegans* (Fig. 2b). This may also help to illustrate why Li/Ca is

137 more strongly correlated to temperature in warm waters (e.g. Hathorne et al., 2013) than in cold  
138 waters (e.g. Case et al., 2010): all else being equal, the shallower slopes of the warm-end lines  
139 result in smaller Li/Ca ranges at a given temperature than do the steeper cold-end lines (Fig. 2b).

140

### 141 **3.2. Comparison to abiotic partition coefficients**

142 We suggest that the slopes of the lines in Figure 2 are set by the ratios between the  
143 temperature-dependent abiotic partition coefficients  $K_{\text{Li/Ca}}$  and  $K_{\text{Mg/Ca}}$ , and that the spread along  
144 each line results from varying calcification rates (Section 3.3) and/or the organisms'  
145 modifications of their calcifying fluids (Sections 3.4-3.5). Constraints on abiotic aragonite  $K_{\text{Mg/Ca}}$   
146 as a function of temperature are provided by the inorganic precipitation experiments of Gaetani  
147 and Cohen (2006), who found an exponential decrease with temperature ( $r^2=0.996$ ). Gaetani and  
148 Cohen (2006) noted that their  $K_{\text{Sr/Ca}}$  results agreed well with values from Kinsman and Holland  
149 (1969), who used the same experimental approach. We make no assumption that these partition  
150 coefficients reflect substitution for  $\text{Ca}^{2+}$ , and indeed  $\text{Mg}^{2+}$  does not appear to occupy the  $\text{Ca}^{2+}$   
151 lattice site in abiotic or coral aragonite (Finch and Allison, 2007; 2008).

152 If we assume that the Gaetani and Cohen (2006)  $K_{\text{Mg/Ca}}$  values are applicable to biogenic  
153 aragonite, then we can combine them with the data in Figure 2b to predict abiotic  $K_{\text{Li/Ca}}$  as a  
154 function of temperature. For each temperature bin, we first find the predicted  $K_{\text{Mg/Ca}}$  at the  
155 central temperature using Gaetani and Cohen's (2006) temperature dependence. We then  
156 combine that coefficient with seawater Mg/Ca to predict an aragonite Mg/Ca, which would be  
157 the mineral's ratio if it were precipitated directly from unmodified seawater. Since modification  
158 of the organism's calcifying fluid hypothetically results in movement along the Li/Mg isotherm  
159 without changing its slope, the slope can be multiplied by the calculated aragonite Mg/Ca to

160 predict the corresponding aragonite Li/Ca if precipitated from unmodified seawater.

161 Combination of that value with seawater Li/Ca yields  $K_{\text{Li/Ca}}$ . This analysis suggests that abiotic

162  $K_{\text{Li/Ca}}$  should decrease exponentially by ~7% per °C:

$$163 \quad K_{\text{Li/Ca}} = 0.0252 \pm 0.0002 e^{-0.0707 \pm 0.0011 T} \quad (4)$$

164 with  $r^2 = 0.999$  (Fig. 3). This temperature sensitivity is close to that calculated by Montagna et al.

165 (2014) using a similar approach (~6.7% per °C). We are not aware of any abiotic aragonite

166 precipitation experiments that determine  $K_{\text{Li/Ca}}$  as a function of temperature. Marriott et al.

167 (2004a) did, however, make two abiotic aragonite determinations at 25°C (and near-seawater

168 salinities) that are within 30% of our predicted value (Fig. 3).  $K_{\text{Li/Ca}}$  in abiotic calcite decreases

169 by ~5% per °C ( $r^2=0.995$ ) (Marriott et al., 2004b) with values that are comparable to our

170 aragonite predictions (Fig. 3). We note that at 25°C the difference in calcite  $K_{\text{Li/Ca}}$  between the

171 two Marriott et al. studies is even larger than between Marriott et al.'s (2004a) aragonite  $K_{\text{Li/Ca}}$

172 and our prediction, so the latter discrepancy may be insignificant. In summary, our predicted

173 abiotic aragonite  $K_{\text{Li/Ca}}$  temperature dependence awaits experimental confirmation, but available

174 data suggest that our derived values are reasonable.

175

### 176 **3.3. Hypothetical effect of precipitation rate**

177 Gaetani and Cohen (2006) noted that their abiotic aragonite  $K_{\text{Mg/Ca}}$ ,  $K_{\text{Sr/Ca}}$ , and  $K_{\text{Ba/Ca}}$  values

178 were all substantially larger than predicted from thermodynamic equilibrium according to lattice

179 strain theory. They proposed that the observations could be explained by surface entrapment

180 during crystal growth (Watson, 2004), with reduced entrapment at higher temperatures due to

181 higher ionic diffusivities in the lattice surface. This model also predicts a positive dependence on

182 precipitation rate, which is borne out for Mg and U in aragonite precipitation experiments:

183 apparent entrapment varies from zero to 100% (relative to the temperature-dependent limit) over  
184 about three orders of magnitude in growth rate (Gabitov et al., 2008). This raises a potential  
185 complication for applying the Gaetani and Cohen (2006)  $K_{Mg/Ca}$  results to biogenic aragonite: if  
186 either their experimental precipitation rates or biogenic precipitation rates are substantially below  
187 the levels at which entrapment asymptotes at 100%, then the two are not directly comparable.

188 Gaetani and Cohen's (2006) precipitation rates were apparently above the level of ~100%  
189 Mg entrapment as measured by Gabitov et al. (2008). However, the Mg/Ca and Li/Ca ratios  
190 measured in *H. elegans* and in corals are substantially lower than predicted in Section 3.2 for  
191 aragonite precipitated from unmodified seawater (black dots in Fig. 4). This could mean that  
192 biogenic  $K_{Mg/Ca}$  and  $K_{Li/Ca}$  are each decreased by a range of lower precipitation rates and less  
193 surface entrapment, with zero-entrapment Mg/Ca and Li/Ca values occurring somewhere close to  
194 the origin in Figure 4 (note that lattice strain theory calculations are exceedingly sensitive to  
195 ionic radii, which are not well known at the 9-coordination of aragonite, so we do not plot the  
196 zero entrapment equilibrium values). Microscale measurements of linear extension rates in some  
197 fibrous ('wall') portions of the *Pocillopora damicornis* skeleton (Brahmi et al., 2012) appear to  
198 be lower (~0.05-0.2 nm s<sup>-1</sup>) than Gabitov et al.'s (2008) 100% entrapment threshold (~0.2 nm s<sup>-1</sup>  
199 or higher), implying that kinetics may be important in corals. Centers of calcification (COCs, or  
200 'rapid accretion deposits') grow faster (Brahmi et al., 2012), and their elevated Li/Ca and Mg/Ca  
201 ratios (by roughly a factor of two) have been attributed to greater entrapment (Montagna et al.,  
202 2014; Rollion-Bard and Blamart, 2015).

203 If this interpretation is correct, the minimal Li/Mg deviations away from isotherms (Figs. 2,  
204 4a) require that the *ratio* between the two partition coefficients remains nearly constant at a  
205 given temperature as precipitation rates vary (i.e. that  $K_{Li/Ca}$  and  $K_{Mg/Ca}$  have approximately the

206 same sensitivity to precipitation rate). Providing some support for this scenario, Gabitov et al.  
207 (2008) demonstrated a sharp drop in both  $K_{\text{Mg/Ca}}$  and  $K_{\text{U/Ca}}$  at linear extension rates below  $\sim 0.2$   
208  $\text{nm s}^{-1}$ , accompanied by no significant change in the ratio between the two. Limited aragonite  
209  $K_{\text{Li/Ca}}$  experimental data confirm a positive growth rate effect, but it does not appear to be as  
210 strong as for  $K_{\text{Mg/Ca}}$  (Gabitov et al., 2011), which would tend to drive the biogenic data off the  
211 isotherms. We infer from this that precipitation rate and degree of entrapment are unlikely to be  
212 *dominant* drivers of the biogenic Li/Mg observations, but additional abiotic growth rate  
213 experiments are required for confirmation. In the following we make the simplifying assumption  
214 of 100% entrapment, and we explore other potential biomineralization dynamics. We return to  
215 kinetics when discussing Sr/Ca in Section 3.6.

