

1 Factors affecting B/Ca ratios in synthetic aragonite

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22 **Abstract**

23 Measurements of B/Ca ratios in marine carbonates have been suggested to record
24 seawater carbonate chemistry, however experimental calibration of such proxies based on
25 inorganic partitioning remains limited. Here we conducted a series of synthetic aragonite
26 precipitation experiments to evaluate the factors influencing the partitioning of B/Ca
27 between aragonite and seawater. Our results indicate that the B/Ca ratio of synthetic
28 aragonites depends primarily on the relative concentrations of borate and carbonate ions
29 in the solution from which the aragonite precipitates; not on bicarbonate concentration as
30 has been previously suggested. The influence of temperature was not significant over the
31 range investigated (20 – 40 °C), however, partitioning may be influenced by saturation
32 state (and/or growth rate). Based on our experimental results, we suggest that aragonite
33 B/Ca ratios can be utilized as a proxy of $[\text{CO}_3^{2-}]$. Boron isotopic composition ($\delta^{11}\text{B}$) is an
34 established pH proxy, thus B/Ca and $\delta^{11}\text{B}$ together allow the full carbonate chemistry of
35 the solution from which the aragonite precipitated to be calculated. To the extent that
36 aragonite precipitation by marine organisms is affected by seawater chemistry, B/Ca may
37 also prove useful in reconstructing seawater chemistry. A simplified boron purification
38 protocol based on amberlite resin and the organic buffer TRIS is also described.

39

40 **1. Introduction**

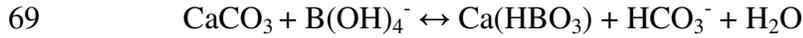
41 Boron concentrations and boron isotopic compositions in marine carbonates are
42 potential archives of past seawater pH and carbonate chemistry (e.g. Sanyal et al., 1996;
43 Pelejero et al., 2005; Pearson and Palmer, 1999; Douville et al., 2010; Rae et al., 2011;
44 Henehan et al., 2013; Penman et al., 2013). In seawater, boron is typically present in

45 two forms, boric acid ($B(OH)_3$) and borate ($B(OH)_4^-$), the relative abundances of which
46 depend largely on pH (e.g. Culberson, 1968; Dickson, 1990; Klochko et al., 2006). The
47 $B(OH)_4^-$ ion is thought to be the primary form of boron incorporated into calcium
48 carbonate (e.g. Sen et al., 1994; Hemming et al., 1995), thus offering the potential to use
49 B/Ca ratios to estimate pH and/or carbonate chemistry (e.g. Yu et al., 2007). However,
50 there is uncertainty as to how boron incorporation may depend upon concentrations of
51 different dissolved inorganic carbon (DIC) species (e.g. Hemming et al., 1995; Uchikawa
52 et al., 2015). In addition, there are suggestions that $B(OH)_3$ may also be incorporated,
53 especially in calcite (e.g. Xiao et al., 2008; Klochko et al., 2009; Rollion-Bard et al.,
54 2011; Mavromatis et al., 2015; Uchikawa et al., 2015), thus potentially complicating the
55 interpretation of B/Ca ratios.

56 Various relationships have been used to explore the range of possible factors
57 controlling B incorporation in both synthetic (e.g. Mavromatis et al., 2015; Uchikawa et
58 al., 2015) and biogenic carbonates (e.g. Ni et al., 2007; Yu et al., 2007; Yu and
59 Elderfield, 2007; Foster 2008; Douville et al., 2010; Allen et al., 2011; Rae et al., 2011;
60 Tripathi et al., 2011; Allen et al., 2012; Allison et al., 2014; Babila et al., 2014; Henehan et
61 al., 2015). Here we consider several of the relationships proposed by previous studies:
62 $B(OH)_4^-/CO_3^{2-}$, $B(OH)_4^-/HCO_3^-$, $B(OH)_4^-/(CO_3^{2-} + HCO_3^-)$, B/HCO_3^- , $B/(CO_3^{2-} + HCO_3^-)$,
63 $B(OH)_4^-/\Delta CO_3^{2-}$ (where ΔCO_3^{2-} is the difference between the actual $[CO_3^{2-}]$ and the
64 $[CO_3^{2-}]$ at which the solution would be saturated with respect to aragonite, $\Omega_{Arag} = 1$). In
65 addition to various empirical relationships, we also consider potential balanced exchange
66 reactions with the following expressions for the distribution coefficient:

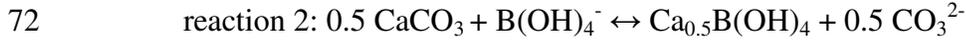
67

68 reaction 1 (Hemming and Hanson 1992):



70
$$K_D = \frac{[\text{HBO}_3^{2-} / \text{CO}_3^{2-}]_{\text{CaCO}_3}}{[\text{B(OH)}_4^- / \text{HCO}_3^-]_{\text{solution}}} \quad \text{eq. 1}$$

71



73
$$K_D = \frac{[\text{B(OH)}_4^- / [\text{CO}_3^{2-}]^{0.5}]_{\text{CaCO}_3}}{[\text{B(OH)}_4^- / [\text{CO}_3^{2-}]^{0.5}]_{\text{solution}}} \quad \text{eq. 2}$$

74



76
$$K_D = \frac{[[\text{BO}_3^{3-}]^2 / [\text{CO}_3^{2-}]^3]_{\text{CaCO}_3}}{[[\text{B(OH)}_4^-]^2 / [\text{CO}_2][\text{HCO}_3^-]^2]_{\text{solution}}} \quad \text{eq. 3}$$

77 Studies of naturally formed samples do provide some insights into the potential
78 controls on boron incorporation (Hemming and Hanson 1992; Sanyal et al., 1996; Wara
79 et al., 2003; Ni et al., 2007; Yu et al., 2007; Yu and Elderfield, 2007; Foster et al., 2008;
80 Rollion-Bard et al., 2011; Allison et al., 2014; Kaczmarek et al., 2015). However, such
81 studies cannot establish how B/Ca is controlled by environmental variables due to
82 inevitable uncertainty as to the conditions during carbonate deposition. This is
83 particularly the case for calcifying organisms that modify the conditions at the site of
84 calcification substantially from the conditions present in the surrounding seawater (e.g.
85 Al-Horani et al., 2003; McCulloch et al., 2012; De Nooijer et al., 2014). Since the
86 chemistry at the site of calcification is generally unknown, most studies have focused on
87 the relationship between B/Ca and seawater chemistry. Thus in studies of biologically

88 formed calcium carbonate, there is uncertainty as to whether B/Ca changes in direct
89 response to environmental conditions, or if it reflects physiological changes in the
90 organism.

91 Laboratory studies on the incorporation of B into calcium carbonate remain
92 limited, and few potentially controlling factors (e.g. temperature, carbonate chemistry,
93 growth rate etc) have been tested (Kitano et al., 1978; Sen et al. 1994; Hemming et al.,
94 1995; Hobbs and Reardon, 1999; Sanyal et al., 2000; Xiao et al., 2008; He et al., 2013;
95 Gabitov et al., 2014; Mavromatis et al., 2015; Uchikawa et al., 2015). Critically only one
96 study has characterized the carbonate chemistry during aragonite precipitation
97 (Mavromatis et al., 2015).

98 We conducted a series of experiments to explore how carbonate chemistry,
99 organic additives, temperature, and boron concentration may influence B/Ca ratios in
100 aragonite formed from seawater-like solutions. Manipulation of pH, DIC, and Ca^{2+} are
101 among the mechanisms potentially driving biogenic calcification, thus our experiments
102 focused on manipulating these variables. In addition to these inorganic variables, there
103 are also a wide range of organic molecules produced by calcifying organisms which may
104 influence calcification (e.g. Mass et al., 2013). We chose to test one specific mechanism
105 by which organic molecules could influence B/Ca, that of buffering pH. In seawater, the
106 two dominant pH buffers are DIC and B species, thus variations in pH (such as might
107 occur adjacent to a growing aragonite crystal) would directly affect DIC and B
108 speciation. By adding an additional buffering agent (such as 2-Amino-2-hydroxymethyl-
109 propane-1,3-diol (TRIS) or 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid
110 (HEPES)), pH could in theory be more stable adjacent to the growing crystal which could

111 alter the relationship between B/Ca and bulk solution chemistry. In addition to biological
112 processes affecting elemental ratios, there is also a potential for some of the compounds
113 used to study crystal growth to influence elemental incorporation. Calcein is among the
114 molecules commonly used to mark growing crystals in living organisms (e.g. Venn et al.,
115 2013), and the influence of calcein on the incorporation of a number of elements has been
116 tested (Dissard et al., 2009), though no information is thus-far available as the effect of
117 calcein on B/Ca, thus it was tested here.

118

119 **2. Methods**

120 *2.1. Aragonite precipitation*

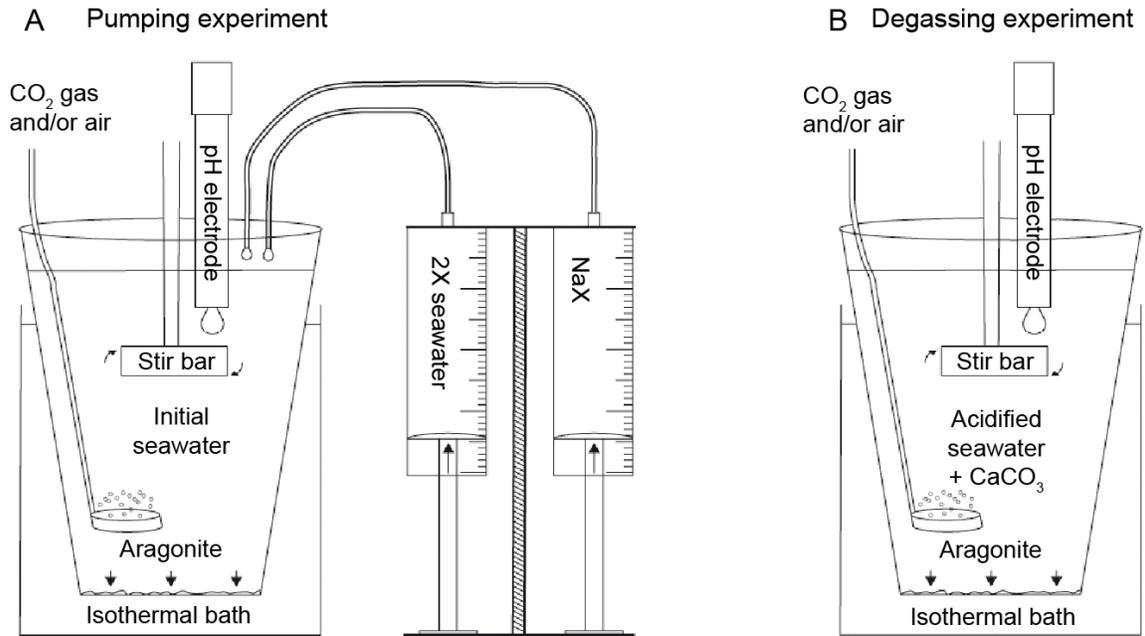
121 Aragonite was precipitated from seawater (0.2 μm filtered to remove living
122 organisms) using several different approaches adapted from existing methods (Kinsman
123 and Holland 1969; Kitano et al., 1978; Gaetani and Cohen 2006; Holcomb et al., 2009;
124 Gabitov et al., 2011; Wang et al., 2013). The range of experimental protocols used was
125 intended to precipitate aragonite under a wide range of solution chemistries in order to
126 encompass the likely compositional range of biologically mediated solutions and thus
127 more fully evaluate the factors that affect boron incorporation during bio-calcification.
128 Detailed descriptions of the protocols used for each of the 65 experiments are provided in
129 the supplementary materials (see section S1 and Table S1 for more details). Briefly, all
130 experiments were carried out in plastic containers held within constant temperature water
131 baths. Two general types of experiments were conducted: degassing (Figure 1B) and
132 pumping (Figure 1A) experiments. Degassing experiments were carried out by
133 dissolving CaCO_3 in seawater at ~ 1 atm pCO_2 with the addition of MgCl_2 , SrCO_3 (to

134 maintain seawater like Mg/Ca and Sr/Ca ratios) and various additives (TRIS, HEPES,
135 calcein, boron, CaCl₂, etc. depending upon the experiment). As CO₂ degassed in these
136 experiments, Ω_{Arag} increased until aragonite began to precipitate. Degassing experiments
137 were bubbled at controlled rates with air or air/CO₂ mixes during precipitation to stabilize
138 pH. Pumping experiments were conducted by adding seawater containing CaCO₃
139 (dissolved by bubbling with CO₂) or concentrated seawater (evaporated to achieve 2x
140 normal salinity = 2xsw) and a NaHCO₃ or Na₂CO₃ or NaOH or mixture there-of solution
141 (here after referred to as NaX solution) to seawater using a syringe pump. The
142 simultaneous injection of 2xsw and NaX solutions allowed carbonate chemistry to be
143 modified while maintaining salinity ~constant. Pumping rates were varied over the
144 course of each experiment to stabilize pH during precipitation. Some of these
145 experiments were additionally bubbled with air or air/CO₂ mixtures, and some contained
146 additional additives. All experiments were stirred continuously.

147 The evolution of solution chemistry during precipitation differed among
148 experiments. In general, in pumping experiments an initial pH and alkalinity was
149 established, precipitation then removed CO₃²⁻ thus reducing DIC (or equivalently total
150 inorganic carbon) and alkalinity, while pumping of the NaX solution added DIC and
151 alkalinity, thus allowing carbonate chemistry to be maintained nearly constant during
152 precipitation. In degassing experiments, though pH was maintained nearly constant,
153 DIC, and alkalinity both declined during precipitation due to the precipitate removing
154 DIC and alkalinity and bubbling removing DIC. To illustrate the relationships between
155 different solution chemistry parameters potentially relevant for B/Ca, Figure 2 shows

156 various chemical parameters plotted versus pH_T for our experiments, as well as the values
157 expected for seawater at different DIC concentrations.

158



159

160 Figure 1. Schematic representation of the experimental setup used for pumping (A) and
161 degassing (B) experiments.

162

163 Over the course of each experiment, samples were taken for pH, alkalinity, and
164 solution chemistry measurements. Samples for alkalinity and solution chemistry were
165 filtered (Millex-HV syringe filter, 0.45 μm PVDF membrane) at the time of collection to
166 remove any aragonite particles potentially present. All seawater samples used for
167 elemental composition measurements were acidified with concentrated HNO_3 to dissolve
168 any material that precipitated post-collection. Details of all measurements, associated
169 calculations, and measured values are provided in the supplementary materials (sections
170 S2, S3, and .xls file).

171

172 *2.2. Precipitate Characterization*

173 *2.2.1. Mineralogy*

174 The mineralogy of most experiments was characterized by XRD (see supplemental
175 materials section S4) and/or Raman spectroscopy (DeCarlo et al., 2015; and supplemental
176 materials S4). Some experiments contained phases other than aragonite and were
177 generally excluded from analysis of B/Ca, with the exception of one sample (10h) which
178 had a faint XRD peak near $2\text{-theta} = 30$, suggesting possible contamination with a calcitic
179 phase, but neither the Raman spectra nor the elemental composition indicated a non-
180 aragonitic phase, thus any contamination was assumed to be sufficiently low as to not
181 compromise the use of the sample.

182

183 *2.2.2. Composition*

184 The elemental composition of all precipitates was measured using Q-ICPMS
185 (supplemental materials S3.1) to verify that the elemental composition was similar to
186 other marine aragonite samples while simultaneously measuring the B/Ca ratio. The
187 coral standard JCp-1 (B/Ca = 0.4596 mmol mol⁻¹, Hathorne et al. (2013)) was used to
188 standardize all measurements, and the validity of this approach for measuring B/Ca was
189 verified using independent measurements of purified boron extracts measured via MC-
190 ICPMS (supplemental materials S3.2.1). Data on the incorporation of Sr/Ca and U/Ca
191 into these precipitates is published elsewhere (DeCarlo et al., 2015).

192

193 *2.3. Solution Characterization*

194 Since natural seawater was used for all experiments, and Ca and B are generally
195 considered uniformly distributed throughout the oceans in proportion to salinity,
196 concentrations were calculated based on salinity and the mass of any added B- or Ca-
197 containing solutions. For a subset of experiments the validity of this assumption was
198 verified via ICP-MS measurements. Measurements are described in the supplemental
199 materials including the description of new simplified chemistry for the purification of
200 boron based on amberlite IRA 743 resin and the organic buffer TRIS (supplemental
201 material S3.3).

202

203 *2.4. Calculations*

204 Carbonate chemistry was calculated using the measured alkalinity, pH, and temperature.
205 When pH measurements were carried out at a temperature different from that of the
206 experimental temperature, the pH at the experimental temperature was calculated using

207 CO2Sys (van Heuven et al., 2009). Salinities were interpolated based on initial and final
208 salinities and estimated evaporation rates. Calcium and boron concentrations in the fluid
209 were calculated based on salinity, estimated amount of precipitate deposited, and any
210 calcium or boron added to the experiment. These experiments were undertaken in
211 conjunction with those reported by DeCarlo et al. (2015), further details are given in the
212 supplemental materials (S2), as are alternative calculations using constants from Hain et
213 al. (2015) (S6).

214 Since aragonite is primarily CaCO_3 , and thus $\text{Ca} \approx \text{CO}_3$, B/Ca can be substituted
215 for B/ CO_3 when calculating distribution coefficients, so though equations 1-3 are
216 expressed relative to CO_3 in the solid, B/Ca will be used for calculations.