216

### 217 **3.4. Hypothetical effect of $\text{Ca}^{2+}$ pumping**

218 The Mg/Ca and Li/Ca ratios observed in *H. elegans* and corals could be consistent with the  
219 abiotic partition coefficients predicted in Section 3.2 (i.e. with 100% entrapment) if Mg/Ca and  
220 Li/Ca ratios in the organisms' calcifying fluids are lower than those in seawater, with *H. elegans*  
221 being lowest of all. Calcifying organisms must exert tight controls over the precipitation of  
222  $\text{CaCO}_3$ , and hence they create a 'privileged space' that is isolated from seawater. Since cytosolic  
223  $[\text{Ca}^{2+}]$  must be kept low ( $< 1 \mu\text{M}$ ) for cell health, vacuolized or extracellular seawater (10 mM  
224  $[\text{Ca}^{2+}]$ ) likely provides a baseline for the calcifying fluid (e.g. Erez, 2003). Seawater  
225 vacuolization, alkalization, and delivery to sites of calcification have been demonstrated in  
226 benthic foraminifera (Bentov et al., 2009; de Nooijer et al., 2009b). Corals sequester their  
227 calcifying fluid extracellularly against the skeleton (Adkins et al., 2003; McConnaughey, 1989)  
228 with tracers documenting at least some direct seawater transport to the site of calcification

229 (Gagnon et al., 2012; Tambutte et al., 2011). Once seawater is isolated and  $\text{CaCO}_3$  precipitation  
230 begins, Rayleigh fractionation will result in modification of the calcifying fluid's Mg/Ca and  
231 Li/Ca ratios (Elderfield et al., 1996), but because Mg and Li are highly incompatible this process  
232 is expected to raise, not lower, those ratios (Section 3.5). Therefore we require another  
233 mechanism to lower Mg/Ca and Li/Ca in the calcifying fluid.

234  $\text{Mg}^{2+}$  is well known to poison calcite precipitation (Berner, 1975), and it has been suggested  
235 that foraminifera actively pump  $\text{Mg}^{2+}$  out of their privileged spaces in order to precipitate low-  
236 Mg calcite (Bentov and Erez, 2006). Such a process could explain our observations if  $\text{Mg}^{2+}$   
237 pumps also export  $\text{Li}^+$  with essentially no discrimination, but this seems unlikely given their  
238 different valence states. Furthermore the  $\text{Mg}^{2+}$  pumping strategy has been shown to be  
239 energetically inferior to raising calcifying fluid pH via  $\text{H}^+$  export (Zeebe and Sanyal, 2002), and  
240 in fact aragonitic organisms have no specific need to exclude  $\text{Mg}^{2+}$ .  $\text{Li}^+$  export would likely  
241 impart a large isotopic fractionation given the low masses of its isotopes ( $^6\text{Li}$  and  $^7\text{Li}$ ), yet  
242 calcitic foraminifera and aragonitic corals exhibit similar  $\delta^7\text{Li}$  to their respective abiotic  
243 precipitates (Marriott et al., 2004a).

244 We therefore consider  $\text{Ca}^{2+}$  import as an alternative, with transmembrane pumps (or  
245 channels) that discriminate almost completely against both  $\text{Mg}^{2+}$  and  $\text{Li}^+$ .  $\text{Mg}^{2+}$  and  $\text{Li}^+$  ionic  
246 radii are small compared to  $\text{Ca}^{2+}$ , which might explain the specificity of a  $\text{Ca}^{2+}$  pump.  $\text{Ca}^{2+}$   
247 pumping carries the advantage of raising pH in the privileged space, thereby promoting  $\text{CaCO}_3$   
248 precipitation (McConnaughey, 1989; Zeebe and Sanyal, 2002; Sinclair and Risk, 2006). Active  
249 concentration of  $\text{Ca}^{2+}$  may also be required to satisfy known biomineralization rates. Allison et  
250 al. (2011) calculated that the coral *Galaxea fascicularis* would need to empty and refill its  
251 privileged space at least 10,000 times per hour if all of its  $\text{Ca}^{2+}$  were supplied from unmodified

252 seawater. Similarly, de Nooijer et al. (2009a) estimated that the calcitic benthic foraminifer  
253 *Ammonia aomoriensis* must process ~75 times its own volume in seawater to obtain enough  $\text{Ca}^{2+}$   
254 to build a single chamber, yet vacuole turnover was observed to be far too slow to accommodate  
255 that need. These observations could implicate the existence of large internal stores of  $\text{Ca}^{2+}$ ,  
256 perhaps in a solid form like amorphous  $\text{CaCO}_3$  (ACC) (Erez, 2003). However, recent *in vitro*  
257 tracer experiments with *A. aomoriensis* led Nehrke et al. (2013) to conclude that the main source  
258 of  $\text{Ca}^{2+}$  is not vacuolized seawater, nor some internal  $\text{Ca}^{2+}$  store like ACC, but rather it is  
259 delivered directly to the privileged space via pumping from seawater. Some vacuolized seawater  
260 does still reach the site of calcification, and most or all of the  $\text{Mg}^{2+}$  and  $\text{Li}^+$  that ends up in the  
261 mineral would be supplied by those vacuoles and/or by breaks in the cytoplasmic sheet covering  
262 the privileged space (or by extracellular openings in the case of corals). Under this scenario the  
263 spread along a Li/Mg isotherm can be considered as a two-component mixture between a  
264 perfectly isolated privileged space (all  $\text{Ca}^{2+}$  actively pumped, represented by the origin in Fig. 4  
265 if the pump completely discriminates against  $\text{Mg}^{2+}$  and  $\text{Li}^+$ ) and passively incorporated seawater  
266 (filled dots). This is numerically equivalent to pumping  $\text{Ca}^{2+}$  into a seawater-derived reservoir  
267 (Sinclair and Risk, 2006), which would cause the chemistry in Figure 4 to migrate from the filled  
268 dots toward the origin.

269 Inferred  $[\text{Ca}^{2+}]$  in the calcifying fluid can be derived by finding the fluid's Mg/Ca (or Li/Ca)  
270 ratio that is required for the biogenic aragonite data to be compatible with the abiotic partition  
271 coefficients, while leaving fluid  $[\text{Mg}^{2+}]$  and  $[\text{Li}^+]$  at their seawater values. The constraint of using  
272 abiotic partition coefficients is an important difference from previous models that used empirical  
273 biogenic partition coefficients (especially critical for Mg), allowing them to match coral  
274 chemistry using minimal elevations of fluid  $[\text{Ca}^{2+}]$  (Sinclair and Risk, 2005; Gagnon et al., 2007,

275 2012). In contrast, our inferred  $[Ca^{2+}]$  ranges from ~13 mM (~30% enrichment over seawater)  
276 for the warmest corals to >400 mM (~40-fold enrichment) for the coldest *H. elegans* (Fig. 4).  
277  $Ca^{2+}$ -ATPases, which exchange  $Ca^{2+}$  for  $H^+$ , have been implicated in various calcifying plants  
278 and animals and have been characterized in the coral *Stylophora pistillata* (Zoccola et al., 2004).  
279  $Ca^{2+}$ -ATPase can maintain a cross-membrane  $[Ca^{2+}]$  gradient of order 10,000-100,000-fold  
280 (Langer et al., 2006), so our inferred concentrations are feasible if pumped directly from  
281 seawater or an intermediary  $Ca^{2+}$  pool, and not adjacent to cytosol. The biogenic aragonite data  
282 imply that less pumping generally occurs in warmer waters, hypothetically due to higher  
283 aragonite saturation states. Microsensor measurements document elevated  $[Ca^{2+}]$  in the  
284 calcifying fluid of the coral *G. fascicularis*, but at levels much more modest than inferred here  
285 (Al-Horani et al., 2003). We note, however, that our inferred  $Ca^{2+}$  concentrations need not be  
286 free in the calcifying fluid, but could be largely sequestered in ACC or organic ligands, which  
287 would also alleviate the thermodynamic limit of  $Ca^{2+}$ -ATPase. In that light the extreme  
288 accumulation of  $Ca^{2+}$  would be less a requirement of raising the saturation state and more a  
289 material necessity of house building (Nehrke et al., 2013). In fact, very high free  $[Ca^{2+}]$  (and  
290 hence pH) does not necessarily translate into higher aragonite precipitation rates, because the  
291 carbon supply may become limited by the  $CO_2$  diffusion rate across membranes at zero  $CO_2$  in  
292 the privileged space (Sinclair and Risk, 2006).

293 If the bulk of the  $Ca^{2+}$  precipitated into aragonite is acquired by pumping, then an isotopic  
294 fractionation would be expected because transmembrane transport likely discriminates against  
295 heavier isotopes. Coccolithophores (Gussone et al., 2006) and corals (Böhm et al., 2006) exhibit  
296 similar  $\delta^{44/40}Ca$  despite an offset of ~0.6‰ between inorganic calcite and aragonite (Gussone et  
297 al., 2005), suggesting a characteristic biological fractionation and no mineralogical fractionation

298 (Böhm et al., 2006; Gussone et al., 2006). *H. elegans*  $\delta^{44/40}\text{Ca}$  is slightly more depleted than  
299 coccolithophores and corals, which might be consistent with a different level of transmembrane  
300 transport (Gussone et al., 2016). It must be noted, however, that other processes can impart  
301 isotopic fractionations during biomineralization, so the  $\delta^{44/40}\text{Ca}$  observations cannot be taken as  
302 conclusive evidence for or against  $\text{Ca}^{2+}$  pumping (Gussone et al., 2016).

303

### 304 **3.5. Rayleigh fractionation**

305 If *H. elegans* and corals calcify from a calcifying fluid that is isolated from seawater, then  
306 depletion of the  $\text{Ca}^{2+}$  in that pool will result in Rayleigh fractionation of the various cations  
307 present, given mathematically by Elderfield et al. (1996). This process has been implicated in  
308 explaining why calcitic benthic foraminiferal trace element ratios tend to vary with calcite  
309 saturation state, with lower saturation leading to a more isolated (infrequently replenished)  
310 reservoir and hence greater fractionations (Elderfield et al., 1996). It has also been included in  
311 various attempts to explain coral trace element ratios (e.g. Case et al., 2010; Gaetani et al., 2011;  
312 Gagnon et al., 2007; Montagna et al., 2014). The case for  $\text{Li}^+$  and  $\text{Mg}^{2+}$  is simple because the  
313 abiotic aragonite partition coefficients for these elements are  $\ll 1$  (Gaetani and Cohen, 2006;  
314 Marriott et al., 2004a). Therefore as calcification proceeds from a closed pool,  $[\text{Ca}^{2+}]$  declines  
315 while  $[\text{Li}^+]$  and  $[\text{Mg}^{2+}]$  remain nearly constant (Case et al., 2010). This has almost exactly the  
316 opposite effect of  $\text{Ca}^{2+}$  pumping:  $\text{Li}/\text{Ca}$  and  $\text{Mg}/\text{Ca}$  ratios in the privileged space rise, and  
317 aragonite chemistry moves away from the origin, approximately along  $\text{Li}/\text{Mg}$  isotherms and with  
318 little resulting impact on the  $\text{Li}/\text{Mg}$  thermometer (Fig. 4b). For 95% precipitation of the  $\text{Ca}^{2+}$   
319 pool ( $f = 0.05$ ),  $\text{Li}/\text{Mg}$  deviations away from isotherms range from  $\sim 0.6\%$  at the warm end to  
320  $\sim 6\%$  at the cold end, regardless of the  $[\text{Ca}^{2+}]$  starting point.

321

### 322 **3.6. Is Sr/Ca consistent with this model?**

323 Much work has been devoted to understanding Sr/Ca in corals because of its utility as a  
324 paleotemperature proxy (see Cohen and Gaetani, 2010, for a review). Here we simply examine  
325 what is required for paired Sr/Ca and Mg/Ca data to fit within the confines of our  
326 biomineralization model. The lack of a positive correlation between Sr/Ca and Mg/Ca in corals  
327 at a given temperature (Fig. 5a) indicates that in contrast to Li/Mg, Sr/Mg ratios in the privileged  
328 space are not constant. This in turn could mean two things: the  $\text{Ca}^{2+}$  pump could be 'leaky' with  
329 respect to  $\text{Sr}^{2+}$ , and/or Rayleigh fractionation may be important. To evaluate the relative impacts  
330 of these two effects we use abiotic aragonite  $K_{\text{Sr/Ca}}$  from Gaetani and Cohen (2006), who found a  
331 decrease with temperature ( $r^2=0.97$ ) in good agreement with Kinsman and Holland (1969).  $K_{\text{Sr/Ca}}$   
332 is slightly above 1 at oceanic temperatures, much higher than  $K_{\text{Mg/Ca}}$ , indicating that Rayleigh  
333 fractionation is likely to be important for Sr/Mg. In Figure 5a we show pre-Rayleigh trajectories  
334 for paired Sr/Ca and Mg/Ca at a single arbitrary temperature ( $12^\circ\text{C}$ ) assuming  $[\text{Ca}^{2+}]$  in the  
335 privileged space is raised by a pump that has various levels of affinity for  $\text{Sr}^{2+}$ . An affinity value  
336 of 1 means that the pump makes no distinction between the two elements and therefore  
337 transports them at the seawater ratio, while values lower than 1 indicate that  $\text{Sr}^{2+}$  is less  
338 efficiently transported than  $\text{Ca}^{2+}$ . This model only projects into the range of the coral data if there  
339 is little discrimination. Since any Rayleigh fractionation will drive aragonite Sr/Ca lower, a  $\text{Sr}^{2+}$   
340 to  $\text{Ca}^{2+}$  transport stoichiometry of  $\sim 0.97$  could be an approximate lower limit that satisfies nearly  
341 all of the data (Fig. 5b). A value that high is mainly constrained by the cold-end coral data where  
342 abiotic  $K_{\text{Sr/Ca}}$  and  $K_{\text{Mg/Ca}}$  are less certain (Gaetani and Cohen, 2006), while warm water data can  
343 accommodate a stoichiometry as low as  $\sim 0.9$ . Berman and King (1990) reported Sr:Ca transport

344 stoichiometries of 0.82-0.93 in  $\text{Ca}^{2+}$ -ATPase from rabbit muscle tissue, so our inferred values  
345 appear to be reasonable. This contrasts with the coral models of Sinclair and Risk (2006) and  
346 Gagnon et al. (2012), who assumed a pump that is impervious to  $\text{Sr}^{2+}$ .

347 In modifying a calcifying fluid that has experienced  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  pumping, Rayleigh  
348 fractionation will drive aragonite Sr/Ca down and Mg/Ca up, with trajectories shown as dashed  
349 lines in Figure 5a for 12°C and two arbitrary starting points. The spread of coral Sr/Ca and  
350 Mg/Ca data from a given temperature bin appears to run quasi-parallel to these trajectories, in  
351 support of this mechanism (Gagnon et al., 2007). Different coral specimens at a given  
352 temperature likely have different Rayleigh starting points due to variable amounts of pumping,  
353 leading to additional spread in the sub-horizontal direction in Figure 5. Rayleigh trajectories vary  
354 with not only with starting point chemistry (Fig. 5a) but also with temperature due to its impact  
355 on  $K_{\text{Sr/Ca}}$  (Fig. 5b). The coral data appear to follow the predicted slopes at different temperatures  
356 (e.g. *Desmophyllum* at 3-6°C vs. *Acropora* at 27-30°C), further supporting the Rayleigh model  
357 and also the applicability of the abiotic  $K_{\text{Sr/Ca}}$ .