217

218 *2.5. Average solution chemistry and partitioning*

219 We evaluated the factors controlling B incorporation into aragonite by comparing the
220 bulk/mean aragonite B/Ca ratio to the average solution composition during precipitation
221 of each of 58 experiments conducted in 2013 (of 65 total experiments). The solution
222 chemistry and bulk precipitation rates varied over the course of each experiment. To
223 estimate the average solution chemistry during the time that aragonite precipitated,
224 chemistry parameters were weighted by the amount of precipitate formed over the given
225 time interval (estimated from the difference between measured and expected alkalinity).
226 The distribution coefficient relationship that best described the data was then used to
227 calculate distribution coefficients for each individual experiment such that the calculated
228 B/Ca ratio for the final precipitate in each experiment matched the measured ratio. Data
229 from experiments run in 2011 (denoted by a '/11' in the experiment name in the

230 supplemental tables) were not included in these comparisons as carbonate chemistry was
231 generally less stable; experiments from 2011 were used only for assessing the effects of
232 calcein.

233

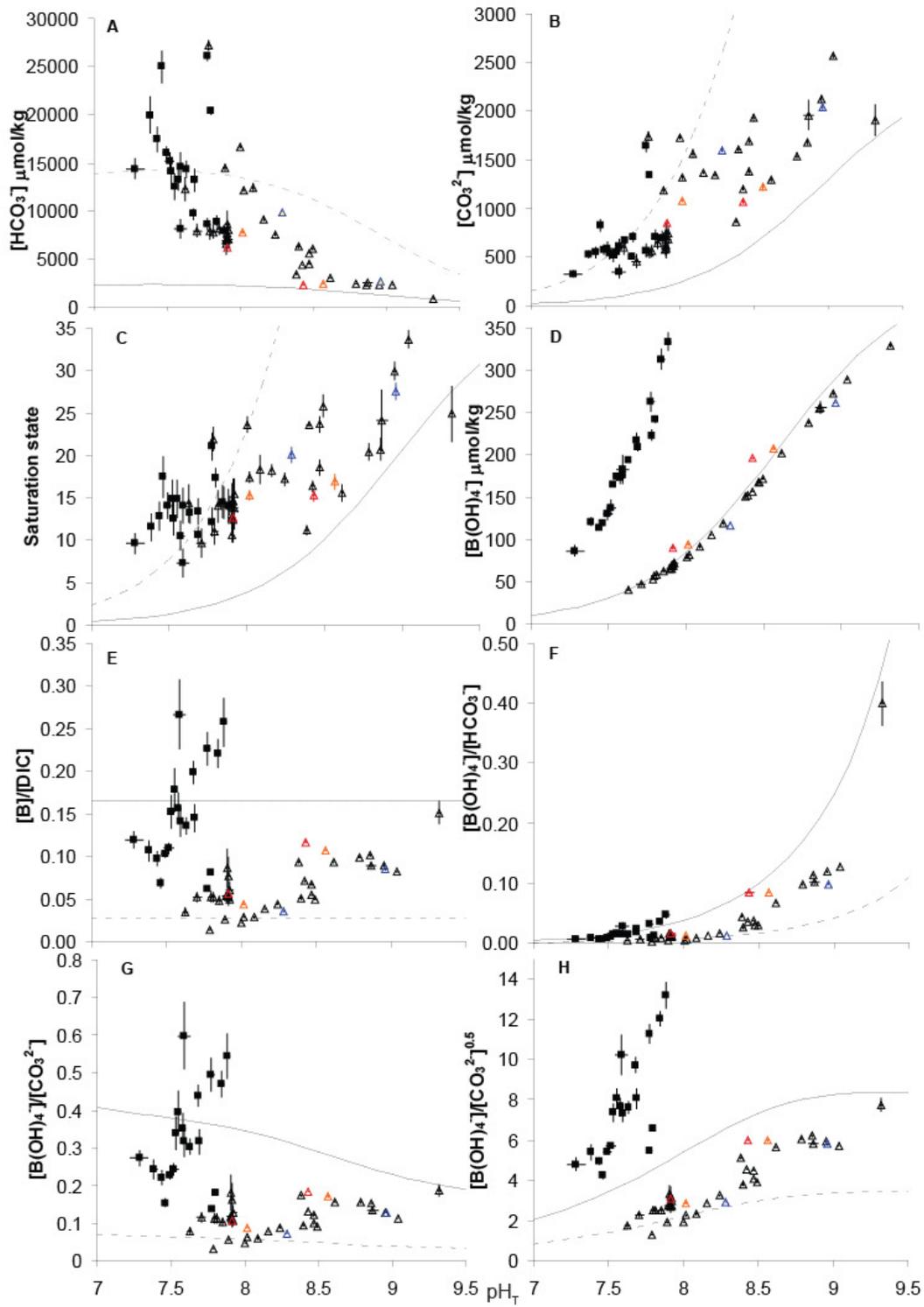
234 **3. Results**

235 Aragonite was precipitated over a wide range of pH_T (7.3 to 9.3, where pH_T is pH
236 measured on the total scale), temperature (~20 °C to 40 °C), and carbonate chemistry
237 conditions (Fig. 2). Within any given experiment, the precipitate formed under a range of
238 solution chemistry conditions, but the range within an experiment was generally small
239 relative to the differences among experiments (Fig. 2). For example, the within-
240 experiment pH variation was typically less than 0.1 pH units, whereas among
241 experiments pH differences of more than 2 pH units were achieved. Likewise, within the
242 course of an experiment, the relative standard deviation (RSD) of $[\text{B}(\text{OH})_4^-]/[\text{CO}_3^{2-}]^{0.5}$
243 was less than 15% (typically less than 5%), while different experiments differed by more
244 than an order of magnitude (Figure 2H, Table S2).

245 The B/Ca ratio in the precipitate showed no significant ($p > 0.05$) correlation with pH_T or
246 any single carbonate chemistry parameter. Significant ($p < 0.001$) correlations were
247 found between B/Ca and the mean solution [B] and $[\text{B}(\text{OH})_4^-]$ (Table 1). However, when
248 considering only precipitates formed under seawater boron concentrations, B/Ca does
249 correlate significantly with a number of carbonate system parameters, most notably pH
250 and parameters closely correlated with pH (e.g. DIC species and $[\text{B}(\text{OH})_4^-]$; Figure 3,
251 Table 1), with $[\text{B}(\text{OH})_4^-]$ remaining the single parameter most strongly correlated with
252 B/Ca.

253

254



255

256 Figure 2. Relationship between different solution chemistry parameters and pH_T (total
257 scale pH) Symbols are means of individual experiments; experiments without added B
258 are represented by triangles, experiments with added B are represented by squares, lines
259 show bi-direction error bars (1 standard deviation (sd)). Experiments conducted at
260 different temperatures are shown in different colors: blue ~ 20, black ~ 25, orange ~ 33,
261 and red ~ 40 °C. Most experiments were conducted at ~ 25 °C, 2 experiments were run at
262 each of the other temperatures. Lines show calculated concentrations of different DIC
263 species and borate ($\mu\text{mol}/\text{kg sw}$) as a function of seawater pH_T . Calculated values are for
264 seawater (S=35, T=25 °C) with either 2500 (solid line) or 15000 (dashed line) μmol
265 DIC/kg sw.

266 Table 1. Pearson correlation coefficients for mean solution chemistry parameters
 267 showing the most significant correlations with the B/Ca ratio of the precipitate, as well as
 268 various proposed ratios suggested to be linked to B/Ca regardless of significance.
 269 Correlation coefficients are given for the data set as a whole (n=58, excluding
 270 experiments run in 2011), for experiments without added B (n=39), and for pumping
 271 experiments without added B (n=28). Significant ($p < 0.05$) individual correlations are
 272 indicated by *.

Species in solution	Correlation with precipitate B/Ca		
	All experiments	Experiments with seawater [B]	Pumping experiments with seawater [B]
pH _T	0.03	0.80*	0.81*
[HCO ₃ ⁻]	-0.16	-0.80*	-0.81*
DIC	-0.18	-0.77*	-0.80*
$\frac{[\text{B}(\text{OH})_4^-]^2}{[\text{CO}_2][\text{HCO}_3^-]^2}$	0.19	0.46*	0.47*
$\frac{[\text{B}(\text{OH})_4^-]}{[\text{HCO}_3^-]}$	0.33*	0.77*	0.76*
$\frac{[\text{B}(\text{OH})_4^-]}{([\text{CO}_3^{2-}] + [\text{HCO}_3^-])}$	0.47*	0.90*	0.90*
[B(OH) ₃]	0.55*	-0.82*	-0.83*
[B]/[Ca]	0.58*	0.38*	0.23
[B]	0.62*	-0.41*	-0.35
$\frac{[\text{B}(\text{OH})_4^-]}{\Delta\text{CO}_3^{2-}}$	0.78*	0.70*	0.92*
[B(OH) ₄ ⁻]	0.79*	0.82*	0.83*
$\frac{[\text{B}]}{[\text{HCO}_3^-]}$	0.81*	0.84*	0.85*
$\frac{[\text{B}(\text{OH})_4^-]}{[\text{CO}_3^{2-}]}$	0.83*	0.81*	0.93*
$\frac{[\text{B}]}{([\text{CO}_3^{2-}] + [\text{HCO}_3^-])}$	0.89*	0.93*	0.97*
[B]/[DIC]	0.89*	0.94*	0.97*
$[\text{B}(\text{OH})_4^-] * [\text{Ca}^{2+}]$	0.92*	0.82*	0.81*
$\frac{[\text{B}(\text{OH})_4^-]}{[\text{CO}_3^{2-}]^{0.5}}$	0.95*	0.94*	0.95*

273

274

275 Since boron is thought to compete with DIC species for incorporation into aragonite (e.g.

276 Hemming et al., 1992), correlations between precipitate B/Ca and various solution

277 boron/DIC relationships were explored (Table 1). In the full data-set, B/Ca and mean
278 $[B(OH)_4^-]/[HCO_3^-]$ were not strongly correlated (Fig. 3b, based on equation 1), nor were
279 the residuals of a $[B(OH)_4^-]$ vs B/Ca regression and $[HCO_3^-]$. Nor was there a significant
280 correlation between B/Ca and average $[B(OH)_4^-]^2/[CO_2][HCO_3^-]^2$ (equation 3). B/Ca in
281 the precipitate was most strongly correlated with the mean $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ (equation
282 2), $[B]/[DIC]$ or $[B]/([CO_3^{2-}] + [HCO_3^-])$ and $[B(OH)_4^-]*[Ca^{2+}]$ (Table 1, Fig. 3). The
283 correlations of B/Ca with $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ and $[B]/[DIC]$ or $[B]/([CO_3^{2-}] + [HCO_3^-])$
284 were important regardless of whether B was added or whether only pumping or degassing
285 experiments were considered. Conversely $[B(OH)_4^-]*[Ca^{2+}]$, though significantly
286 correlated with B/Ca, did not necessarily correlate more strongly than $[B(OH)_4^-]$ alone
287 (Table 1). When only a subset of the experiments is considered, some of the other
288 potential relationships become significant (Table 1). For instance, $[B(OH)_4^-]/[CO_3^{2-}]$ is
289 highly correlated with B/Ca, especially for pumping experiments, as is $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$,
290 yet these two ratios show opposite behaviors in seawater as a function of pH (Fig.
291 2G,H). Given the range of DIC (2.8 – 29 mmol/kg sw) and [B] (0.39 – 2.1 mmol/kg sw)
292 among experiments (Table S2), DIC and [B] would be expected to have a greater
293 influence on $[B(OH)_4^-]/[CO_3^{2-}]$ and $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ than pH, thus a positive
294 correlation is expected. Similarly mean $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ and $[B]/[DIC]$ were highly
295 correlated (Pearson correlation coefficient: 0.954) as would be expected given the large
296 ranges of DIC and [B] and their consequent influence on $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ (e.g. Fig.
297 2). Since DIC is nearly equivalent to $[CO_3^{2-}] + [HCO_3^-]$, no separate treatment will be
298 given of the $[B]/([CO_3^{2-}] + [HCO_3^-])$ relationship. Linear least squares regression
299 (excluding one outlier, experiment 1c) gave the following fits:

300

301 $B/Ca \text{ (mmol/mol)} = .0604 (\pm 0.0022) [B(OH)_4^-]/[CO_3^{2-}]^{0.5} + 0.0411 (\pm 0.012)$ eq. 4

302

303 $B/Ca \text{ (mmol/mol)} = 2.88 (\pm 0.13) [B]/[DIC] + 0.085 (\pm 0.014)$ eq. 5

304

305 where $[B(OH)_4^-]$, $[CO_3^{2-}]$, $[B]$, and $[DIC]$ are in units of $\mu\text{mol kg sw}^{-1}$, values in
306 parentheses are 1 standard error, all parameter estimates were significant ($p \leq 0.001$,
307 $R^2 = 0.93$ for eq. 4, $R^2 = 0.89$ for eq. 5).

308 Although our data provide no means of assessing whether B/Ca in the aragonite
309 precipitate depends upon solution $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ or $[B]/[DIC]$, the relationship
310 based on borate and carbonate was chosen for further investigation as CO_3^{2-} was
311 considered to be more relevant for precipitation than total DIC (see supplemental section
312 S6 for calculations based on DIC as well as Ca^{2+}).

313 Within any given experiment, the precipitate formed under a range of solution chemistry
314 conditions. However, the range within an experiment was generally small relative to the
315 differences among experiments. Thus K_D was assumed to be constant for a given
316 experiment allowing K_D values to be calculated for each individual experiment i :

317
$$\frac{B_i}{Ca_i} = \frac{B_i}{(CO_3)_i^{0.5}} = K_{D_i} \times \sum_{j=1}^{j=n} \frac{[B(OH)_4^-]_{i,j} \times w_{i,j}}{[CO_3^{2-}]_{i,j}^{0.5}}$$

318 Where B/Ca is measured and is in mmol/mol, $[B(OH)_4^-]$ and $[CO_3^{2-}]$ are in units of μmol
319 kg sw^{-1} , w is the fraction of total aragonite formed in time interval j as estimated from the
320 difference in expected and measured alkalinity, i signifies an individual experiment, and j
321 is one of n measurements taken during the course of aragonite precipitation in experiment

322 *i.* Aragonite is assumed to be pure CaCO₃, thus Ca = CO₃ with activities = 1, so the
323 exponent can be dropped for the solid phase. Calculated K_D values ranged from 0.042-
324 0.103, with an average of 0.071 +/- 0.011 sd. K_D values were correlated with a number
325 of solution chemistry parameters (Fig. S4), but regressions with [B] and either [CO₃²⁻] or
326 saturation state with respect to aragonite (Ω) explained much of the variance:

327

$$328 \quad K_D = -0.0109 (\pm 0.00157) [B] - 0.001106 (\pm 0.00021) \Omega + 0.0994 (\pm 0.00432) \quad \text{eq. 6}$$

329

$$330 \quad K_D = -0.01215 (\pm 0.00159) [B] - 0.0000119 (\pm 0.000002) [\text{CO}_3^{2-}] + 0.09474 (\pm 0.00323)$$

331 eq. 7

332 where [B] is in units of mmol kg sw⁻¹, and [CO₃²⁻] is in units of μmol kg sw⁻¹, with

333 R²=0.49, p<0.001 and R²=0.53, p<0.001 for equation 6 and 7 respectively. Note that

334 Ω and [CO₃²⁻] were highly correlated (Pearson correlation coefficient: 0.94).

335 Using eqs. 6-7, the B/Ca ratio for each precipitate was predicted based on each

336 measurement time-point. The differences between the measured and predicted B/Ca

337 ratios showed no significant correlation with any solution chemistry parameter (see

338 supplemental .xls file), nor was there any significant effect of temperature, calcein, nor of

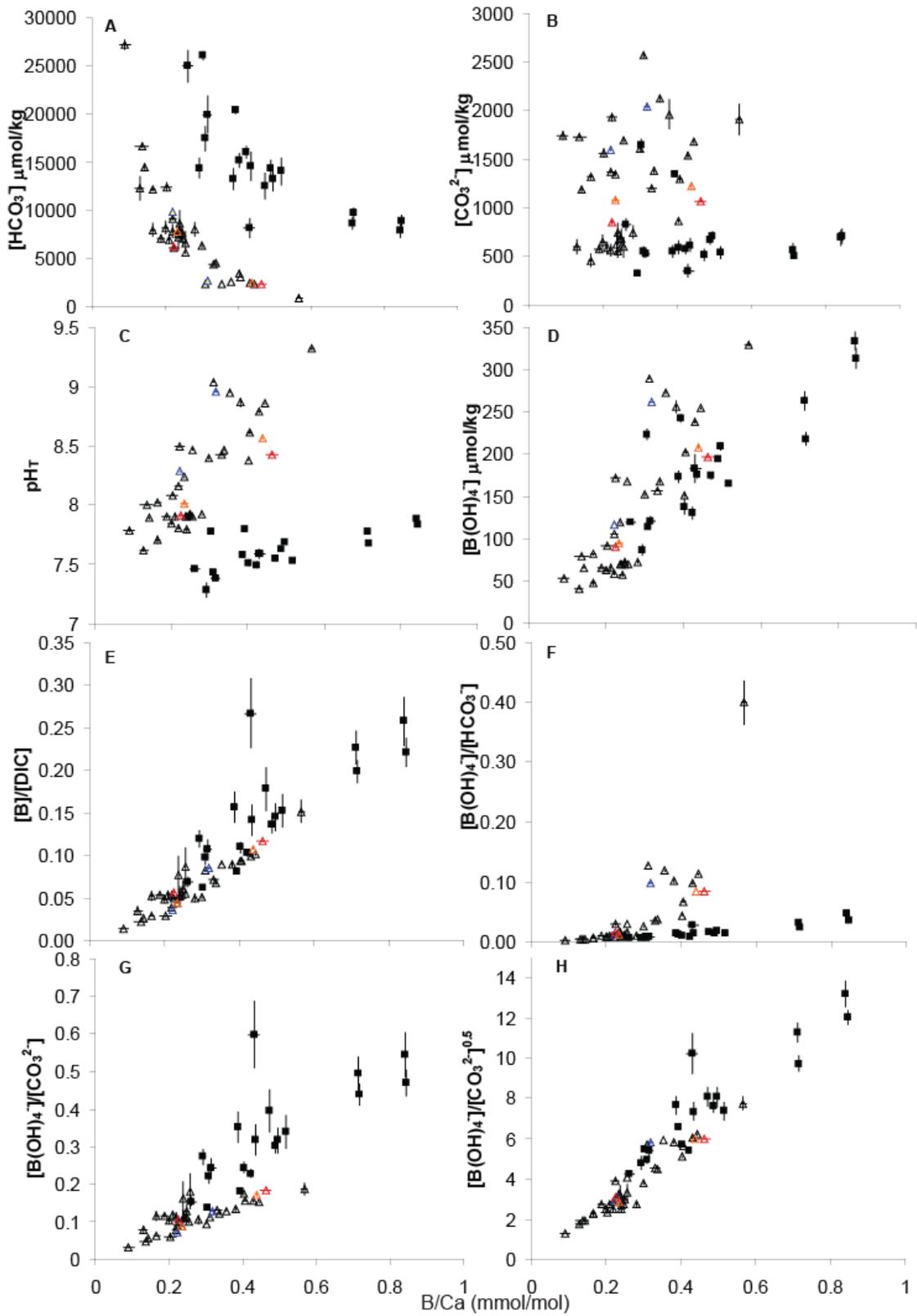
339 organic buffering compounds (though precipitates formed in the presence of HEPES

340 tended to have B/Ca ratios higher than predicted, while those formed in the presence of

341 TRIS tended to be lower). Differences between measured and predicted (for both

342 equations 6 and 7) B/Ca ratios were typically less than 0.03 mmol/mol or 8% relative

343 difference.