358 The Sr/Ca and Mg/Ca measurements in Figure 5 primarily represent fibrous aragonite, but  
359 some samples may hypothetically include admixtures of COC aragonite. If systemic, such  
360 admixtures could contribute to the observed horizontal scatter because COCs are consistently  
361 elevated in Mg/Ca (and Li/Ca) but not in Sr/Ca (Meibom et al., 2004; Gagnon et al., 2007;  
362 Montagna et al., 2014). As noted above, this could be related to greater  $\text{Mg}^{2+}$  and  $\text{Li}^+$  entrapment  
363 in faster growing COCs, whereas limited abiotic aragonite observations suggest that  $\text{Sr}^{2+}$  may be  
364 insensitive to entrapment over coral-relevant growth rates (Gabitov et al., 2006; Holcomb et al.,  
365 2009).

366 In contrast to corals, Sr/Ca and Mg/Ca in *H. elegans* are positively correlated, and both tend  
367 to increase with temperature (Rosenthal et al., 2006). This is surprising given the inverse  
368 relationship between Sr/Ca and temperature in both abiotic and coral aragonite. *H. elegans*  
369 Sr/Mg behavior is, in fact, more akin to Li/Mg than to coral Sr/Mg (Fig. 6). This may indicate  
370 that Ca<sup>2+</sup> pumping discriminates more strongly against Sr<sup>2+</sup> in *H. elegans*, and a Sr<sup>2+</sup> to Ca<sup>2+</sup>  
371 transport stoichiometry of ~0.2-0.3 results in a reasonably good fit to the data. This model  
372 therefore requires a great deal of pumping but relatively little Rayleigh fractionation, which  
373 would drive values to the right in Figure 6. It furthermore suggests that the empirical correlations  
374 between Sr/Ca, Mg/Ca, and temperature in *H. elegans* are actually dominated by the amount of  
375 pumping, with greater pumping in colder waters. Much of the correlation to temperature may  
376 actually be spurious because temperature is well correlated to seawater  $\Delta\text{CO}_3^{2-}$  with respect to  
377 aragonite in these data sets (Rosenthal et al., 2006), and indeed a dominant role for  $\Delta\text{CO}_3^{2-}$  has  
378 been implicated (Yu et al., 2014). Rosenthal et al. (2006) suggested that the  $\Delta\text{CO}_3^{2-}$  influence is  
379 limited to saturation states below  $\sim 15 \mu\text{mol kg}^{-1}$ , with temperature prevailing above that level.  
380 According to our model the apparent  $\Delta\text{CO}_3^{2-}$  effect may be explained by greater Ca<sup>2+</sup> pumping in  
381 less saturated waters ( $< 15 \mu\text{mol kg}^{-1}$  is shown as triangles in Fig. 6), and it probably extends  
382 above  $15 \mu\text{mol kg}^{-1}$  albeit with a weaker influence (circles in Fig. 6). The predicted temperature  
383 influence on *H. elegans* paired Sr/Ca and Mg/Ca is overwhelmed by Ca<sup>2+</sup> pumping and Rayleigh  
384 fractionation according to this model.

385 Alternatively the positive correlation between Sr/Ca and Mg/Ca in *H. elegans* could be a  
386 consequence of surface entrapment due to slow but variable precipitation rates. The differing  
387 behavior between organisms would require  $K_{\text{Sr/Ca}}$  to be insensitive to the precipitation rates  
388 found in corals (Gabitov et al., 2006; Holcomb et al., 2009), but sensitive to lower rates

389 hypothetically found in *H. elegans*. In that case some of the coral Mg/Ca lowering at near-  
390 constant Sr/Ca (Fig. 5) could be attributable to reduced Mg entrapment instead of  $\text{Ca}^{2+}$  pumping.  
391 The *H. elegans* Sr/Ca and Mg/Ca pattern (Fig. 6) might then accommodate a  $\text{Ca}^{2+}$  pump with a  
392 high affinity for  $\text{Sr}^{2+}$  (pushing chemistry to the left as in Fig. 5a), combined with Rayleigh  
393 fractionation (pushing chemistry to the right as in Fig. 6b). The observed correlation between  
394 Sr/Ca and temperature (Rosenthal et al., 2006) could again be spurious and due to the co-varying  
395  $\Delta\text{CO}_3^{2-}$ , with lower precipitation rates and less entrapment in undersaturated waters. We  
396 reiterate, however, that this scenario also requires the ratio between  $K_{\text{Li/Ca}}$  and  $K_{\text{Mg/Ca}}$  to remain  
397 nearly constant at a given temperature as growth rates vary, to satisfy the requirement that paired  
398 biogenic Li/Ca and Mg/Ca data remain along isotherms (Figs. 2, 4a), whereas limited  
399 experimental data suggest that is not the case (Gabitov et al., 2011).

400

### 401 **3.7. Implications for paleotemperature estimation**

402 We agree with prior workers (Bryan and Marchitto, 2008; Montagna et al., 2014; Raddatz et  
403 al., 2013) that Li/Mg is a promising paleotemperature proxy in *H. elegans* and various corals. If  
404 our hypothesis is correct, then Li/Mg may effectively account for ‘vital effects’ associated with  
405 organisms’ modification of their calcifying fluids, e.g. in response to seawater  $\Delta\text{CO}_3^{2-}$ . This  
406 could lead to greater paleotemperature accuracy (since ancillary parameters like  $\Delta\text{CO}_3^{2-}$  need not  
407 be known) and precision (if the model is a reasonably complete description of  
408 biomineralization). The proxy is clearly not perfect however, as instances of anomalous Li/Mg  
409 ratios have been demonstrated in a portion of a *Porites* record from Japan (Hathorne et al., 2013)  
410 and between forereef and backreef *Siderastrea* from Belize (Fowell et al., 2016). The  
411 hypothetical influence of crystal growth rate on cation entrapment might account for some of the

412 observed scatter around our simple model, and thereby place limits on both accuracy and  
413 precision. If that is the case, then in corals it would be important to avoid mixing fibrous  
414 aragonite and faster growing COCs when generating temperature reconstructions (Montagna et  
415 al., 2014).

416 The standard errors of estimate for Li/Mg range from 0.22 mmol mol<sup>-1</sup> for corals (Equation  
417 2) to 0.29 mmol mol<sup>-1</sup> for *H. elegans* (Equation 1). At cold temperatures where the relationship is  
418 steepest this translates to slightly better than ±1°C uncertainty, while at the warm end it balloons  
419 to several degrees. However, this analysis does not account for the fact that Li/Mg scatter is  
420 decreased in warm waters compared to cold waters, which counteracts the effect of the  
421 exponential response (Fig. 1c). Regressing the data with temperature as the dependent variable  
422 yields standard errors of estimate of 1.3°C (*H. elegans*) to 1.5°C (corals), which we take to be  
423 better measures of the temperature uncertainty.

424 We note that the cold-end scatter is substantially reduced if we regress Mg/Li (rather than  
425 Li/Mg) against temperature, but this also puts the flat part of the exponential curve in cold  
426 waters, negating the apparent gain in sensitivity (Fig. 7). Alternatively fitting *H. elegans* Mg/Li  
427 with a second-order polynomial produces an equation that is relatively steep at the cold end:

$$428 \quad \text{Mg/Li} = 0.150 \pm 0.012 + 0.0209 \pm 0.0027T - 0.0002 \pm 0.0001T^2 \quad (5)$$

429 with  $r^2 = 0.95$ . Since the shape of this response is substantially different from the polynomial fit  
430 to the coral Mg/Li data (which is virtually identical to the coral exponential fit), we favor the  
431 exponential fits as better descriptors of the fundamental similarity between *H. elegans* and coral  
432 aragonite. However, preliminary downcore measurements suggest that *H. elegans* Equation (5)  
433 provides more realistic deep sea temperatures than Equation (1), so Equation (5) may serve as an  
434 empirically superior choice for paleotemperature reconstruction until additional calibration data

435 become available. The standard error of estimate for Mg/Li according to Equation (5) is 0.022  
436 mol mmol<sup>-1</sup>, which translates to ±1.0°C at 0°C and ±1.7°C at 20°C.

437 Some of the scatter in our compilations could further be related to combining data from  
438 different laboratories that are not intercalibrated or that employ different cleaning procedures,  
439 and some could be due to imprecise knowledge of calcification temperatures, so true precision  
440 might be better. In the deep ocean where reliable paleotemperature proxies are lacking,  
441 uncertainties of ~1°C would represent a step forward. If the overall Li/Mg error is random, then  
442 repeated measurements on the same samples could reduce the paleotemperature uncertainty  
443 below 1°C.

444 It is tempting to try extending our biomineralization model to calcitic foraminifera. For  
445 several calcitic benthic foraminiferal taxa, Mg/Li is strongly correlated to temperature ( $r^2 = 0.71$ -  
446 0.90) but this represents only a slight improvement over Mg/Ca, in contrast to the case for *H.*  
447 *elegans* (Bryan and Marchitto, 2008). Importantly, different calcitic taxa yield significantly  
448 distinct Mg/Li slopes and intercepts, implying that additional unknown factors must be affecting  
449 their Mg/Li ratios. Langer et al. (2015) proposed that Ca<sup>2+</sup> channels in *Amphistegina lessonii* are  
450 more permeable to Li<sup>+</sup> than to Mg<sup>2+</sup>, which would cause calcite Mg/Li to vary somewhat with  
451 the extent of pumping at a given temperature. For planktonic foraminifera there is no apparent  
452 correlation between Mg/Ca and Li/Ca within a given temperature range (Allen et al., 2016). This  
453 latter observation is reassuring for the use of Mg/Ca as a temperature proxy, as it suggests that  
454 Ca<sup>2+</sup> pumping (with Mg<sup>2+</sup> and Li<sup>+</sup> exclusion) is not so important for planktonic foraminifera. We  
455 conclude that our simple biomineralization model and its implications for Li/Mg-based  
456 temperature reconstruction are only directly applicable to certain biogenic aragonites.

457 The impact of Rayleigh fractionation on the coral Sr/Ca thermometer has been noted  
458 previously (e.g. Gaetani and Cohen, 2006; Gagnon et al., 2007). The relationship between Sr/Ca  
459 and temperature can vary between different taxa, different localities, and even different growth  
460 axes on the same coral head (e.g. de Villiers et al., 1995; Marshall and McCulloch, 2002;  
461 Corrège, 2006). These variations may be attributable to differing amounts of Rayleigh  
462 fractionation. The impact of  $\text{Ca}^{2+}$  pumping on the Sr/Ca thermometer appears to be  
463 comparatively smaller because of the pump's high affinity for  $\text{Sr}^{2+}$  (Fig. 5b). We encourage the  
464 continued use of multiple elements to isolate the temperature signal, whether it be Li/Mg, Mg-Sr-  
465 Ba (Gaetani et al., 2011), U/Sr (DeCarlo et al., 2016), or some other combination.

466

#### 467 **4. Conclusions**

468 We present a simple conceptual model that explains the remarkably similar behavior of  
469 Li/Mg between the aragonitic foraminifer *H. elegans* and various aragonitic coral taxa. We  
470 suggest that Li/Mg reflects the ratio between the abiotic partition coefficients  $K_{\text{Li/Ca}}$  and  $K_{\text{Mg/Ca}}$   
471 because neither  $\text{Ca}^{2+}$  pumping nor Rayleigh fractionation significantly alters the Li/Mg ratio of  
472 the calcifying fluid. This model is consistent with coral Sr/Ca if the  $\text{Ca}^{2+}$  pump barely  
473 discriminates against  $\text{Sr}^{2+}$ . In contrast *H. elegans* Sr/Ca appears to require either a large  
474 discrimination against pumping  $\text{Sr}^{2+}$ , or an important role for aragonite precipitation rate through  
475 its impact on surface cation entrapment. In either case Li/Mg appears to be largely unaffected by  
476 such 'vital effects,' and therefore it holds unusual promise as a paleotemperature proxy.

477

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484

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**Table 1.** New trace element measurements on core top *H. elegans*. Elemental ratios are given in mmol mol<sup>-1</sup>, except Li/Ca which is in μmol mol<sup>-1</sup>.

Core	Depth in core (cm)	Latitude	Longitude	Water depth (m)	Temperature (°C)	Li/Ca	Mg/Ca	Sr/Ca	Li/Mg
AII107-71GGC	5-7	31°31' S	35°56' W	1887	2.9	2.93	0.62	0.85	4.73
AII107-71GGC	5-7	31°31' S	35°56' W	1887	2.9	2.88	0.58	0.78	4.95
CHN82-15PC	0-6	43°22' N	28°14' W	2151	3.7	2.60	0.72	0.77	3.62
CHN82-15PC	0-6	43°22' N	28°14' W	2151	3.7	2.52	0.61	0.74	4.13
KNR166-2-16MC	0-1	24°24' N	83°14' W	248	10.8	3.87	1.41	2.32	2.75
KNR166-2-76MC	0-1	23°35' N	79°25' W	539	11.0	4.11	1.49	2.27	2.76
KNR166-2-89MC*	0-1	24°34' N	79°14' W	353	17.8	4.78	1.57	2.51	3.04
KNR166-2-123MC	0-1	24°46' N	79°16' W	632	10.6	3.58	1.30	2.18	2.75
RC13-140	10	2°52' N	87°45' W	2246	2.0	2.11	0.47	0.44	4.54
RC23-15	5	1°13' N	87°45' W	3612	2.0	1.39	0.26	0.45	5.35
RC23-22	10	1°00' N	83°37' W	3215	2.0	1.39	0.25	0.35	5.54

\*3σ Li/Mg outlier omitted from figures

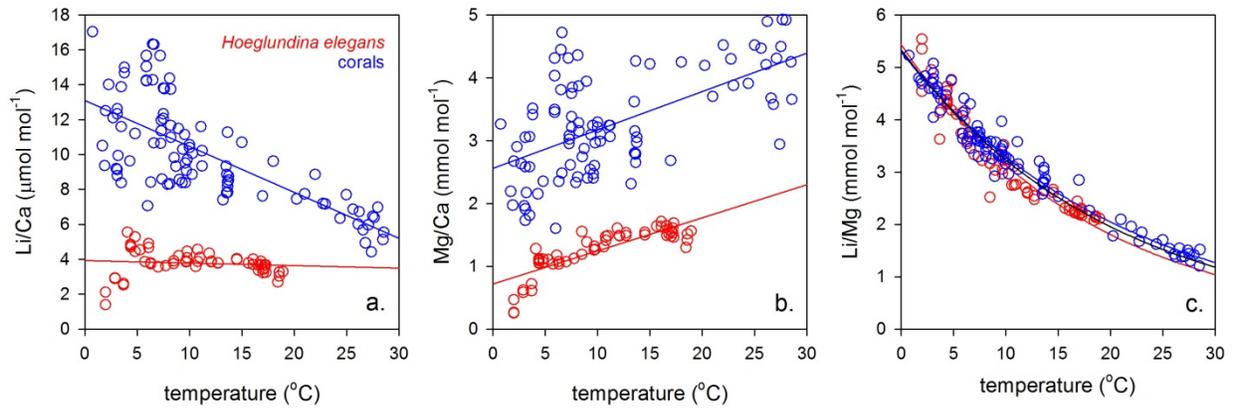
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**Table 2.** Laser ablation ICP-MS Sr/Ca measurements ( $\text{mmol mol}^{-1}$ ) made on fibrous aragonite from a subset of the corals in Montagna et al. (2014).