346 Figure 3. Relationship between B/Ca (mmol/mol) in aragonite and various solution
347 chemistry parameters. Units for all species in solution are $\mu\text{mol/kg sw}$. Symbols are as
348 described for figure 2.

349 **4. Discussion**

350 How boron is incorporated into aragonite remains uncertain. Many relationships (e.g.
351 Eqs. 1-3) have been proposed to explain how B/Ca depends on solution chemistry. The
352 wide range of solution chemistries achieved in our experiments allows us to evaluate
353 many of the proposed relationships.

354 In contrast to previous work (Hemming and Hanson, 1992), we found no significant
355 relationship between the B/Ca ratio in aragonite and the $[B(OH)_4^-]/[HCO_3^-]$ ratio in
356 solution (Fig. 3f). Rather, our results indicate that B/Ca depends on $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$
357 (Fig. 3h), suggesting that equation 2 represents the appropriate expression for the
358 distribution coefficient. A dependence of B/Ca on $[B(OH)_4^-]$ and $[CO_3^{2-}]$ is the most
359 likely scenario, due both to data suggesting $B(OH)_4^-$ to be the primary form of B
360 incorporated (e.g. Hemming et al., 1995; Mavromatis et al., 2015), and the involvement
361 of CO_3^{2-} in the formation of $CaCO_3$ (but see Wolthers et al., 2012). For a reaction
362 involving $B(OH)_4^-$ and CO_3^{2-} , a $B(OH)_4^-$ can balance the charge of only $1/2$ a CO_3^{2-} , thus a
363 dependence on $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ would be expected, consistent with our data (Fig.
364 3D).

365 Other possibilities do, however, exist. The significant correlation between B/Ca and
366 $[B(OH)_4^-]*[Ca^{2+}]$ could suggest the involvement of $CaB(OH_4)^+$, though it could also
367 reflect the importance of $[B(OH)_4^-]$ combined with a negative correlation between $[CO_3^{2-}]$
368 and $[Ca]$ in a sub-set of experiments (discussed further in the supplement). Variations in
369 $[B]/[DIC]$ were strongly correlated with B/Ca and $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ reflecting the
370 dependence of $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ on $[B]$ and $[DIC]$ combined with the pH
371 dependencies of both B and DIC species; thus we cannot rule out the possibility of B/Ca

372 being controlled by [B]/[DIC]. For calcite, existing work points to [B]/[DIC] and growth
373 rate being the primary controls on B/Ca (Uchikawa et al., 2015). However, recalculating
374 the data of Uchikawa et al. (2015) as B/Ca / [B(OH)₄⁻]/[CO₃²⁻]^{0.5} versus growth rate gives
375 a very similar fit to that obtained with [B]/[DIC] (R²=0.86 vs 0.88), again reflecting the
376 difficulty of experimentally decoupling these parameters without simultaneously
377 changing other chemical parameters.

378

379 *4.1. Partition coefficient K_D*

380 Using our experimental data, we calculated partition coefficients (K_D) for [B(OH)₄⁻
381]/[CO₃²⁻]^{0.5} between aragonite and solution. This allows us to identify which factors
382 influence B/Ca ratios in addition to the primary control of the solution [B(OH)₄⁻]/[CO₃²⁻
383]^{0.5} ratio. The K_D appears to depend upon the boron concentration and the saturation state
384 or [CO₃²⁻] (equation 6, 7, Fig. S4). A dependence upon boron concentration is consistent
385 with previous work (Hemming et al., 1995), though our experiments likely did not cover
386 a large enough range of [B] to fully describe this dependence (discussed below). In
387 addition, we found a relationship between K_D and saturation state, which may reflect the
388 influence of growth rate because aragonite crystals precipitate faster from solutions of
389 greater supersaturation (e.g. Burton and Walter 1987). Other studies have also suggested
390 a growth rate influence on boron incorporation in calcite (Hobbs and Reardon, 1999;
391 Gabitov et al., 2014; Uchikawa et al., 2015) and aragonite (Mavromatis et al., 2015).
392 However, in contrast to the positive relationships between B/Ca and precipitation rate
393 observed previously, we found a negative, albeit weak, correlation between B/Ca and
394 precipitation rate (see supplemental .xls file for rates) or saturation state.

395 Several possibilities exist to explain the different signs of the effect of precipitation rate
396 on B/Ca between our experiments and previous studies. For studies on calcite, such
397 differences may reflect fundamental differences in how B is incorporated in calcite versus
398 aragonite (e.g. Kitano et al., 1978; Mavromatis et al., 2015), but such an explanation
399 cannot account for differences between our results and those of Mavromatis et al. (2015)
400 for aragonite. However, for experiments conducted at similar [B] to ours, B/Ca data of
401 Mavromatis et al., (2015) correlated with $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ (calculated from Table 1 of
402 Mavromatis et al., (2015)) and when expressed as $B/Ca / [B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ their K_D
403 values were consistently lower than those reported here (Table 2). The experiments of
404 Mavromatis et al. (2015) were conducted at lower saturation states than those used in our
405 study; thus such differences may reflect an effect of growth rate on B/Ca which is
406 particularly pronounced at low super-saturation states. It should also be noted that the
407 experiments of Mavromatis et al. (2015) were not conducted using seawater, so the ionic
408 composition of the fluid may influence partitioning (e.g. Kitano et al., 1978).

409

410 Alternatively, the expression used for the partition coefficient may play some role in the
411 observed correlations between B/Ca and precipitation rate. Since K_D could be fit almost
412 equally well using saturation state (eq. 6) or $[CO_3^{2-}]$ (eq. 7), any dependence of K_D on Ω
413 may reflect the dependency of Ω on $[CO_3^{2-}]$. Thus the dependence of K_D on $[CO_3^{2-}]$ may
414 not reflect a growth rate effect associated with Ω , instead it could indicate that equation 2
415 does not fully describe the exchange reaction and that the relationship between $B(OH)_4^-$
416 and $[CO_3^{2-}]$ deviates from the 1 : 0.5 ratio used. Although a few of our experiments were
417 conducted at different $[CO_3^{2-}]$ but similar Ω , and vice-versa, and thus could potentially be

418 used to determine whether $[\text{CO}_3^{2-}]$ or Ω drives partitioning, no clear pattern was
419 observed.
420 Any influence of temperature or various additives was small relative to other sources of
421 variability as no significant effects were detected, which contrasts with some studies of
422 natural samples as well as one study of synthetic aragonite which point to a temperature
423 effect (Sinclair et al., 1998; Wara et al., 2003; Yu et al., 2007; Mavromatis et al., 2015).
424 It should be noted that because temperature influences saturation state, B and DIC
425 speciation, such effects, if not corrected for, could give rise to an apparent temperature
426 dependency for B/Ca. In the case of Mavromatis et al., (2015), the K_D expression used
427 was based on [B] and not $[\text{B}(\text{OH})_4^-]$, thus changes in boron speciation with temperature
428 could account for the temperature influence; recalculating their data per equation 2
429 however shows no evidence for a temperature effect on K_D based on the same data
430 points.

431

432 *4.2. Prior K_D estimates*

433 Although the partitioning of B into aragonite has previously been investigated (Kitano et
434 al., 1978; Hemming et al., 1995; Mavromatis et al., 2015), only the study of Mavromatis
435 et al. (2015) characterized carbonate chemistry, thus making it difficult to compare our
436 results with much of the prior work. The experiments of Kitano et al. (1978) were similar
437 to our degassing experiments, but carbonate chemistry was not reported during
438 precipitation; given the range of carbonate chemistry values which can potentially be
439 generated during such an experiment we cannot satisfactorily estimate carbonate
440 chemistry for these experiments. Hemming and Hanson (1992) estimated $K_D \sim 0.012$ via

441 equation 1 (or 12 to be consistent with expressing B/Ca as mmol/mol as used elsewhere
442 in our paper) for biogenic calcium carbonate samples, which is well within the range
443 estimated in our study (Table 2). For the experiments of Hemming et al. (1995) detailed
444 carbonate chemistry measurements are lacking, however using their measured pH and
445 calculated $[Ca^{2+}]$, and our observation that precipitation typically starts near $\Omega = 20$, we
446 can make rough estimates of the relevant parameters: $[HCO_3^-] = 1000 \mu\text{mol/kg}$, $[CO_3^{2-}] =$
447 $100 \mu\text{mol/kg}$, and, depending upon the experiment, $[B(OH)_4^-] = 0.012, 0.107, \text{ or } 0.78$
448 mmol/kg . Using these values, we can estimate K_D via equation 1 and 2 (Table 2).
449 Despite experimental differences, the K_D estimates based on Hemming et al. (1995) fall
450 within the range of values found in the current study. Further, if we use equation 6 to
451 estimate K_D using the above constraints, we would predict a K_D range of 0.08 to 0.04,
452 and with equation 7: 0.09 to 0.05. At the boron concentration closest to seawater used by
453 Hemming et al. (1995), the difference between K_D predicted minus that calculated is -
454 0.001 for equation 6, and 0.01 for equation 7. The range of boron concentrations used by
455 Hemming et al. (1995) includes concentrations well below (~13% of seawater values)
456 those used in the current study, and at $[B]$ well below seawater values, both equations 6
457 and 7 underestimate K_D . The study of Mavromatis et al. (2015) included boron
458 concentrations ranging from near seawater values to ~20x seawater values. At high $[B]$,
459 both equation 6 and 7 predict negative K_D values for the Mavromatis et al. (2015) data,
460 indicating that neither equation can be reliably extrapolated far beyond the concentration
461 range used for fitting the equations. Within the range for which $[B]$ was similar,
462 equations 6 and 7 both predicted K_D values higher (up to a factor of 10x) than those
463 calculated from Mavromatis et al. (2015). The highest Ω (5.8) used by Mavromatis et al.

464 (2015) was below the lowest values used in the current study, so a growth rate or
465 saturation state influence on K_D could be involved. Our experiment 1c, which
466 precipitated at a lower Ω than any of our other experiments had the lowest K_D , consistent
467 with a positive effect of growth rate at low Ω values.

468 The agreement between K_D estimates both across the diverse conditions used in the
469 current study and for independent studies, suggests that equations 6 and 7 provide
470 reasonable estimates of K_D over a wide range of conditions, except at $[B] \ll \text{seawater}$,
471 $[B] \gg \text{seawater}$, and $\Omega < \sim 9$.

472

473

474 Table 2. K_D values calculated using different equations for the current study and the
 475 studies of Hemming et al. (1995) and Mavromatis et al. (2015). See discussion for
 476 further details on the calculations. Note that K_D values expressed here are for expressing
 477 B/Ca as mmol/mol. For the current study, mean values are expressed ± 1 standard
 478 deviation.

Study	equation 1 K_D	equation 2 K_D
Hemming	4.5 (37 ppm B) - 10 (0.59 ppm B)	0.04 (37 ppm B) - 0.1 (0.59 ppm B)
Mavromatis	0.3 – 40	0.0003 – 0.03
Current	1.4 – 52, mean 23 ± 14	0.042 - 0.103, mean 0.071 ± 0.011

479

480

481 4.3. Nernst partition coefficient

482 An alternative means of expressing partitioning is to use the single element or Nernst
 483 partition coefficient (D_B), which is expressed as the ratio of the mass percent B in the
 484 solid relative to the mass percent in solution (e.g. Gaetani and Cohen 2006). The use of
 485 Nernst partition coefficients allows different studies to be compared as prior studies have
 486 generally provided the necessary data. Values for Nernst partition coefficients are
 487 dependent upon the specific experimental conditions (temperature, pH, competing
 488 species, etc) (e.g. McIntire 1963), as they do not necessarily take into account speciation
 489 changes or other factors influencing incorporation, thus comparisons should be
 490 interpreted with this in mind. Values for D_B were calculated for each experiment as
 491 described for K_D calculations, and are summarized in Table 3 along with those of other
 492 studies. D_B values from the current study were strongly correlated with pH_T (pearson
 493 correlation coefficient: 0.888), as well as with a wide range of other solution chemistry

494 parameters (Figure 4), likely reflecting changes in boron and carbon speciation with pH.

495 The following equations described much of the variance in D_B values:

496

$$497 \quad D_B = 8.215 (\pm 0.40) \text{ pH}_T - 0.297 (\pm 0.035) \Omega - 55.69 (\pm 2.81) \quad \text{eq. 8}$$

$$498 \quad D_B = 7.954 (\pm 0.378) \text{ pH}_T - 0.267 (\pm 0.034) \Omega + 0.124 (\pm 0.038) T - 57.3 (\pm 2.6) \quad \text{eq. 9}$$

$$499 \quad D_B = 7.429 (\pm 0.423) \text{ pH}_T - 0.260 (\pm 0.033) \Omega + 0.114 (\pm 0.037) T - 0.491 (\pm 0.203) [B] -$$

$$500 \quad 52.5 (\pm 3.2) \quad \text{eq. 10}$$

501

502 Where Ω is the saturation state with respect to aragonite, pH_T is the pH on the total scale,

503 T is temperature in Celsius. All parameter estimates were significant at the $p < 0.05$ level,

504 those for the constant, pH and saturation state were all highly significant ($p < 0.001$), $R^2 =$

505 0.9, 0.92, and 0.93 for equation 8, 9, and 10 respectively. Note that D_B depends on

506 factors such as pH and temperature, whereas the K_D values did not, likely reflecting

507 changes in speciation of B and DIC as a function of pH and temperature which were

508 taken into account when calculating K_D .

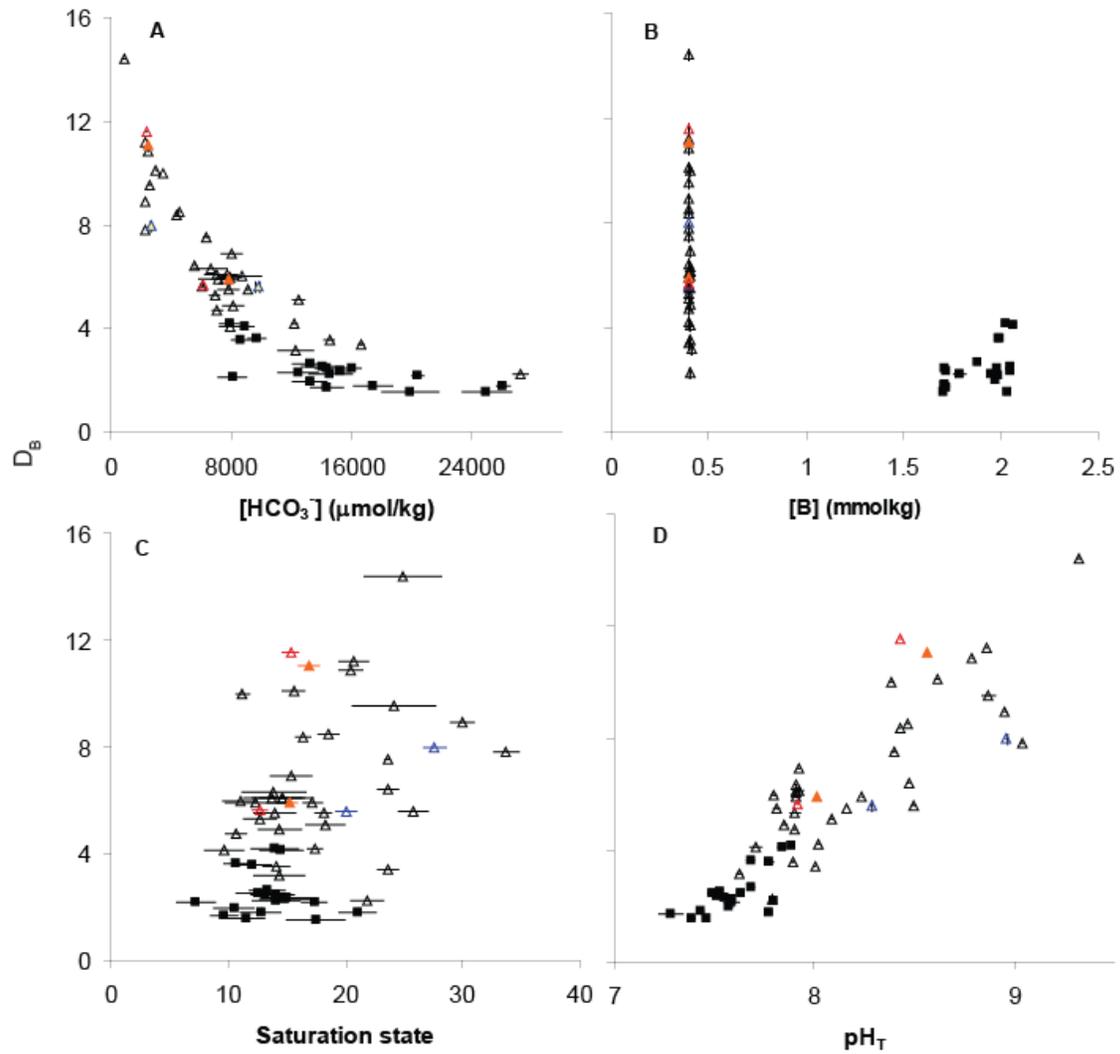
509 Differences between the predicted (using equation 10) and measured solid composition

510 were not strongly correlated with any solution chemistry parameter, though there was a

511 weak positive correlation with growth rate and with salinity; no significant effects of

512 organic buffers were detected. Relative differences between measured and predicted

513 values were generally less than 16%.



515

516 Figure 4. Relationship between the Nernst partition coefficient (D_B) and various solution
 517 chemistry parameters. Symbols are as described for figure 2.

518

519 Table 3. Nernst coefficients (D_B) estimated from different studies. Note that for
 520 estimating D_B for the Hemming and Hanson (1992) study, it was assumed that the
 521 biogenic CaCO_3 samples precipitated from a solution with 4.676 ppm B, all other studies
 522 represent synthetic aragonites and $[B]$ was specified in the study.

Study	D _B
Kitano et al., 1978	~0.53 – 1.5
Hemming and Hanson, 1992	2-15
Hemming et al., 1995	10.2 – 22.8
Mavromatis et al., 2015	0.07 – 9
Current	1.5 – 14.4, mean 5.4 ± 3.0

523

524 Our estimates of D_B agree well with existing values – our experimental range covers the
525 range estimated for natural aragonite (Table 3). Our highest values overlap the lower
526 estimates of Hemming et al. (1995); for the two highest [B] used by Hemming et al., their
527 values are only slightly higher than some of our estimates at similar [B]. Estimates of D_B
528 from Kitano et al. (1978) and Mavromatis et al. (2015), though below those of Hemming
529 et al. (1995), also overlap our values, with their estimates for their lowest [B] being
530 similar to our values at similar [B]. Although both the D_B values of Kitano et al. (1978)
531 and Hemming et al. (1995) overlap ours, the values in the two studies do not overlap
532 (Table 3). This lack of agreement between these two previous studies likely reflects
533 differences in the carbonate chemistry during aragonite precipitation. In the experiments
534 performed by Hemming et al (1995), CO_2 diffusion into the solution controlled
535 precipitation, thus aragonite was formed under low [DIC] and low $[\text{CO}_3^{2-}]$ conditions,
536 with $[\text{CO}_3^{2-}]$ likely lower than any of our experiments or those of Kitano et al. (1978).
537 Such low $[\text{CO}_3^{2-}]$ conditions would in-turn lead to an increase in the $[\text{B}(\text{OH})_4^-]/[\text{CO}_3^{2-}]^{0.5}$
538 ratio relative to other studies, thus a higher percentage of solution B would be expected to
539 be incorporated into the aragonite, consistent with high D_B estimates (Table 3). In
540 contrast, Kitano et al. (1978) used CO_2 degassing experiments, with much lower $[\text{Ca}^{2+}]$
541 and higher [DIC]. Although insufficient detail is given to estimate $[\text{CO}_3^{2-}]$ for these
542 experiments, concentrations were likely much higher than those of Hemming et al.
543 (1995), potentially similar to ours, consistent with similar D_B estimates. However,
544 Kitano et al. (1978) also used boron concentrations much higher than those used in the
545 current study, and high [B] resulted in lower D_B values.
546 The pattern of lower D_B or K_D values at higher [B] is consistent across studies.

547 Such observations have previously been suggested to be due to saturating defect sites at
548 which incorporation is more favorable at relatively low concentrations leaving only
549 structural sites for further substitution (Hemming et al., 1995). Changes in boron
550 speciation may also occur at high concentrations (e.g. Williams and Strack 1966) which
551 could further affect partitioning. It should also be noted that boron can influence the
552 growth of crystals along different axes (Ruiz-Agudo et al., 2012) and solution chemistry
553 influences surface charging which may further influence B incorporation (Hobbs and
554 Reardon 1999). Although our data provide insight into the controls on B incorporation
555 into aragonite in terms of bulk solution influences, there remains considerable research to
556 be done to understand the detailed mechanisms of B incorporation, particularly with
557 regards to the reactions and molecular rearrangements occurring near the crystal surface,
558 which ultimately control B incorporation and B/Ca ratios.

559

560 *4.4. Environmental proxies*

561 Although our results show patterns consistent with some studies of biologically formed
562 calcium carbonates e.g. $[B(OH)_4^-]/\Delta CO_3^{2-}$ was strongly correlated with B/Ca (Table 1;
563 Yu and Elderfield, 2007), such results cannot be directly compared. Here we directly
564 measure the chemistry during precipitation and thus correlate B/Ca in aragonite to the
565 chemistry in the solution from which that aragonite formed, whereas studies of material
566 in the natural environment usually measure seawater chemistry, not the chemistry of the
567 solution from which precipitation occurs, and thus make an assumption about the link
568 between seawater chemistry and the chemistry of the fluid responsible for precipitation.
569 Biologically formed aragonite is often formed from a solution substantially modified

570 from seawater, for instance, in corals aragonite growth occurs from a solution in which
571 pH and $[\text{CO}_3^{2-}]$ are elevated relative to the surrounding seawater (e.g. Al-Horani et al.,
572 2003; McCulloch et al., 2012; DeCarlo et al., 2015; Cai et al., 2016). Similarities in
573 relationships between B/Ca and seawater chemistry reported for biological samples and
574 relationships between B/Ca and directly measured solution chemistry in synthetic
575 precipitates suggests that variations in seawater chemistry affect the internal calcifying
576 environment of calcifying organisms. With the relationships described here for synthetic
577 aragonite, B/Ca holds potential as a proxy to determine how the chemistry of the internal
578 calcifying environment of biomineralizing organisms is linked to the external
579 environment. With this framework, B/Ca ratios of the shells and skeletons of calcifying
580 organisms can improve our understanding of how environmental conditions are recorded
581 in biogenic aragonite.

582

583

584 ***5. Summary***

585 The B/Ca ratio in aragonite appears to be primarily a function of $[\text{B}(\text{OH})_4^-]/[\text{CO}_3^{2-}]^{0.5}$ in
586 the solution from which aragonite growth occurs, with possible influences of [B] and
587 saturation state/ $[\text{CO}_3^{2-}]$. For aragonites formed from seawater-like solutions, [B] can be
588 estimated from salinity, and since pH can be estimated from boron isotopes (e.g. Trotter
589 et al., 2011), $[\text{B}(\text{OH})_4^-]$ can be calculated (assuming T is known), thus the remaining
590 variables influencing B/Ca are $[\text{CO}_3^{2-}]$ and potentially $[\text{Ca}^{2+}]$. B/Ca can be used to
591 estimate $[\text{CO}_3^{2-}]$, thus allowing the full carbonate chemistry under which the aragonite
592 formed to be estimated. If it can be shown that the solution chemistry from which

593 aragonite precipitates in a particular organism varies in a predictable way with seawater

594 chemistry, it may further be possible to use B/Ca in biogenic carbonates to infer past

595 seawater conditions.

596

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611

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788

789

790

791 **Supplemental materials**

792 Detailed methods and associated discussion, figures, and tables

793

794 *SI. Precipitation details*

795 *SI.1. Reagents*

796 Seawater drawn continuously from ~4 m depth, ~200 m off-shore in Vineyard Sound

797 (Massachusetts, USA), passed through a sand filter and distributed throughout the

798 Environmental Systems Laboratory (WHOI) was used for all experiments. The seawater

799 used for experiments was further passed through pleated Flow Max cartridge filters (final

800 size 0.35 μm), and finally a 0.2 μm Whatman Polycap 36tc filter (lot y830) and stored in

801 HDPE carboys (all filters and carboys were rinsed repeatedly prior to collecting

802 seawater). Seawater was collected on three different dates in 2011 and 2013 and stored

803 in the dark for no more than 6 weeks prior to use in experiments.

804 Concentrated seawater (2xsw) was prepared by placing seawater in pre-washed ~1 L

805 polypropylene (PP) containers (MicroLite, Anchor Packaging) held within warm water

806 baths (50 – 70 °C) and allowing it to evaporate until the mass halved. 2xsw used in 2011

807 was not filtered, while that used in 2013 was passed through a 0.45 μm filter (Millipore

808 HAWP) prior to use.

809 Calcium carbonate was from Alfa Aesar (puratronic stock 43073 lot 116Q78 - used for

810 runs in 2011 and degassing runs 1-4 in 2013, or stock 10996 lot C24U037 for runs 5 - 7

811 in 2013 as well as the fsw containing CaCO_3 used in pumping runs 13g and 8f).

812 Strontium carbonate was from Alfa Aesar (puratronic stock 36618, lot 23557 used in

813 2011, lot 23399 in 2013), as was sodium carbonate (puratronic stock 10861 lot 23390 or

814 23776). Other reagents were obtained from various suppliers: NaHCO₃ (Acros
815 424270010 lot a0200805001 for 2011 and 13g, 10h, 6c, and 7d in 2013; Alfa Aesar stock
816 10863 lot S70421 for other 2013 experiments), calcein (Alfa Aesar L10255 lot
817 10132899), OTC (oxytetracycline dihydrate, Acros 123840100 lot A0275864), TRIS
818 base (Fisher t395 lot 064221 used in 2011, or lot 104689 used in 2013), Na₂B₄O₇ 10H₂O
819 (Baker 3568 lot C13634), NaOH (Fisher s318 lot 975017), HEPES sodium salt (Fisher
820 BP2939 lot 107739), CaCl₂ (Alfa Aesar 10043-52-4, stock L13191 lot 10113722), MgCl₂
821 (Alfa Aesar stock 12315 lot f18w011).
822 Water used for preparing solutions and cleaning was either quartz distilled (used in 2011)
823 or filtered (18 MΩ, Barnstead Nanopure; used in 2013).

824

825 *S.1.2. Aragonite growth set-up*

826 All experiments conducted in 2011 used ~1 L PET containers (Deli Gourmet, Solo) for
827 aragonite growth, while in 2013 ~1 L PP containers (MicroLite, Anchor Packaging) were
828 used for most experiments. The choice of container has little impact on the experiment
829 (unpublished data). Precipitates grown in PET containers were generally easier to
830 recover than those grown in PP containers, but, PET tends to be damaged by acid
831 washing, thus when precipitates were to be used primarily for trace element composition
832 and thus all glass and plastic ware acid (HCl) washed prior to use, PP containers were
833 used.

834

835 Some experiments were bubbled with air, CO₂, or mixtures there-of. Air/CO₂ mixtures
836 were prepared using mass flow controllers. The pCO₂ of both the mixed gasses and air

837 was determined using a NDIR CO₂ analyzer (Qubit S-151). Atmospheric pressure in the
838 lab was recorded (dial barometer, Fisher) each time the gas composition was measured –
839 values were generally near 770 mmHg. Gas flows to individual experiments were
840 controlled with rotameters. All gasses were bubbled through de-ionized water prior to
841 being introduced into experimental containers to humidify the air and thus reduce
842 evaporation of the experimental solution. Gasses were introduced into a given
843 experiment via a glass tube with a glass frit to diffuse the air near the bottom of each
844 experimental container.

845

846 For pumping experiments, glass and teflon syringes (SGE gastight) were used to add
847 reagents in 2011, polypropylene/polyethylene syringes (Norm-ject, Henke-Sass Wolf) in
848 2013. Vinyl tubing (Cole-Parmer 30526-18) was used to carry reagents from the syringe
849 to the experimental container. Syringes and tubing were washed with dilute HCl, H₂O,
850 and the given reagent prior to use.

851 Details specific to individual experiments are provided in Table S1.

852

853 *SI.3. Weights*

854 All solutions added to or removed from an experiment were weighed using an Ohaus
855 precision standard model ts4kd balance, the calibration was verified using reference
856 masses prior to each group of experiments (measured reference values were within 0.03%
857 of expected). Most reagents and all dilutions of alkalinity samples were weighed to four
858 or five decimal places (Sartorius cpa124s or bp211d balances); reference weights were
859 within 0.006% of expected values.

860

861 *S1.4. Stirring*

862 All solutions were stirred continuously during precipitation. This was affected using one
863 of three different methods. An overhead stirrer set at 120 rpm was used to rotate a PTFE
864 impeller with 4 angled blades (~4 cm diameter) for all 2013 experiments ending “g” or
865 “h” and 2011 experiments ending “1” or “2”. Experiments ending a-f were stirred with
866 PTFE coated octagonal magnetic stir bars ~5.1 cm long and 0.8 cm diameter at a rate of
867 130 rpm. In 2011, stir bars were placed directly on the bottom of the containers. To
868 reduce problems with the stir bar grinding the growing precipitates, stir bars were
869 suspended ~2 cm from the bottom of the container using nylon monofilament line for
870 experiments conducted in 2013. The line was attached to a swivel, thus the stir bar could
871 rotate freely.

872

873 *S2. Solution chemistry and calculations*

874 *S2.1. Salinity*

875 The final salinity as well as the initial salinity of seawater based reagents was
876 measured using a conductivity probe (Hach). Conductivity values were converted to
877 salinity using equations of Fofonoff (1985). The initial seawater and a sub-set of final
878 solutions were also measured using a Guildline autosal model 8400B salinometer.
879 IAPSO standard seawater (batch P-153) was used to standardize the autosal before runs.
880 For samples measured using both methods, agreement was generally within 0.5, though
881 values measured using the Hach conductivity probe were invariably offset from the

882 autosal values, thus a correction was applied to the values measured using the Hach probe
883 to better match the autosal values.

884

885 *S2.2. Alkalinity and pH*

886 Alkalinity measurements were carried out per Holcomb et al. (2012), most samples were
887 diluted with a ~39 g NaCl/L solution at the time of collection to prevent precipitation
888 prior to measurement and to reduce the alkalinity to <5200 μmol alkalinity/kg sw. When
889 appropriate, the calculations were corrected for the presence of added buffers. Due to the
890 experimental solutions departing from seawater composition, a number of modifications
891 were made to otherwise standard calculations – see section S2.3.

892 All pH measurements (recorded to 0.1 mV) were made on unfiltered samples using an
893 Orion Ross 8165 pH electrode and an Orion 3-star meter calibrated against NBS buffers
894 (Ricca). Solutions for pH measurement were placed in a tube in a temperature controlled
895 bath (~ 25 °C) and stirred during pH measurement. Periodic measurements of either
896 certified seawater reference material (CRM-107 or 117, supplied by Andrew Dickson,
897 Scripps Institute of Oceanography) or an in-house standard were made to estimate the
898 offset between pH_{NBS} and pH_{T} . The pH_{T} for the standard seawater solutions was
899 calculated based on TA and DIC using CO2Sys (van Heuven et al., 2009) with constants
900 from Mehrbach et al. (1973) as refit by Dickson and Millero (1987), and Dickson (1990)
901 for sulfate. Measurements were then corrected to the total scale assuming that drift in the
902 offset value was linear with time between times at which it was determined.

903 Occasionally values for alkalinity or pH were not obtained at a given measurement time-
904 point. When this occurred, values were interpolated based on measurements made before

905 and after the missing value and calculated rates of alkalinity depletion – the rate of
906 alkalinity depletion was assumed to remain stable over the period affected by a missing
907 alkalinity value.

908

909

910 *S2.3. Salinity corrections*

911 Due to the addition of different compounds to seawater, standard seawater salinity to
912 composition and ion activity relationships do not apply to most time-points in our
913 experiments. For example, addition of MgCl_2 adds conductivity (and thus changes
914 salinity) and affects ion activities, yet makes no contribution to alkalinity, nor does it
915 contribute other species which usually vary in direct proportion to salinity. A number of
916 calculations (titration alkalinity, carbonate chemistry parameters, etc.) make use of
917 salinity to composition relationships to simplify calculations. To compensate for
918 compositional differences, a number of modifications were made to these otherwise
919 standard calculations.