Sample code	Location	Latitude	Longitude	Depth (m)	Temperature ( $^{\circ}\text{C}$ )	Species	Sr/Ca
<i>Field specimens</i>							
POS-325-433-1	Stjemsund, Norway	70°16' N	22°28' E	277-365	5.9	<i>Lophelia pertusa</i>	10.33
POS-325-433-2	Stjemsund, Norway	70°16' N	22°28' E	277-365	5.9	<i>Lophelia pertusa</i>	10.30
POS-228-216	Sula Ridge, Norway	64°07' N	8°07' E	250-320	7.52	<i>Lophelia pertusa</i>	10.15
POS-228-217	Sula Ridge, Norway	64°07' N	8°07' E	250-320	7.52	<i>Lophelia pertusa</i>	10.12
ALK-232-1050 BG	Oslofjord, Norway	59°06' N	10°41' E	105	8.2	<i>Lophelia pertusa</i>	9.88
DW13831#1	Darwin Mounds, UK	59°49' N	7°22' W	950	6.31	<i>Lophelia pertusa</i>	10.00
POS-292-544-1	Pelagia Mound, UK	55°31' N	15°40' W	835-858	7.92	<i>Lophelia pertusa</i>	9.91
POS-265-499	Propeller Mound, UK	52°09' N	12°46' W	729	9.6	<i>Lophelia pertusa</i>	9.93
VH-97-351	Galicia Bank, Spain	42°30' N	11°30' W	775-880	11.2	<i>Madrepora oculata</i>	10.22
M701-Dive111	Gondola Slide, Italy	41°44' N	17°03' E	674-710	13.55	<i>Lophelia pertusa</i>	9.76
M70-1-721-red	Santa Maria di Leuca, Italy	39°34' N	18°27' E	556-630	13.65	<i>Lophelia pertusa</i>	9.90
M70-1-721-white	Santa Maria di Leuca, Italy	39°34' N	18°27' E	556-630	13.65	<i>Lophelia pertusa</i>	9.84
M70-1-677	Urania Bank, Italy	36°50' N	13°09' E	440-654	13.65	<i>Lophelia pertusa</i>	10.06
GoM	Gulf of Mexico, US	29°10' N	88°01' W	434-465	9.3	<i>Lophelia pertusa</i>	10.22
N'Zeta	Offshore N'Zeta, Angola	7°17' S	12°03' E	370	8.72	<i>Lophelia pertusa</i>	9.96
<i>Culturing experiments</i>							
Clado-15					15.0	<i>Cladocora caespitosa</i>	9.60
Clado-18					18.0	<i>Cladocora caespitosa</i>	9.41
Clado-21					21.0	<i>Cladocora caespitosa</i>	9.14
Clado-23					23.0	<i>Cladocora caespitosa</i>	9.21

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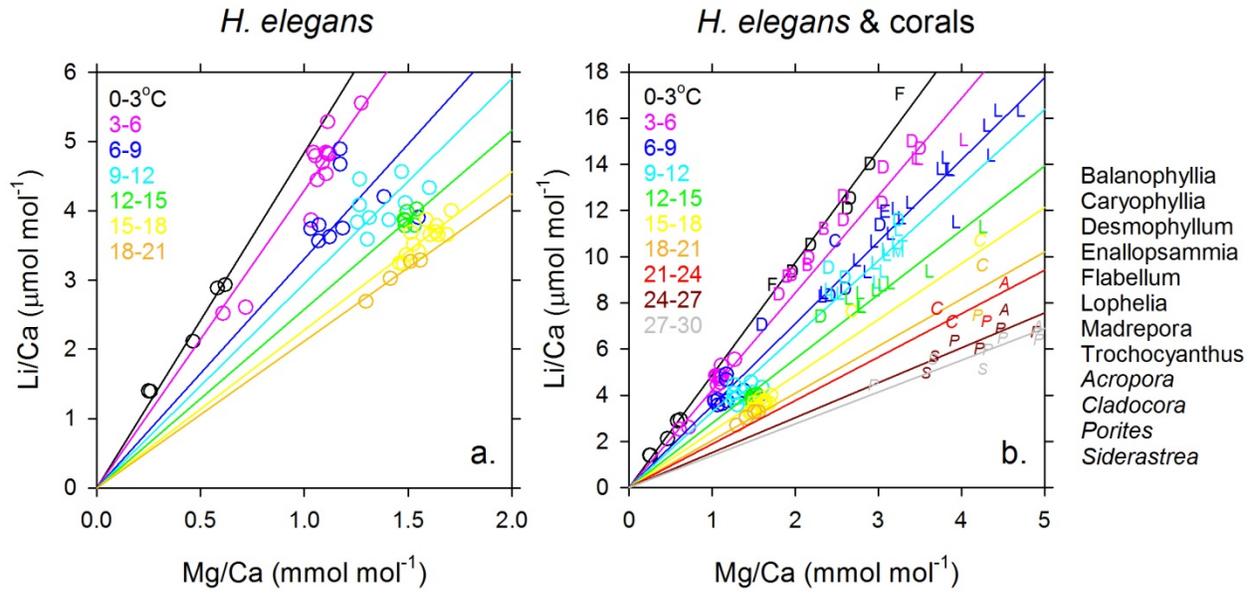
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697 **Figure 1.** Li/Ca (a.), Mg/Ca (b.), and Li/Mg (c.) versus estimated growth temperature for the  
 698 aragonitic benthic foraminifer *H. elegans* (red) and various aragonitic coral taxa (blue). Fits  
 699 corresponding to Equations 1-3 are shown in panel (c.) in red, blue, and black, respectively.

700 References for published data are given in the text.

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704 **Figure 2.** Li/Ca versus Mg/Ca in *H. elegans* (a.) and *H. elegans* combined with corals (b.). Data

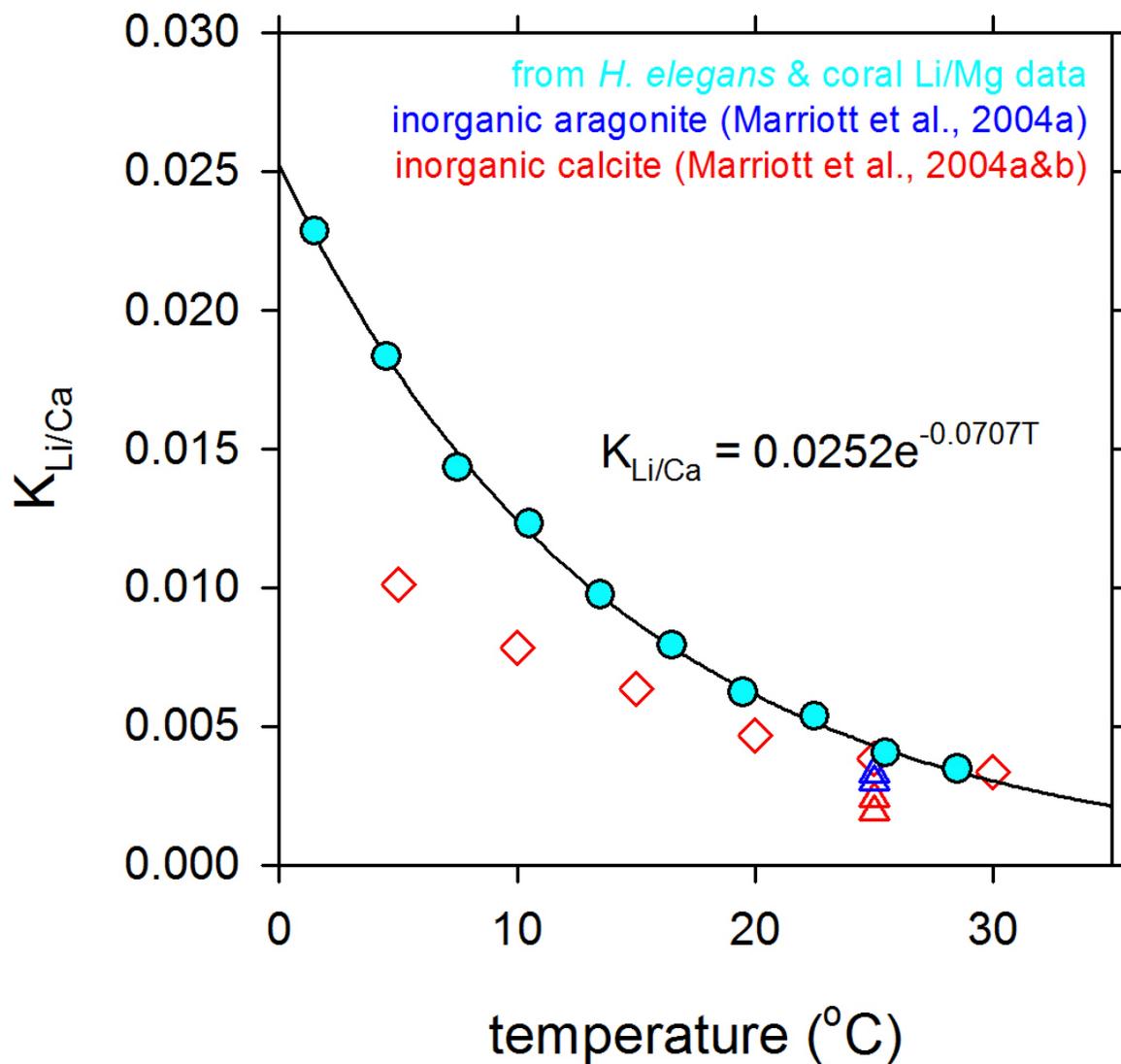
705 are color-coded by growth temperature according to the legend, and lines are best fits for each

706 temperature bin, forced through the origin. Coral taxa are indicated using the first letter of the

707 genus, with deep sea corals in roman type and shallow hermatypic corals in italics. References

708 for published data are given in the text.

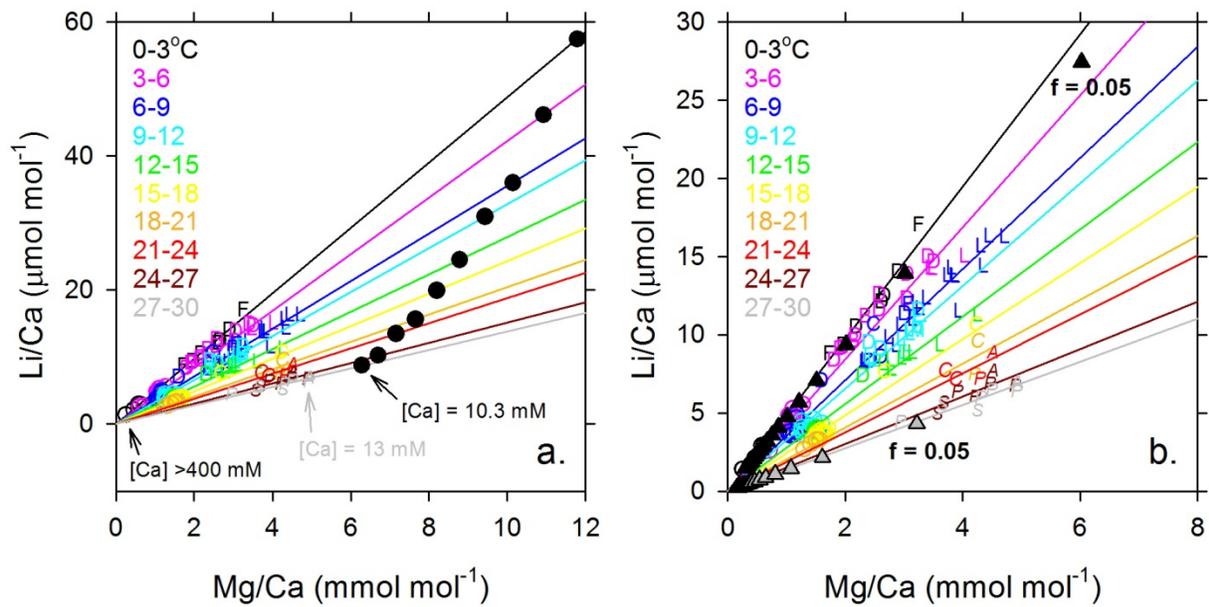
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712 **Figure 3.** Predicted Li partition coefficients into aragonite as a function of temperature (cyan),  
 713 based on the *H. elegans* and coral Li/Mg regressions shown in Fig. 2b combined with the  
 714 temperature sensitivity of abiotic aragonite Mg partition coefficients from Gaetani and Cohen  
 715 (2006). Equation 4 is plotted in black. Data from abiotic aragonite (blue) and calcite (red) are  
 716 shown for comparison (Marriott et al., 2004a, b).

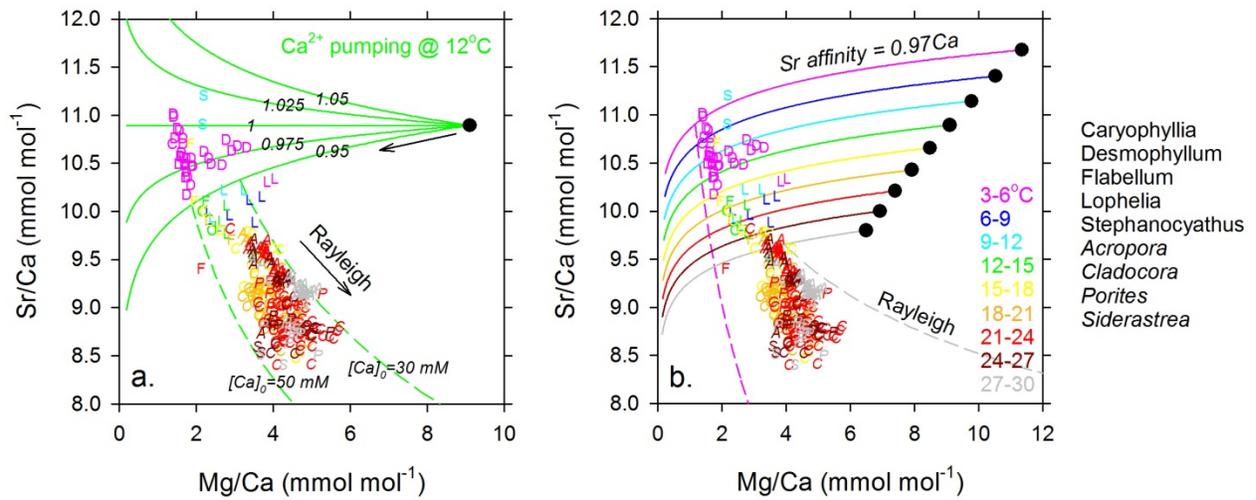


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719 **Figure 4. (a.)** *H. elegans* and coral Li/Ca versus Mg/Ca as in Fig. 2b, but now including the  
 720 composition of aragonite predicted if precipitated from unmodified seawater (black circles,  
 721 plotted at the central temperature of each bin), based on the partition coefficients from Gaetani  
 722 and Cohen (2006) and Fig. 3. The biogenic data may be explained by elevated Ca<sup>2+</sup> within the  
 723 calcifying fluid, and two extremes of the observations are indicated ([Ca<sup>2+</sup>] = 13 and >400 mM).  
 724 **(b.)** As in (a.) but showing the effects of Rayleigh fractionation acting on a closed calcification  
 725 pool (Elderfield et al., 1996) with an arbitrary initial [Ca<sup>2+</sup>] of 400 mM. Triangles show the  
 726 evolution of aragonite away from the origin as f (fraction of initial Ca<sup>2+</sup> remaining) declines in  
 727 0.05 increments, at 1.5°C (black) and 28.5°C (gray).

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731 **Figure 5.** Coral Sr/Ca versus Mg/Ca, with taxa and growth temperatures coded as in Fig. 2b,

732 compared to aragonite precipitated from unmodified seawater at various temperatures (black

733 circles) based on the partition coefficients from Gaetani and Cohen (2006). (a.) Solid lines show

734 the impact of Ca<sup>2+</sup> pumping, moving away from the seawater value at 12°C, assuming five

735 different hypothetical values for the pump's Sr:Ca transport stoichiometry. Rayleigh trajectories

736 are also shown (dashed lines) for two arbitrary initial Ca<sup>2+</sup> concentrations (30 and 50 mM). (b.)