920

921 *S2.3.1. Titration alkalinity corrections*

922 For the calculation of titration alkalinity, a regression analysis was used (Holcomb et al.,
923 2012). This code uses salinity to concentration relationships to calculate concentrations
924 of B, F, etc., as well as salinity dependencies for estimating carbonate equilibrium
925 constants. The concentrations of NH_4 , H_2SiO_4 , and PO_4 were assumed to be 0 in all
926 solutions, and all reagents used were assumed to be free from compounds that would
927 affect alkalinity calculations except for those specifically considered. TRIS, HEPES, and

928 boron were added to certain experiments. The contribution of boron is normally
929 considered in calculating alkalinity, so only the B concentration was adjusted to account
930 for the added B. To account for the contribution of TRIS we used a pKa value calculated
931 from equation 27 of Dickson (1993). For HEPES, we are unaware of reported pKa
932 values for seawater media, thus a pKa of 7.5 was assumed. Since most alkalinity samples
933 were diluted with a NaCl solution (~39 g NaCl/L – with an assumed salinity of 32 and no
934 contribution to alkalinity), concentrations of different species (B, F, etc.) and salinities
935 were corrected for sample dilution. Due to the addition of various reagents over the
936 course of each experiment, the measured final salinities (calculated from conductivity) do
937 not reflect seawater composition, nor do they capture the evolution of solution chemistry
938 over time. However, for most pumping experiments, the error introduced by ignoring
939 such salinity changes is less than 1 μmol alkalinity/kg sw, whereas the typical relative
940 standard deviation for repeated alkalinity measurements is 0.2%, or ± 5 μmol alkalinity/kg
941 sw at a typical seawater alkalinity, thus no attempt was made to further correct salinity,
942 and the final measured salinity was used for calculations. For degassing experiments
943 there was a greater difference between measured salinity and that of seawater (due to the
944 addition of MgCl_2), thus a salinity of 32.5 was used for calculating the concentrations of
945 different species in the experimental fluid, while the measured final salinity was used for
946 calculating equilibrium constants. All NaX solutions were assumed to have a salinity of
947 0 for calculating concentrations of species contributing to alkalinity, and $S = 4.5$ for
948 calculating equilibrium constants – though due to samples being substantially diluted
949 with the NaCl solution prior to measurement, the final salinity used for calculating
950 constants was invariably near 32.

951

952 *S2.3.2. Carbonate chemistry corrections*

953 Calculations of the full carbonate system chemistry and concentrations of different
954 species are more sensitive to errors in salinity estimates than titration alkalinity
955 calculations, thus a more rigorous set of corrections were used for these calculations.
956 Two different salinity values were used for calculations. The empirical equilibrium
957 constants used for calculating inorganic carbon, boron, etc. speciation are functions of
958 salinity (reflecting the influence of ionic strength on ion activities). Thus the addition of
959 ions (such as contributed by NaX solutions, or MgCl₂) affects salinity, ionic strength, and
960 in-turn, equilibrium constants. Although the influence of the ions added in this
961 experiment on equilibrium constants likely differs from that expected based purely on
962 changes in salinity (estimated from conductivity), we assumed that the compositional
963 changes were sufficiently small that seawater derived salinity relationships could still be
964 used for calculating equilibrium constants. For estimating concentrations of species such
965 as B, F, SO₄, Ca, etc., the measured salinity values could not be used due to ions added
966 with the NaX or MgCl₂ solutions contributing to salinity but not affecting concentrations
967 of other species present in seawater. Thus, measured salinities were corrected for the
968 contribution of the added ions. The ionic equivalent conductivities reported by
969 Pawlowicz (2010) were used to estimate the contribution of the added NaX or MgCl₂ to
970 conductivity, and equations from Fofonoff (1985) to convert conductivity to salinity.
971 Due to differences in how different experiments were conducted, slightly different
972 procedures were used for calculating salinity at different time-points.

973

974 For degassing experiments, the initial salinity of the solution was unknown due to
975 evaporation potentially occurring during the dissolution of reagents with CO₂. The final
976 measured salinity was however known. Since the degassing experiments used a modified
977 seawater solution in which the primary salt added was MgCl₂, the salinity values used for
978 calculating concentrations were corrected for the presence of MgCl₂ by subtracting the
979 MgCl₂ contribution from the total salinity. To compensate for evaporation, the
980 evaporation rate was estimated from the difference in expected and measured final
981 solution mass relative to the total time for each experiment. For each group of
982 experiments (run simultaneously from the same starting solution), the median
983 evaporation rate was used to correct the salinity for each time point. Most experiments
984 from a given group were run for a similar length of time and had similar evaporation rates
985 (typically 0.5 to 2 g/day, depending upon the set of experiments; excluding suspect
986 values, the range within a group was less than 0.7 g/day), but one experiment departed
987 from this pattern (we suspect the final weight recorded was incorrect). By using the
988 median evaporation rate for each group of experiments we were able to avoid one
989 potentially erroneous value influencing the interpretation. Precipitation of CaCO₃ was
990 not included in correcting salinity values as it had relatively little impact.

991

992 For pumping experiments, the salinity of the initial seawater was known, thus the
993 expected salinity at any point in time could be calculated based on the initial salinity and
994 the salinity of solutions added to the experiment. The 2xsw solution was assumed to
995 have a salinity of 64, which contributed both to the salinity value used to calculate
996 constants and to that used for concentrations. The sw solution containing CaCO₃ and

997 SrCO₃ added in two of the pumping experiments was assumed to have S = 31.9. The
998 NaX solutions were assumed to contribute nothing to the salinity value used to calculate
999 concentrations, but for constants, contributed 3, 2.5, 2, and 0.75 to the salinity for
1000 NaHCO₃, NaHCO₃/Na₂CO₃, Na₂CO₃, and Na₂CO₃ added during the period in which
1001 precipitation was occurring respectively. The use of 0.75 during precipitation reflects an
1002 assumption that for every unit of Na₂CO₃ added, a unit of CaCO₃ precipitates, thus
1003 reducing the overall change in salinity. Based on the measured final salinity, an
1004 evaporation rate was calculated to allow the expected salinity to match (within 0.1) the
1005 measured salinity. Using the salinity based evaporation rate the expected final mass was
1006 calculated, values were generally in good agreement with measured values (difference of
1007 1 ± 2 g (average \pm standard deviation, excluding one suspect value)).

1008 To calculate carbonate chemistry and borate concentrations, a Matlab version of CO2sys
1009 (adapted from van Heuven et al., 2009, using constants from Mehrbach et al., 1973 as fit
1010 by Dickson and Millero 1987; Dickson 1990 for borate, and Dickson 1990 for sulfate)
1011 was used. In addition to the standard species considered, additional buffers were
1012 included (per alkalinity calculations, see above), and boron concentrations were
1013 calculated based on the boron:salinity relationship of Lee et al. (2010), plus any added
1014 boron when appropriate. Although nutrient chemistry was not measured in the seawater
1015 batches used in these experiments, previous studies have monitored nutrients in seawater
1016 from the same source (Holcomb et al., 2010; 2012), based on these data we assumed NH₃
1017 = 0, H₂SiO₄ = 5, and PO₄ = 0.25 μ mol/kg sw at S=32 for all calculations. A wide range
1018 of species (SO₄²⁻, F⁻, etc.) are incorporated into aragonite and could influence the
1019 calculation of carbonate chemistry, however the likely effects were deemed insufficient

1020 to justify corrections in the calculation of carbonate chemistry (a typical S/Ca ratio
1021 measured in a synthetic precipitate was ~6 mmol/mol (unpublished data), which,
1022 assuming a concentration of 28 mmol SO₄²⁻/kg sw represents less than 0.5% removed by
1023 the precipitate; for F, although a greater percentage of total F was removed (~5
1024 mmol/mol Tanaka et al., unpublished data), the low concentration present in seawater
1025 combined with the low pKa should result in little effect on alkalinity). Although the
1026 amount of boron removed by precipitation was trivial relative to measurement
1027 uncertainty, values were corrected by assuming the precipitate formed with a constant
1028 B/Ca ratio and the amount of precipitate formed corresponded to the difference between
1029 measured and expected (assuming no precipitation) alkalinity. Ca²⁺ values used to
1030 calculate saturation states were corrected for added calcium or calcium removed (based
1031 on the expected calcium concentration and the amount of calcium removed as estimated
1032 from alkalinity depletion). For a subset of experiments, solution [Ca²⁺] was measured
1033 (DeCarlo et al., 2015). Measured values showed similar patterns to calculated values,
1034 though measured values tended to be ~0.5 mmol/kg higher than expected.

1035

1036 *S3. ICPMS measurements*

1037 *S3.1. X-Series*

1038 Preparation of aragonite samples for measurement of B/Ca (and other element) ratios via
1039 Q-ICPMS (X-Series II, Thermo Fisher Scientific) followed standard protocols (Holcomb
1040 et al., 2015). Briefly powders were rinsed repeatedly with H₂O (18.2 MΩ, Millipore
1041 Integral 5), and most were cleaned with NaOCl. Cleaned powders were dried, weighed
1042 (~20 mg sub-sample), and dissolved in ~0.58 N HNO₃ (prepared from sub-boiling

1043 distilled (Savillex DST-1000) HNO₃), final acid concentration ~0.1 N. For X-Series
1044 measurements, samples were diluted in 2% HNO₃ containing various elemental spikes to
1045 a final concentration of ~100 ppm Ca or 10 ppm Ca, depending upon the elements to be
1046 measured (e.g. Zinke et al., 2014; Holcomb et al., 2015). The coral standard JCp-1 was
1047 used as the standard, with an accepted B/Ca ratio of 0.4596 mmol B/mol Ca (Hathorne et
1048 al., 2013).
1049 Ca measurements were also carried out on the X-Series using the same solutions used for
1050 measuring elemental ratios. Standards containing various concentrations of [Ca]
1051 (prepared from a 10000 ppm Ca standard (Fisher j/8240 lot 1147827)) were run to
1052 calibrate Ca count ratios relative to the Sc spike included in all solutions.

1053

1054 *S3.1.1. Sample purity*

1055 Aragonite is known to contain a wide range of cations and anions other than Ca²⁺ and
1056 CO₃²⁻, with concentrations of each approaching 50 mmol/mol in aragonite formed in
1057 marine environments. Thus assuming just CaCO₃ is present may bias results. However,
1058 given our measurement reproducibility (~1.5%), fairly large changes in the composition
1059 of the sample would be needed before we would be able to identify a change in Ca. This
1060 is consistent with our measured calcium contents giving an average of 0.010 mol Ca/g
1061 sample, the value expected for pure CaCO₃. We thus considered the precipitates to be
1062 composed of pure CaCO₃ for calculations, though for illustration purposes we include
1063 one figure with B normalized to the measured Ca content in addition to mass based (Fig.
1064 S1).

1065

1066 *S3.2. MC-ICPMS*

1067 Boron in most samples was measured via MC-ICPMS (Neptune Plus, ThermoFisher
1068 Scientific or NU Plasma II, NU instruments). Cation and anion resin purification
1069 procedures were used for all aragonite samples (McCulloch et al., 2014), except the
1070 solutions were weighed to the nearest 0.00001 g to allow for more accurate calculation of
1071 B concentrations. A subset of samples was also prepared with the chemistry described in
1072 section S3.3. Boron concentrations were estimated based on the total B 10+11 intensity
1073 for the sample relative to bracketing standards of known [B]. B/Ca ratios in aragonite
1074 samples were calculated based on both the sample mass and the measured [Ca] (from X-
1075 Series measurements).

1076

1077 *S3.2.1. Agreement amongst B/Ca estimates*

1078 The validity of measurements of B/Ca ratios made using the X-Series could be
1079 compromised due to the use of the coral standard JCp-1 to calculate all ratios, despite
1080 some of the synthetic aragonites having B/Ca ratios substantially different from JCp-1
1081 (ranging from ~0.1 to 0.9 mmol/mol versus a value of 0.4596 mmol/mol for JCp-1).
1082 Although all measurements were made at similar Ca concentrations, B concentrations
1083 could deviate substantially from those of the standard, thus any non-linearity in the
1084 response could bias calculated ratios. To assess any potential bias in the X-Series
1085 measurements, B/Ca was also estimated from boron measurements made via MC-ICP-
1086 MS. Repeated measurements of B/Ca ratios made on different days via the X-Series
1087 gave a reproducibility (1 standard deviation) of 0.02 mmol B/mol Ca or better for any
1088 given sample, while MC-ICP-MS based measurements were reproducible to better than

1089 0.04 mmol B/mol Ca (1 standard deviation). In all cases the average standard deviation
1090 was less than 0.01 mmol/mol. Ratios determined with the X-Series differed from those
1091 determined via MC-ICP-MS. However, on average X-Series measurements were 0.016
1092 mmol/mol lower, which is within measurement error. The relationship between
1093 measurements made with the X-Series, and those made via MC-ICP-MS using different
1094 extraction and normalization approaches is shown in Fig. S1.

1095

1096 *S3.3. B purification chemistry using TRIS*

1097 Since seawater samples contain ions not efficiently removed by the cation/anion resins
1098 used for carbonate samples (Holcomb et al., 2014; McCulloch et al., 2014), the boron
1099 specific resin Amberlite IRA 743 was used to purify the B from solution. Although
1100 several protocols exist for purifying boron using this resin (e.g. Lecuyer et al., 2002;
1101 Lemarchand et al., 2002; Foster 2008; Trotter et al., 2011; Dissard et al., 2012), existing
1102 protocols require either careful control of pH during boron absorption to avoid the
1103 formation of precipitates, pre- or post-purification, or are conducted under low pH
1104 conditions at which the capacity of the resin to absorb boron is reduced. To avoid these
1105 problems, we used an organic buffer, TRIS (Tris(hydroxymethyl)aminomethane), to
1106 stabilize the pH during boron absorption at ~8, thus reducing problems with hydroxides
1107 precipitating yet allowing boron absorption to occur at relatively high pH, thus taking
1108 advantage of the absorption capacity of the resin. To a 5 ml polypropylene tube we
1109 added ~0.05 ml of pre-cleaned Amberlite resin (in 0.075 N HNO₃), 2.5 ml H₂O
1110 containing ~0.01 mg phenol red, varying amounts of sample (typically 0.1 ml, though for
1111 NaX solutions and other samples expected to have low [B] 0.4 ml were used), and TRIS

1112 buffer (0.5:1 to 2:1 ratio TRIS to sample volume, depending upon the nature of the
1113 sample). The TRIS buffer solution used was ~ 0.3 M TRIS (Acros 424571000 lot
1114 A0326538) prepared in ~ 0.07 N HNO₃ and stored in contact with Amberlite IRA 743
1115 resin. TRIS was prepared in dilute acid to limit the possibility of achieving too high a
1116 pH. Samples were incubated overnight on a shaker table, the supernatant discarded, resin
1117 rinsed 4x with H₂O, and then the boron eluted with 4 successive 0.6 ml volumes of 0.15
1118 N HNO₃ with at least 6 h incubation on the shaker table for each elution volume. In
1119 addition to solution samples, some precipitates and coral standards were also extracted
1120 following this protocol – precipitates were dissolved as described above prior to
1121 extraction. Nitric acid blanks were extracted as well to verify procedural blanks each
1122 time samples were extracted.

1123

1124 *S3.4. Validating TRIS extraction*

1125 To verify the veracity of the TRIS based extraction protocol, a number of samples were
1126 prepared using both the method described above as well as established techniques using
1127 either cation and anion column chemistry (McCulloch et al., 2014), or traditional
1128 amberlite based extraction techniques using NaOH to adjust the pH (e.g. Holcomb et al.,
1129 2014). Results show similar B/Ca ratios for aragonite samples prepared with the various
1130 methods (Fig. S1). Repeated measurements of seawater samples prepared with amberlite
1131 resin and TRIS gave a reproducibility of boron concentration estimates of better than 6%
1132 RSD, with an average reproducibility of 1.6% RSD. Measured seawater boron
1133 concentrations agreed with calculated concentrations with an average difference of
1134 <0.2%.

1135

1136 *S4. XRD and Raman*

1137 Verification of the mineral form present in all experiments run in 2013 was made via
1138 powder x-ray diffraction (XRD). Precipitates were loaded onto a Si holder on a rotating
1139 stage and diffraction patterns collected using a PANalytical Empyrean diffractometer (at
1140 the Centre for Microscopy, Characterisation & Analysis, UWA) using Ni filtered Cu K α
1141 radiation (generator at 40 kV, current 40 mA). For reference purposes, a coral aragonite
1142 sample was run each day patterns were obtained for precipitates. A subset of
1143 experiments run in 2011 were characterized by XRD at WHOI by M. Sulanowska. A
1144 raman microscope was also used to determine the mineralogy of individual grains for
1145 many of the experiments per Holcomb et al. (2009) for experiments run in 2011; DeCarlo
1146 et al. (2015) for experiments run in 2013.

1147 In one experiment, in which precipitation was induced by adding a solution containing
1148 NaOH (experiment 11h) Mg(OH)₂ was likely formed, however no clear peaks associated
1149 with Mg(OH)₂ were detected with Raman nor XRD. Visual observation of the sample
1150 suggested aragonite was not the primary phase, and the elemental composition showed
1151 Mg/Ca ratios (~ 100x typical aragonite values) inconsistent with aragonite being the only
1152 phase present. Such observations point to a need for caution in relying on any single
1153 means of identifying the mineral phase formed in synthetic experiments – for instance,
1154 although XRD patterns for sample 11h were atypical (weak peak near $2\theta = 19^\circ$),
1155 aragonite peaks were clearly present (Fig. S2). Given the wide range of peak
1156 shapes/heights observed for different precipitates (likely reflecting variations in crystal
1157 sizes and orientations amongst experiments), the presence of a phase other than aragonite

1158 would not necessarily have been detected from an XRD pattern alone, particularly if a
1159 smaller range of scan angles targeting calcium carbonates were used.

1160

1161 *S5. Additional statistics*

1162 Since all temperature experiments represented pumping experiments without added B, K_D
1163 values from pumping experiments without added B conducted at ~ 25 °C were regressed
1164 against mean experimental saturation state and $[\text{CO}_3^{2-}]$ (variations in [B] were too small
1165 to justify inclusion). The regressions gave the following fits: $K_D = -0.000865 \cdot \Omega$
1166 $+0.0887$, $R^2 = 0.435$ and $K_D = 0.00000945 \cdot [\text{CO}_3^{2-}] + 0.0856$ $R^2 = 0.343$. Residuals (K_D
1167 $-$ calculated K_D) were then calculated for all pumping experiments without added boron
1168 and plotted against temperature (Fig. S3). There was no trend in residuals with
1169 temperature regardless of the regression used, thus suggesting any effect of temperature
1170 on K_D is small relative to experimental variability. Equations 6 and 7 were also used for
1171 calculating the expected B/Ca ratio of each experiment, the difference between the
1172 measured and expected B/Ca ratio calculated, and again the values compared with
1173 temperature; no trend was detected. Tests for the effects of Tris, Hepes, and calcein were
1174 conducted in the same manner, regressions were calculated based on the full data-set
1175 (excluding experiments run in 2011, experiment 1c, and experiments containing Tris,
1176 Hepes, or calcein, (resulting equations: $K_D = 0.0997 - 0.0111 \cdot [\text{B}] - 0.00111 \cdot \Omega$ $R^2=0.53$,
1177 and $K_D = 0.0945 - 0.0124 \cdot [\text{B}] - 0.0000116 \cdot [\text{CO}_3^{2-}]$ $R^2=0.55$) residuals calculated and
1178 tested for significant ($p < 0.01$) differences from 0 (t-test). In all cases, no significant
1179 differences were detected, though precipitates formed from solutions containing HEPES
1180 tended to have higher B/Ca than expected, while the opposite was observed for TRIS.

1181

1182 *S6. Effects of [Mg] and [Ca]*

1183 Since our experiments were conducted over a wide range of Ca and Mg concentrations,
1184 departing substantially from standard seawater conditions, there is the potential for the
1185 seawater based carbonate chemistry constants used in the main text to be inappropriate
1186 for our data. The inclusion of seawater carbonate chemistry constants in common
1187 programs used for calculating carbonate chemistry leads to their application in modeling
1188 biogenic calcification, and thus our choice to use them, however both Ca and Mg
1189 influence DIC and B speciation (Reardon 1976; Bassett 1980; Hain et al., 2015), thus
1190 taking such effects into account is essential for a robust treatment of our data. We
1191 modified CO2Sys to use the DIC (K_0 , K_1 , K_2), boric acid (K_B), water (K_W), hydrogen
1192 sulfate (K_{SO_4}), and aragonite solubility constants of Hain et al. (2015). We further
1193 modified the MyAMI code of Hain et al. (2015) used to calculate these constants to
1194 include variable $[H^+]$ (estimated from measured pH) and $[B(OH)_4^-]$ (estimated with
1195 CO2Sys without corrections for Mg and Ca) for estimating Pitzer activity coefficients.
1196 To estimate what parameters are likely to be affected by [Mg] and [Ca], we calculated
1197 concentrations of different DIC species and borate using constants from Hain et al (2015)
1198 at both normal seawater [Mg] and [Ca] and ~2x elevated (Fig. S5). For B/DIC the
1199 change in constants had no effect, while for $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ there was a slight
1200 influence. In contrast many of the individual DIC or B species show substantial effects
1201 (Fig. S5, S6), thus the relationship between B/Ca and individual chemical species is
1202 likely to change. Correlations between B/Ca and various solution chemistry parameters
1203 are presented in Table S3 and Figure S7 (a summary table with all solution chemistry

1204 parameters calculated using the adjusted constants is given in the supplemental data file).
1205 The use of different constants affected the correlations between B/Ca in the precipitate
1206 and some individual solution chemistry parameters (Table S3), however the strong
1207 correlations between B/Ca and mean $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$, $[B]/[DIC]$ or $[B]/([CO_3^{2-}] +$
1208 $[HCO_3^-])$ and $[B(OH)_4^-]*[Ca^{2+}]$ remain consistent regardless of the constants used.

1209 Linear least squares regression (excluding experiment 1c for equations S1 and S2) using
1210 $[Mg]$ and $[Ca]$ corrected constants for solution chemistry calculations gave the following
1211 fits:

1212
1213 $B/Ca \text{ (mmol/mol)} = .0648 (\pm 0.002) [B(OH)_4^-]/[CO_3^{2-}]^{0.5} + .0359 (\pm 0.013)$ eq. S1

1214
1215 $B/Ca \text{ (mmol/mol)} = 2.795 (\pm 0.133) [B]/[DIC] + 0.089 (\pm 0.014)$ eq. S2

1216
1217 $B/Ca \text{ (mmol/mol)} = 0.000148 (\pm 0.000009) [B(OH)_4^-]*[Ca^{2+}] + 0.0957 (\pm 0.0178)$ eq. S3

1218
1219 $B/Ca \text{ (mmol/mol)} = 0.001674 (\pm 0.000144) [B(OH)_4^-] + 0.0799 (\pm 0.0253)$ eq. S4

1220
1221 where $[B(OH)_4^-]$, $[CO_3^{2-}]$, $[B]$, and $[DIC]$ are in units of $\mu\text{mol kg sw}^{-1}$, $[Ca^{2+}]$ is in mmol
1222 kg sw^{-1} values in parentheses are 1 standard error, all parameter estimates were
1223 significant ($p \leq 0.001$, $R^2 = 0.93$ for eq. S1, $R^2 = 0.89$ for eq. S2, $R^2 = 0.82$ for eq. S3, and
1224 $R^2 = 0.71$ for eq. S4). Note that all coefficient estimates for eq. S1 and S2 are within one
1225 standard error of those in equations 4 and 5.

1226 Apparent partition coefficients (relationships based on $[B]/[DIC]$, $[B(OH)_4^-]/[Ca^{2+}]$ and
 1227 $[B(OH)_4^-]$ are not for balanced reactions) of the form $K = (B/Ca)/\text{solution chemistry}$
 1228 value were calculated for each experiment as described in the main text (Table S4). The
 1229 K_D values based on $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ thus calculated tend to be slightly higher than
 1230 those calculated without taking the effects of $[Mg^{2+}]$ and $[Ca^{2+}]$ into account, reflecting
 1231 slightly lower $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ ratios (Fig. S5)

1232
 1233 Although we consider a K_D expression based on $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ to provide
 1234 the best fit to our data, involve species likely incorporated into aragonite, as well as
 1235 providing a charge balanced reaction, there are a number of apparent partitioning
 1236 relationships which fit our data nearly as well, some of which have been suggested to be
 1237 important by other authors, thus we present alternative fits for K_D relationships. For the
 1238 following fits all solution chemistry parameters were calculated using $[Ca]$ and $[Mg]$
 1239 corrected constants, experiment 1c was excluded for relationships based on $[B(OH)_4^-]$
 1240 $/[CO_3^{2-}]^{0.5}$ and $[B]/DIC$.

1241
 1242 $K = B/Ca/[B(OH)_4^-]/[CO_3^{2-}]^{0.5} = -0.00008035 (0.0000158) [B(OH)_4^-] + 0.0878 (0.00278),$
 1243 $R^2=0.32$ eq. S5

1244
 1245 $K = B/Ca/[B(OH)_4^-]/[CO_3^{2-}]^{0.5} = -0.00001634 (0.00000276) [CO_3^{2-}] -0.00001062$
 1246 $(0.00000177) [B] +0.104 (0.004), R^2=0.49$ eq. S6

1247

1248 $K = B/Ca/[B(OH)_4^-]/[CO_3^{2-}]^{0.5} = -0.001243 (0.0002) \Omega - 0.00001065 (0.00000173) [B] +$
1249 $0.1072 (0.00457), R^2=0.51$ eq. S7

1250

1251 $K = B/Ca/[B]/DIC = -0.005306 (0.001164) [B(OH)_4^-] - 0.214 (0.0275) [Ca^{2+}] + 7.356$
1252 $(0.385), R^2=0.57$ eq. S8

1253

1254 $K = B/Ca/[B(OH)_4^-]*[Ca^{2+}] = -0.0000117 (0.00000114) [Ca^{2+}] - 0.00000776$
1255 $(0.00000059) \Omega - 0.0000000462 (0.00000000488) [B] + 0.000535 (0.0000197), R^2 = 0.87$
1256 eq. S9

1257

1258 $K = B/Ca/[B(OH)_4^-] = -0.000001377 (0.000000097) [CO_3^{2-}] - 0.0000003825$
1259 $(0.000000062) [B] + 0.00433 (0.00015), R^2 = 0.79$ eq S10

1260 where $[B(OH)_4^-]$, $[CO_3^{2-}]$, $[B]$, and $[DIC]$ are in units of $\mu\text{mol kg sw}^{-1}$, $[Ca^{2+}]$ is in mmol
1261 kg sw^{-1} values in parentheses are 1 standard error, all parameter estimates were
1262 significant ($p \leq 0.001$). B/Ca ratios were calculated based on each of the above K_D
1263 expressions and compared to measured values (Table S5). Equations S6, S7, and S9
1264 provided the best fits. Residuals showed no significant effect of TRIS; for HEPES
1265 measured values were significantly ($p < 0.01$) higher than expected based on equation S9.
1266 Residuals from equation S8 were negatively correlated with temperature, whereas
1267 residuals from equations S3 and S4 were weakly positively correlated with temperature.

1268 Although in the full data set the correlation between B/Ca in the precipitate and
1269 $[B(OH)_4^-]*[Ca^{2+}]$ was nearly equivalent to correlations with $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ and

1270 [B]/DIC, when data were separated by pumping vs degassing experiments, the use of
1271 $[B(OH)_4^-][Ca^{2+}]$ provided no improvement in the correlation relative to $[B(OH)_4^-]$ alone
1272 (e.g. Table 1). In contrast, $[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$ was consistently more strongly
1273 correlated with B/Ca than $[B(OH)_4^-]$ alone. This suggests that rather than $[Ca^{2+}]$ being
1274 important in and of itself, it reflects a difference amongst degassing versus pumping
1275 experiments. Indeed $[Ca^{2+}]$ was generally higher in degassing experiments, while
1276 carbonate was generally lower (relative to pumping experiments) leading to a negative
1277 correlation between $[CO_3^{2-}]$ and $[Ca^{2+}]$ in both the overall data-set and certain subsets of
1278 the data. Thus we consider the strong correlation of B/Ca with $[B(OH)_4^-][Ca^{2+}]$ to
1279 reflect $[B(OH)_4^-]$ and a negative correlation between $[Ca^{2+}]$ and $[CO_3^{2-}]$ rather than an
1280 effect of $[Ca^{2+}]$.

1281

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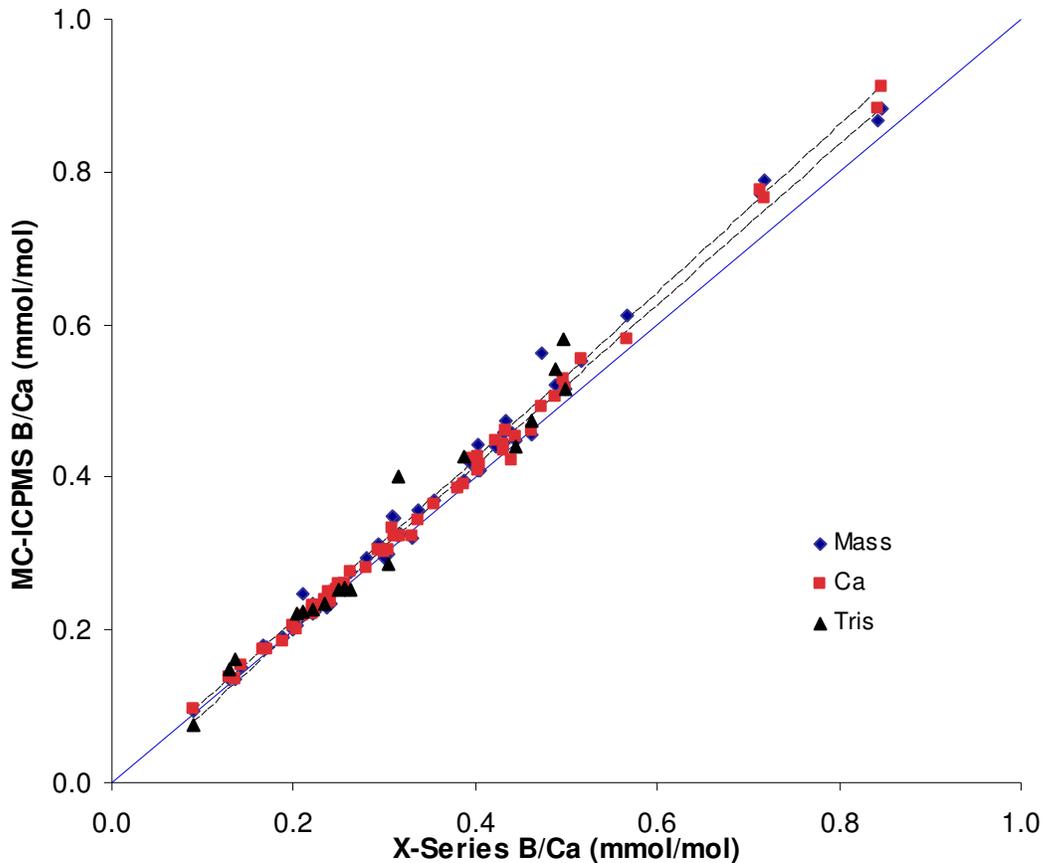
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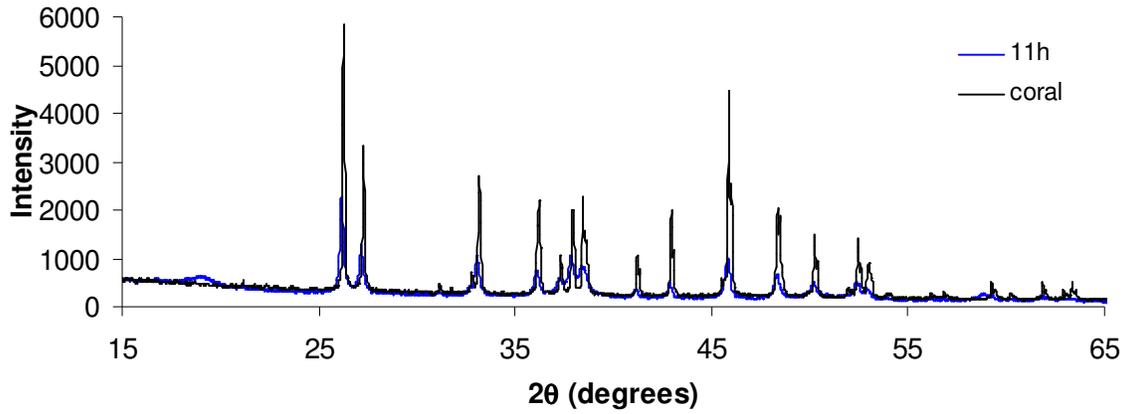
1344



1345

1346 Figure S1. Relationship between different methods of determining B/Ca ratios. B/Ca
 1347 ratios measured on the X-Series are plotted on the x-axis versus measurements made via
 1348 MC-ICPMS (y-axis). Samples for which B (measured via MC-ICPMS) was extracted
 1349 using column chemistry were normalized to Ca based on sample mass (blue diamonds),
 1350 or measured Ca contents (red-orange squares). Samples for which B was extracted using
 1351 Amberlite resin and TRIS buffer were normalized to Ca based on sample mass (black
 1352 triangles). The 1:1 line is shown for reference (blue line). The relationship between the
 1353 X-series measurements and MC-ICPMS measurements (normalized based on sample
 1354 mass) was described by the following linear regression: $B/Ca_{MC-ICPMS} = B/Ca_{X-series} * 1.07 - 0.009$ ($R^2=0.99$); the 95% confidence intervals for this regression are
 1355 shown as dashed lines.
 1356

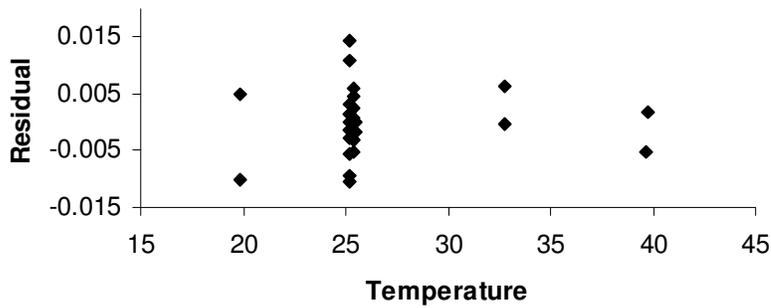
1357



1358

1359 Fig S2. XRD patterns of a coral aragonite powder (black) and synthetic precipitate 11h
1360 (blue) containing a Mg rich phase in addition to aragonite.