737 As in panel (a.) but showing pump trajectories over a range of temperatures with a Sr:Ca

738 transport stoichiometry of 0.97 (solid lines, plotted at the lowest temperature of each bin).

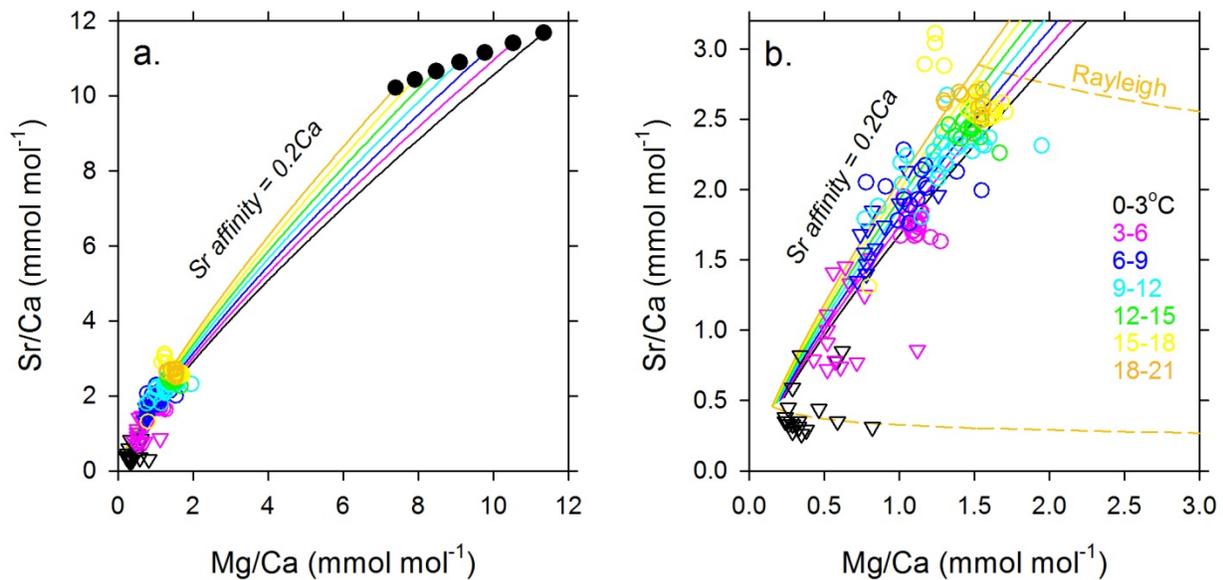
739 Rayleigh trajectories are plotted at 3°C and 27°C for two arbitrary initial Ca<sup>2+</sup> concentrations

740 (dashed lines). Coral taxa are indicated using the first letter of the genus, with deep sea corals in

741 roman type and shallow hermatypic corals in italics. References for published data are given in

742 the text.

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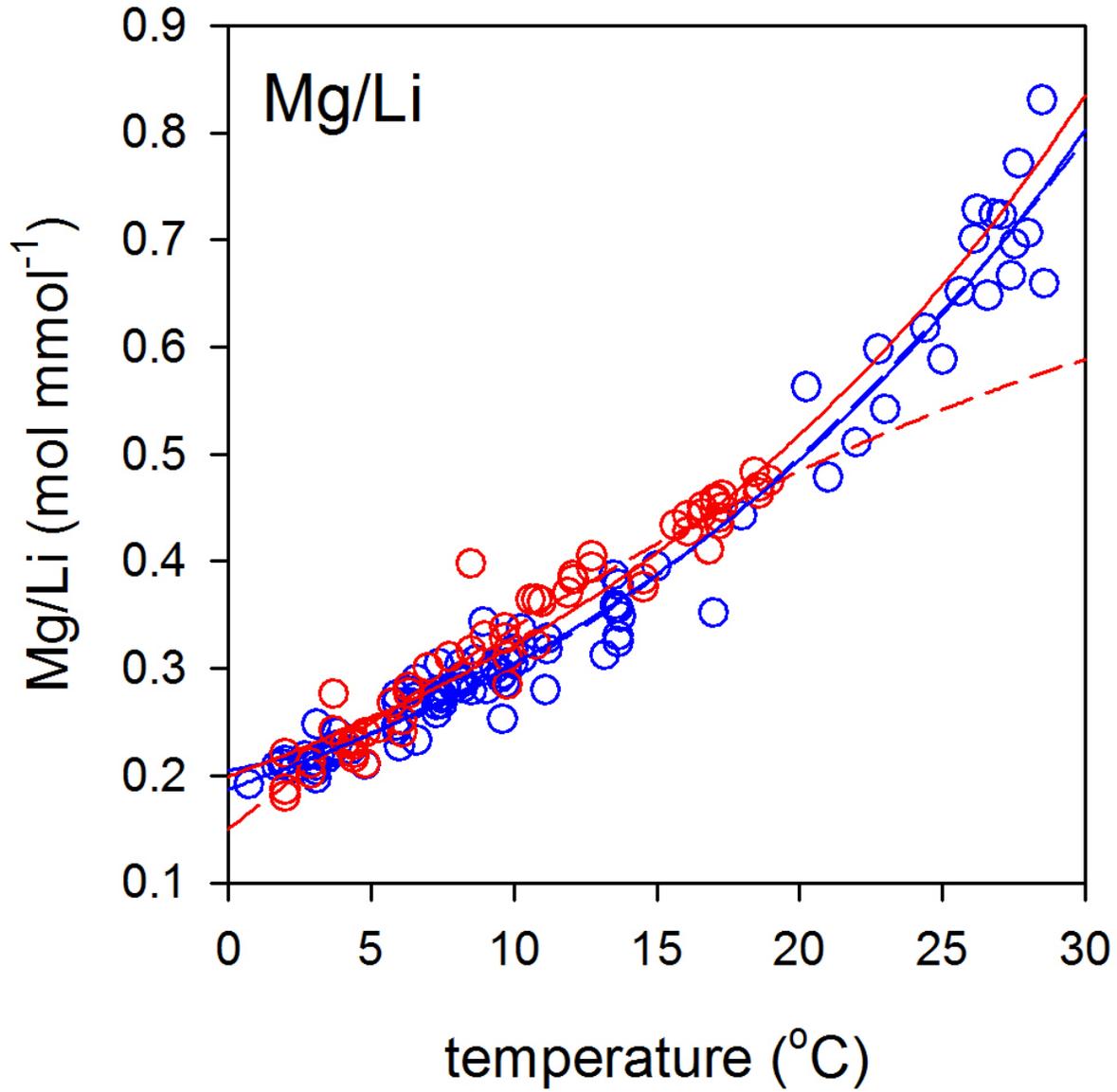


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746 **Figure 6.** *H. elegans* Sr/Ca versus Mg/Ca, color coded by temperature as in previous figures,  
 747 with samples from  $<15 \mu\text{mol kg}^{-1}$  bottom water  $\Delta\text{CO}_3^{2-}$  plotted as inverted triangles. (a.) Lines  
 748 show  $\text{Ca}^{2+}$  pumping trajectories away from aragonite precipitated from seawater (black circles)  
 749 assuming a Sr:Ca transport stoichiometry of 0.2 (plotted at the highest temperature of each bin).  
 750 (b.) As in panel (a.) but including Rayleigh trajectories at  $21^\circ\text{C}$  for two arbitrary initial  $\text{Ca}^{2+}$   
 751 concentrations (dashed lines). References for published data are given in the text.

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755 **Figure 7.** Mg/Li versus estimated growth temperature for the *H. elegans* (red) and various  
 756 aragonitic coral taxa (blue). The data are fit with exponentials (solid lines) and second-order  
 757 polynomials (dashed lines), including *H. elegans* Equation (5).