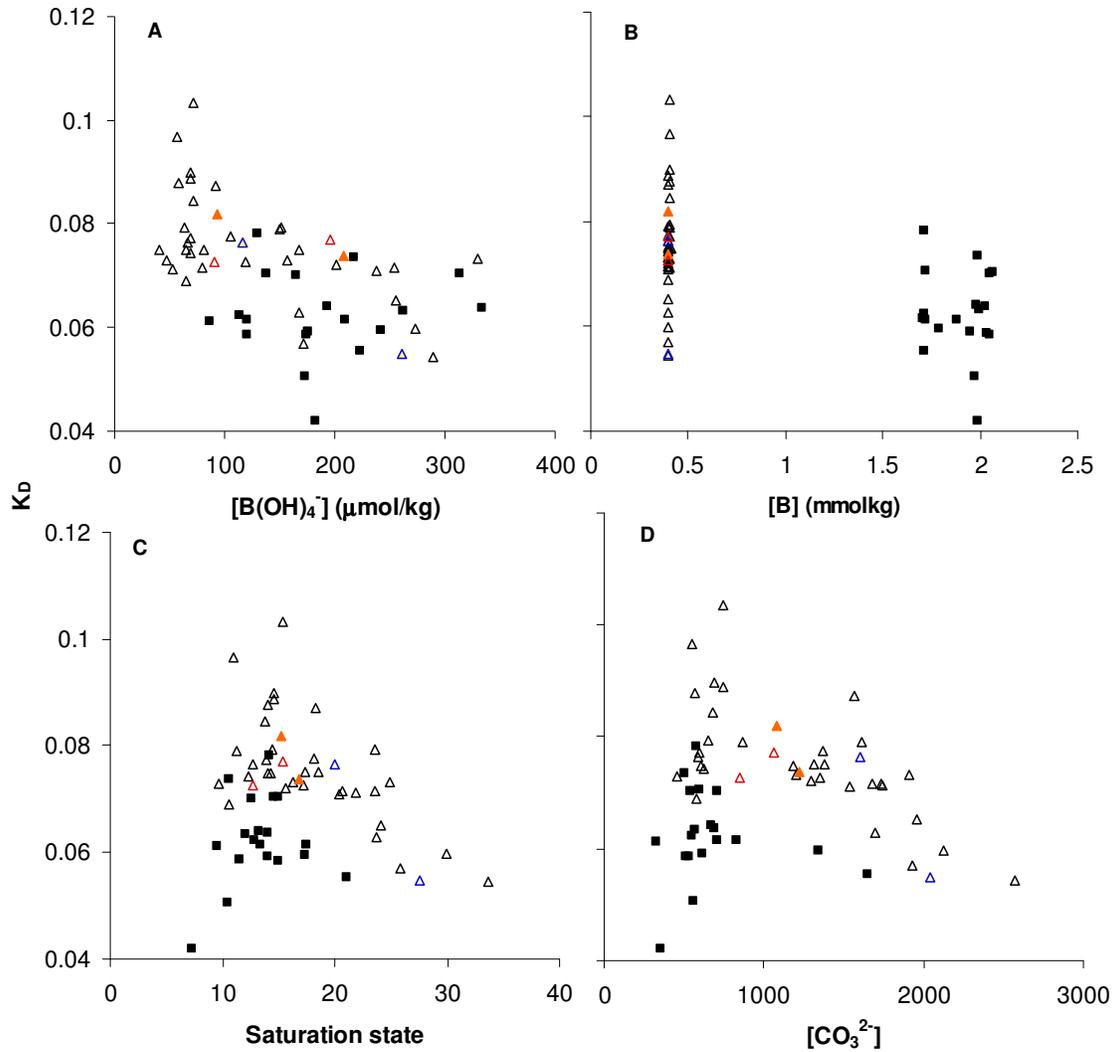
1361



1362

1363 Figure S3. Residuals (experimental $K_D - K_D$ calculated from $K_D = -0.000865 * \Omega$
1364 $+0.0887$) plotted versus temperature for pumping experiments without added B.

1365



1366

1367 Figure S4. Relationship between different solution chemistry parameters and K_D .

1368 Symbols are means of individual experiments; experiments without added B are

1369 represented by triangles, experiments with added B are represented by squares, error bars

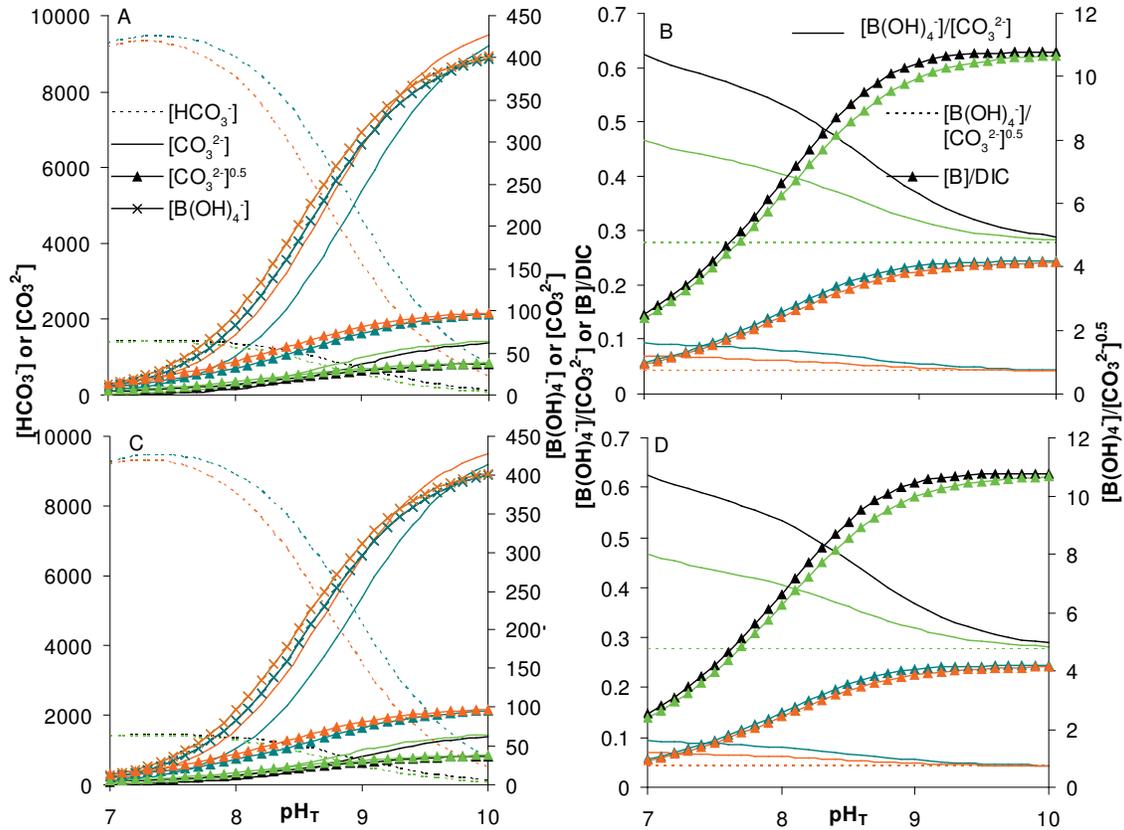
1370 are omitted for clarity. Experiments conducted at different temperatures are shown in

1371 different colors: blue ~ 20, black ~ 25, orange ~ 33, and red ~ 40 °C. Most experiments

1372 were conducted at ~ 25 °C, 2 experiments were run at each of the other temperatures.

1373

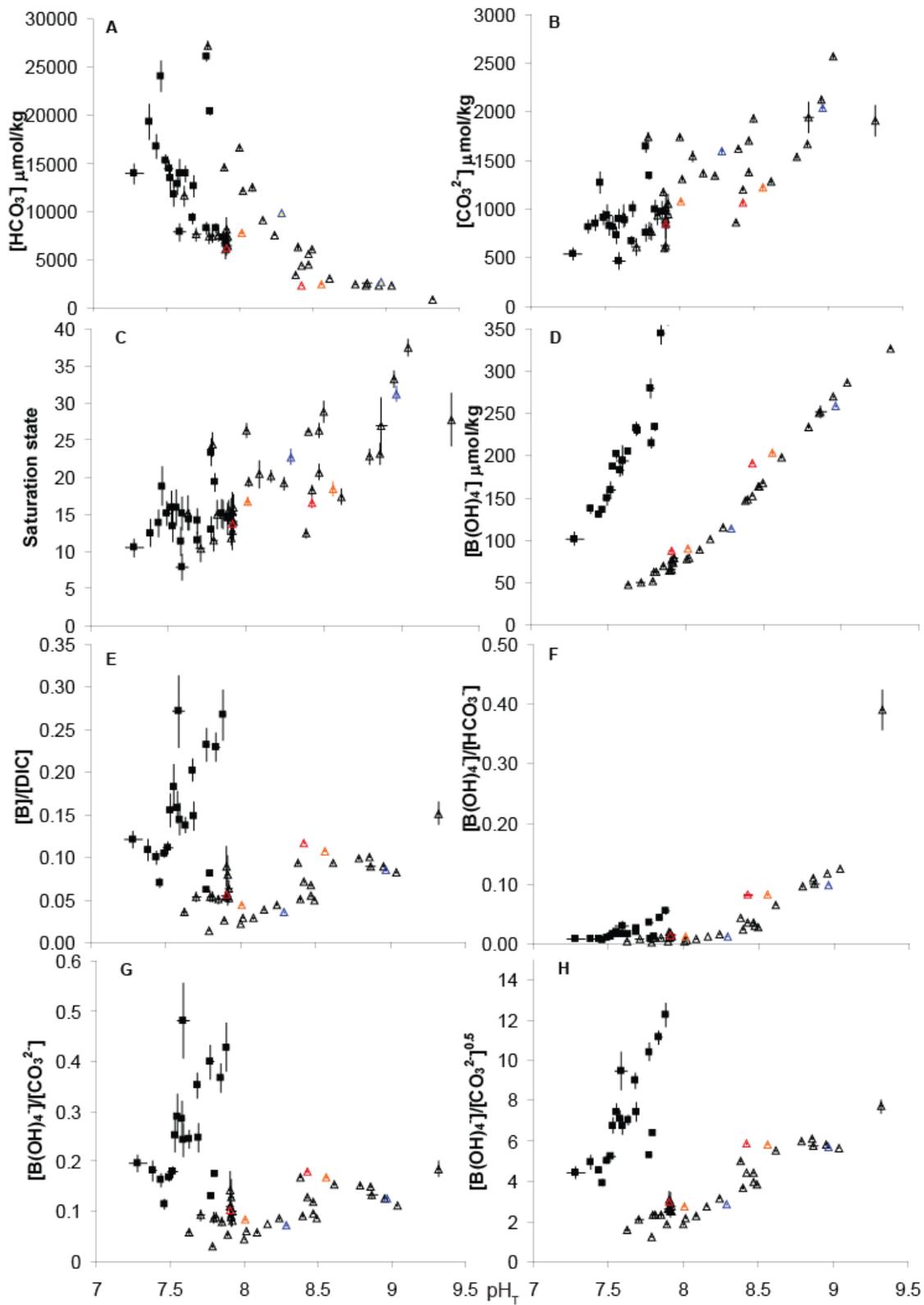
1374



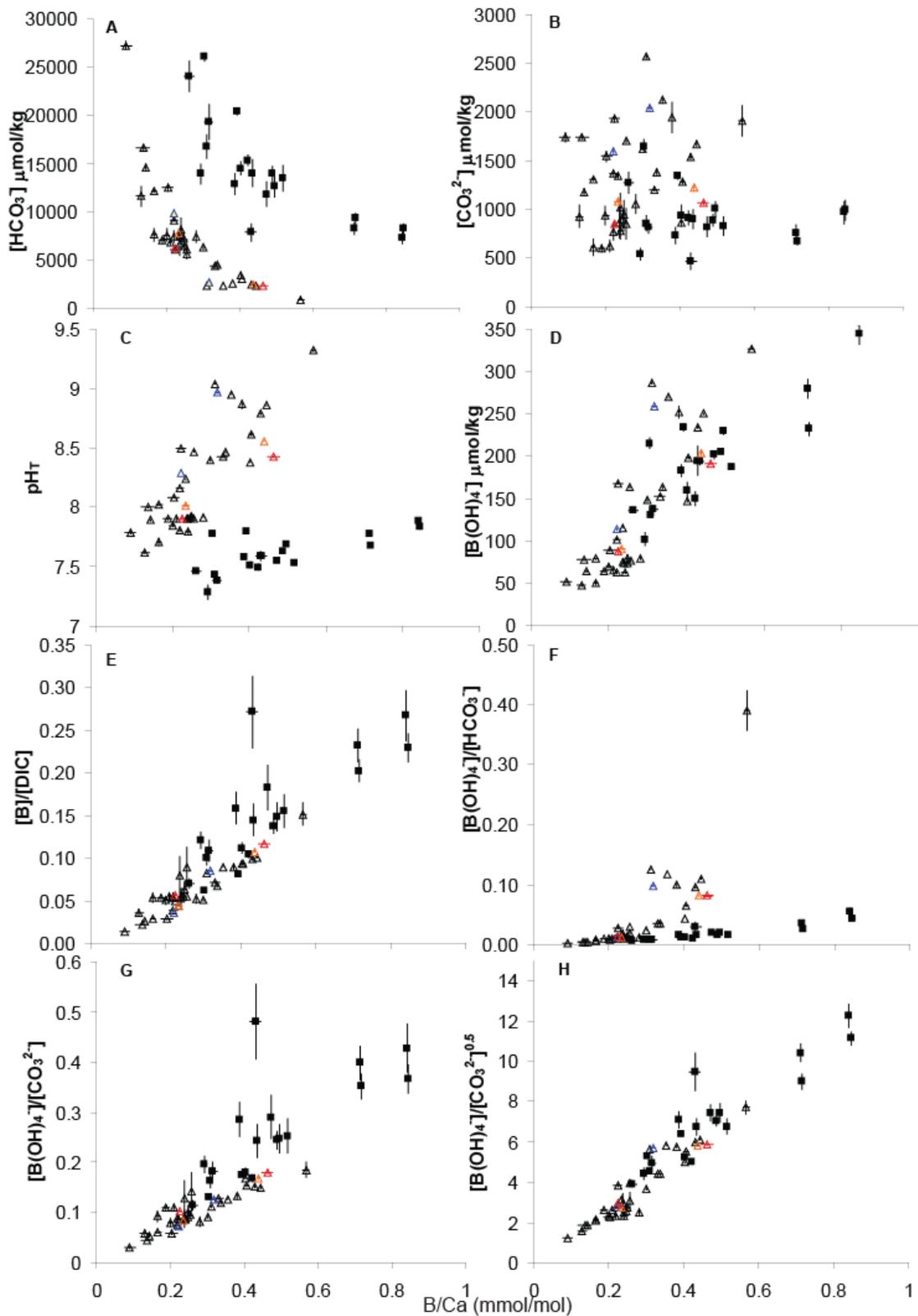
1375
 1376 Figure S5. Relationships amongst DIC species as a function of pH calculated using
 1377 constants from Hain et al. (2015). In A and B, two different DIC levels are used (1500 =
 1378 black and green, 10000 = blue and orange); for each DIC, carbonate chemistry constants
 1379 are calculated using the Pitzer model from the MyAMI code under standard seawater
 1380 [Ca] and [Mg] (black and blue) or 2x [Ca] and [Mg] (green and orange). In C and D the
 1381 same calculations are made but with additional corrections for the effects of pH
 1382 variations on ion activity coefficients.

1383

1384



1386 Figure S6. Relationship between different solution chemistry parameters and pH_T as
1387 calculated using [Mg] and [Ca] corrected constants from Hain et al. (2015). Symbols are
1388 means of individual experiments; experiments without added B are represented by
1389 triangles, experiments with added B are represented by squares, lines show bi-direction
1390 error bars (1 sd). Experiments conducted at different temperatures are shown in different
1391 colors: blue ~ 20, black ~ 25, orange ~ 33, and red ~ 40 °C. Most experiments were
1392 conducted at ~ 25 °C, 2 experiments were run at each of the other temperatures.



1393

1394 Figure S7. Relationship between B/Ca (mmol/mol) in aragonite and various solution

1395 chemistry parameters. Units for all species in solution are $\mu\text{mol/kg sw}$. Symbols are as
1396 described for Figure S6.

1397

1398

1399 Table S1. Experiment name, general description of precipitation approach used and any
 1400 organic additives added. All experiments were carried out at 25 – 25.5 °C unless
 1401 specified otherwise. Those carried out at ~20 °C are highlighted in blue, ~33 °C in
 1402 orange, ~40 °C in red.

Experiment name/ precipitate	Description	Additives
1/19/11 a	Degassing, bubbled with air	calcein, OTC, alizarin
1/19/11 c	Degassing, bubbled with air	calcein
1/19/11 d	Degassing, bubbled with air	
1/19/11 f	Degassing, bubbled with air	
1/20/11 1	Pumping with Na ₂ CO ₃	calcein, OTC
1/20/11 2	Pumping with Na ₂ CO ₃	
1a	Degassing	
1c	Degassing with added B	
1e	Degassing with added B	TRIS
1f	Pumping with Na ₂ CO ₃	
1g	Pumping with Na ₂ CO ₃	
1h / ts20	Pumping with Na ₂ CO ₃	
2a / ts9	Degassing, bubbled with air	
2b / ts8	Degassing, bubbled with air, added CaCl ₂	
2c / ts6	Degassing, bubbled with air, added B	
2d / ts11	Degassing, bubbled with air, added B	HEPES
2e / ts5	Degassing, bubbled with air, added B	TRIS
2f / ts10	Pumping with Na ₂ CO ₃ /NaHCO ₃ , Na ₂ CO ₃ during precipitation	
2g / ts1	Pumping with Na ₂ CO ₃ /NaHCO ₃	
2h / ts2	Pumping with Na ₂ CO ₃ , 20 °C	
3a / ts19	Degassing, bubbled with air	
3b / ts16	Degassing, bubbled with air	
3c / ts18	Degassing, bubbled with air, added B	
3d / ts17	Degassing, bubbled with air, added B	
3e / ts15	Degassing, bubbled with air, added B	TRIS
3f / ts12	Pumping with Na ₂ CO ₃	
3g / ts3	Pumping with Na ₂ CO ₃ /NaHCO ₃ , Na ₂ CO ₃ during precipitation	
3h	Pumping with Na ₂ CO ₃ , 33 °C	
4a / ts26	Degassing, bubbled with air	
4b / ts33	Degassing, bubbled with air, added CaCl ₂	
4c / ts28	Degassing, bubbled with air, added CaCl ₂	
4d / ts29	Degassing, bubbled with air, added Na ₂ CO ₃ and 2xsw	

4e / ts32	Degassing, bubbled with air, added Na ₂ CO ₃	
4f / ts22	Pumping with NaHCO ₃ , Na ₂ CO ₃ during precipitation	
4g / ts4	Pumping with Na ₂ CO ₃ /NaHCO ₃ , Na ₂ CO ₃ during precipitation	
5a / ts41	Degassing, bubbled with ~5000 ppmv CO ₂	
5b / ts39	Degassing, bubbled with ~5000 ppmv CO ₂ , added Na ₂ CO ₃ and B	
5c / ts40	Degassing, bubbled with ~5000 ppmv CO ₂ , added CaCl ₂ and B	
5d / ts42	Degassing, bubbled with ~5000 ppmv CO ₂ , added B	HEPES
5e / ts38	Degassing, bubbled with ~5000 ppmv CO ₂ , added B	TRIS
5f / ts24	Pumping with Na ₂ CO ₃	
5g / ts14	Pumping with NaHCO ₃ , Na ₂ CO ₃ during precipitation	
5h / ts7	Pumping with Na ₂ CO ₃ , 40 °C	
6a / ts54	Degassing, bubbled with ~15000 ppmv CO ₂ , added B	
6b / ts49	Degassing, bubbled with ~15000 ppmv CO ₂ , added CaCl ₂ and B	
6c / ts52	Degassing, bubbled with ~15000 ppmv CO ₂ , added NaHCO ₃ and B	
6d	Degassing, bubbled with ~15000 ppmv CO ₂ , added B	HEPES
6e / ts43	Degassing, bubbled with ~15000 ppmv CO ₂ , added B	TRIS
6f / ts50	Pumping with Na ₂ CO ₃	
6g / ts23	Pumping with NaHCO ₃ , Na ₂ CO ₃ during precipitation	
6h / ts13	Pumping with NaHCO ₃ , Na ₂ CO ₃ during precipitation, 40 °C	
7g / ts25	Pumping with NaHCO ₃ , Na ₂ CO ₃ during precipitation	
7h / ts21	Pumping with NaHCO ₃ , Na ₂ CO ₃ during precipitation, 33 °C	
8f / ts44	Pumping with seawater containing CaCO ₃ and SrCO ₃ (dissolved with CO ₂), bubbled with air	
8g / ts27	Pumping with Na ₂ CO ₃ /NaHCO ₃ , Na ₂ CO ₃ during precipitation	
8h / ts31	Pumping with NaHCO ₃ , Na ₂ CO ₃ during precipitation, 20 °C	

9g / ts30	Pumping with NaHCO ₃ , Na ₂ CO ₃ during precipitation	
9h / ts37	Pumping with NaHCO ₃ , Na ₂ CO ₃ during precipitation, bubbled with ~5000 ppmv CO ₂	
10g / ts36	Pumping with NaHCO ₃ , Na ₂ CO ₃ during precipitation, bubbled with ~2000 ppmv CO ₂	
10h / ts45	Pumping with NaHCO ₃ , Na ₂ CO ₃ during precipitation, added B	
11g / ts46	Pumping with NaHCO ₃ , Na ₂ CO ₃ during precipitation, added B, bubbled with ~15 000 ppmv CO ₂	
11h / ts48	Pumping with Na ₂ CO ₃ /NaOH	
12g / ts51	Pumping with Na ₂ CO ₃	calcein
13g / ts53	Pumping with seawater containing CaCO ₃ and SrCO ₃ (dissolved with CO ₂), bubbled with air	
13h / ts47	Pumping with Na ₂ CO ₃ /NaOH	

1403

Table S2. Summary of experimental chemistry during precipitation, B/Ca ratios in the precipitate, and K_D values. The standard deviation for solution chemistry values is given in the corresponding “sd” column. Experiments performed at different temperatures are in different colors: blue ~20 °C, black ~25 °C, orange ~33 °C, and red ~40 °C. TA, pH_T , and B/Ca (X-Series measurement) were measured, other values were calculated. For a subset of experiments B was also measured (see supplemental .xls file).

Exp.	pH_T	sd	TA ($\mu\text{mol}/\text{kg}$)	sd	TC ($\mu\text{mol}/\text{kg}$)	sd	HCO_3^- ($\mu\text{mol}/\text{kg}$)	sd	CO_3^{2-} ($\mu\text{mol}/\text{kg}$)	sd	Ω_{Arag}	sd	B (mmol/ kg)	sd	Borate ($\mu\text{mol}/\text{kg}$)	sd	B/Ca (mmol/ mol)	K_d
1/19/11a	7.72	0.05	11575	1914	11103	1862	10376	1752	573	96	13.4	3.2	0.404	0.000	49	5	0.22	0.097
1/19/11c	7.61	0.05	11684	2057	11401	2038	10740	1933	450	74	10.5	2.5	0.405	0.000	39	5	0.16	0.080
1/19/11d	7.78	0.04	11358	1961	10794	1881	10033	1753	633	118	15.0	3.8	0.402	0.000	54	5	0.21	0.087
1/19/11f	7.64	0.05	11586	2066	11268	2054	10605	1953	468	64	10.8	2.2	0.405	0.000	42	5	0.18	0.085
1/20/11- 1	8.33	0.04	4282	176	3486	86	2819	47	656	86	8.6	1.6	0.395	0.001	136	9	0.62	0.115
1/20/11- 2	8.34	0.06	4015	129	3248	57	2614	76	624	80	8.4	1.4	0.395	0.000	138	12	0.58	0.105
1a	7.71	0.03	8890	808	8491	758	7924	696	458	64	9.6	1.6	0.403	0.000	47	3	0.17	0.073

1c	7.59	0.04	8992	1049	8609	1015	8105	950	351	64	7.3	1.7	1.988	0.001	183	16	0.43	0.042
1e	7.58	0.02	20294	1313	14021	1179	13222	1105	555	62	10.5	1.7	1.970	0.000	173	7	0.39	0.051
1f	8.61	0.01	5826	54	4313	36	3017	22	1291	19	15.6	0.9	0.400	0.000	202	1	0.41	0.072
1g	8.79	0.01	5813	65	3999	40	2454	20	1542	25	20.4	1.0	0.396	0.000	238	1	0.43	0.071
1h	8.86	0.01	5907	73	3932	44	2251	19	1679	28	20.7	1.3	0.397	0.000	254	1	0.44	0.072
2a	7.91	0.01	9152	852	8456	789	7703	714	687	71	14.5	1.9	0.404	0.000	69	1	0.25	0.090
2b	7.81	0.01	9019	784	8475	732	7826	669	565	59	14.0	1.8	0.404	0.000	57	1	0.22	0.088
2c	7.77	0.02	10045	754	9311	699	8639	638	570	62	12.1	1.7	1.994	0.000	263	11	0.71	0.063
2d	7.68	0.02	16782	778	10312	624	9663	588	508	33	10.6	1.0	1.990	0.000	217	7	0.72	0.074
2e	7.63	0.00	22300	915	15281	905	14377	852	668	39	13.2	1.2	1.977	0.000	194	2	0.49	0.064
2f	8.47	0.01	7492	100	5936	71	4544	48	1381	32	18.5	0.9	0.398	0.000	167	2	0.34	0.075
2g	8.40	0.01	9715	270	7956	253	6327	231	1611	23	23.6	0.2	0.399	0.000	152	2	0.30	0.079
2h	8.96	0.00	7034	62	4700	40	2656	19	2041	22	27.6	1.0	0.397	0.001	261	1	0.32	0.055
3a	7.92	0.01	9615	843	8855	784	8038	712	750	67	15.4	1.8	0.406	0.000	72	1	0.28	0.103
3b	7.79	0.02	9040	893	8521	852	7885	791	547	55	11.0	1.5	0.406	0.000	56	2	0.24	0.097
3c	7.88	0.02	9597	844	8637	763	7875	681	691	80	14.0	2.0	2.022	0.000	334	11	0.84	0.064
3d	7.84	0.02	10623	705	9689	632	8897	562	704	72	14.5	1.8	2.063	0.000	313	12	0.85	0.070
3e	7.69	0.01	21855	1166	14118	1241	13218	1170	709	51	13.3	1.5	1.877	0.000	209	4	0.50	0.061

3f	8.95	0.01	6876	67	4426	34	2299	3	2124	32	29.9	1.0	0.396	0.000	273	1	0.35	0.060
3g	8.43	0.00	6976	61	5614	46	4400	32	1201	17	16.3	0.6	0.397	0.000	157	1	0.33	0.073
3h	8.56	0.01	5174	63	3708	35	2484	11	1220	27	16.9	0.9	0.398	0.000	208	2	0.44	0.074
4a	7.92	0.02	8452	945	7750	851	7011	751	681	102	13.7	2.5	0.405	0.000	72	3	0.25	0.085
4b	7.90	0.00	7884	1337	7268	1243	6614	1130	597	104	13.9	2.7	0.405	0.000	69	0	0.26	0.077
4c	7.85	0.01	9536	819	8894	760	8161	690	654	67	14.4	1.9	0.406	0.000	63	2	0.20	0.079
4d	7.91	0.02	10246	1522	9502	1442	8677	1332	748	98	14.6	2.6	0.397	0.000	69	3	0.24	0.089
4e	7.91	0.02	8433	1503	7802	1412	7118	1294	620	106	12.4	2.5	0.400	0.000	69	2	0.24	0.074
4f	8.16	0.00	11956	136	10522	122	9111	107	1365	15	18.1	0.7	0.398	0.000	105	0	0.22	0.078
4g	8.47	0.00	9161	83	7294	64	5586	48	1695	21	23.6	0.9	0.398	0.000	167	1	0.26	0.063
5a	7.62	0.01	13509	1317	13058	1258	12258	1172	604	72	14.3	2.2	0.412	0.000	41	1	0.13	0.075
5b	7.59	0.01	16006	1586	15475	1555	14594	1468	617	61	14.1	2.0	1.949	0.000	175	3	0.43	0.059
5c	7.55	0.01	13669	1460	13217	1419	12466	1336	513	61	14.9	2.2	2.050	0.000	174	3	0.47	0.059
5d	7.53	0.01	19533	1550	14885	1476	14061	1393	537	57	12.5	1.9	2.046	0.000	164	2	0.52	0.070
5e	7.38	0.02	25217	1844	21058	1981	19938	1877	531	39	11.5	1.6	2.032	0.000	121	5	0.32	0.059
5f	9.04	0.00	7783	50	4855	25	2281	6	2573	24	33.7	1.1	0.397	0.000	290	1	0.31	0.054
5g	8.02	0.00	14910	180	13591	171	12194	160	1314	14	17.4	0.6	0.398	0.000	81	1	0.17	0.075
5h	8.43	0.01	4718	33	3406	20	2335	14	1066	14	15.3	0.7	0.399	0.000	196	1	0.46	0.077

6a	7.52	0.03	16546	884	16130	809	15220	747	593	68	14.9	2.1	1.724	0.000	138	9	0.40	0.071
6b	7.28	0.06	15110	1087	15331	1226	14368	1065	327	33	9.6	1.1	1.719	0.000	86	6	0.29	0.061
6c	7.44	0.01	18640	1395	18416	1372	17432	1296	546	50	12.8	1.7	1.715	0.000	114	2	0.31	0.062
6d	7.49	0.02	22684	1084	16951	639	16018	600	577	45	14.1	1.5	1.715	0.000	130	7	0.42	0.078
6e	7.46	0.01	31275	1792	26396	1744	24973	1648	829	64	17.5	2.4	1.703	0.000	120	2	0.26	0.062
6f	8.38	0.01	5348	42	4324	32	3446	27	868	13	11.2	0.6	0.402	0.000	150	2	0.40	0.079
6g	8.24	0.00	10397	146	8952	136	7573	125	1348	14	17.2	0.8	0.397	0.000	119	1	0.23	0.073
6h	7.91	0.01	7949	104	7033	92	6139	85	852	24	12.7	0.6	0.399	0.000	90	2	0.23	0.073
7g	8.00	0.00	20209	219	18509	211	16657	199	1733	18	23.6	0.9	0.399	0.000	79	1	0.14	0.072
7h	8.01	0.01	10056	110	8919	110	7793	108	1078	14	15.3	0.6	0.397	0.000	94	1	0.23	0.082
8f	7.90	0.03	8138	409	7545	363	6897	321	585	57	12.7	1.4	0.396	0.000	66	4	0.21	0.076
8g	8.49	0.01	10083	143	7974	114	6028	87	1932	34	25.8	1.3	0.397	0.000	172	1	0.22	0.057
8h	8.28	0.00	13102	185	11418	168	9777	149	1600	19	20.1	0.9	0.399	0.000	116	1	0.22	0.076
9g	7.79	0.01	30772	528	29287	503	27224	468	1746	42	21.9	1.4	0.402	0.000	53	1	0.09	0.071
9h	7.89	0.01	16954	402	15830	385	14510	360	1187	27	14.1	1.1	0.402	0.000	65	1	0.14	0.075
10g	8.09	0.01	15660	461	14071	428	12436	390	1562	41	18.3	1.6	0.398	0.000	92	1	0.20	0.087
10h	7.78	0.01	29597	532	28033	485	26074	441	1648	61	21.0	1.6	1.716	0.017	223	6	0.30	0.055
11g	7.80	0.01	23314	436	21955	419	20382	395	1343	26	17.3	1.1	1.790	0.028	242	4	0.39	0.060

12g	8.87	0.03	6744	306	4489	145	2530	10	1956	150	24.1	3.6	0.398	0.000	256	7	0.38	0.065
13g	7.90	0.01	8296	392	7711	363	7069	329	579	34	10.6	0.9	0.396	0.000	65	1	0.19	0.069
13h	9.32	0.01	5177	382	2809	227	895	72	1913	156	24.9	3.3	0.394	0.000	329	1	0.57	0.073

Table S3. Pearson correlation coefficients for mean solution chemistry parameters showing the most significant correlations with the B/Ca ratio of the precipitate, as well as various proposed ratios suggested to be linked to B/Ca regardless of significance. Correlation coefficients are given for the data set as a whole as calculated in the main text (Table 1), for calculations using the Pitzer model of Hain et al. (2015), and for calculations using the Pitzer model of Hain et al. (2015) taking into account the effects of [Mg] and [Ca].

Species in solution	Correlation with B/Ca (main text)	Correlation with B/Ca (Pitzer model)	Correlation with B/Ca (correcting for [Mg] and [Ca])
pH _T	0.03	0.03	0.03
[HCO ₃ ⁻]	-0.16	-0.16	-0.18
DIC	-0.18	-0.17	-0.18
$\frac{[\text{B}(\text{OH})_4^-]^2}{[\text{CO}_2][\text{HCO}_3^-]^2}$	0.19	0.19	0.19
$\frac{[\text{B}(\text{OH})_4^-]}{[\text{HCO}_3^-]}$	0.33	0.32	0.35
$\frac{[\text{B}(\text{OH})_4^-]}{([\text{CO}_3^{2-}] + [\text{HCO}_3^-])}$	0.47	0.47	0.51
[B(OH) ₃]	0.55	0.55	0.55
[B(OH) ₄ ⁻]	0.79	0.78	0.84

$[B]/[HCO_3^-]$	0.81	0.79	0.83
$[B(OH)_4^-]/[CO_3^{2-}]$	0.83	0.83	0.86
$[B]/([CO_3^{2-}] + [HCO_3^-])$	0.89	0.89	0.89
$[B]/[DIC]$	0.89	0.89	0.89
$[B(OH)_4^-]*[Ca^{2+}]$	0.92	0.92	0.91
$[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$	0.95	0.95	0.95

Table S4. Apparent partition coefficients for potential relationships between B/Ca in the precipitate and solution chemistry parameters. Solution chemistry was calculated using constants from Hain et al. (2015) taking into account the effects of [Mg] and [Ca]. B/Ca is in mmol/mol, units are $\mu\text{mol/kg}$ for all solution chemistry parameters except $[Ca^{2+}]$ which is in mmol/kg.

	$K = B/Ca/[B(OH)_4^-]/[CO_3^{2-}]^{0.5}$	$K = B/Ca/[B]/[DIC]$	$K = B/Ca/[B(OH)_4^-]*[Ca^{2+}]$	$K = B/Ca/[B(OH)_4^-]$
average K	0.0748	4.16	0.000227	0.00237
minimum K	0.0455	1.59	0.000123	0.00108
maximum K	0.111	7.12	0.000359	0.00388
standard deviation	0.0123	1.11	0.0000577	0.000645

Table S5. Mean absolute differences between measured and calculated B/Ca as calculated with equations S1-S10 relative to the measured value and standard deviation.

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
mean	0.107	0.141	0.166	0.201	0.104	0.083	0.082	0.139	0.081	0.093
standard deviation	0.082	0.118	0.145	0.188	0.76	0.066	0.065	0.140	0.067	0.074

A supplemental .zip file is available which contains detailed data for each run, XRD patterns and/or Raman spectra for each precipitate, a full summary of precipitation chemistry and precipitate chemistry as determined with different measurement and extraction techniques.