**Core-top calibration of B/Ca in Pacific Ocean *Neogloboquadrina incompta* and
Globigerina bulloides as a surface water carbonate system proxy**

Quintana Krupinski, Nadine B.^{1,2,*}; Russell, Ann D.³; Pak, Dorothy K.⁴; Paytan,
Adina¹.

14 **1. Abstract**

15

16 Practical methods for reconstructing past ocean carbonate chemistry are needed to
17 study past periods of ocean acidification and improve understanding of the marine
18 carbonate system's role in the global climate cycles. Planktic foraminiferal B/Ca may
19 fill this role, but requires better understanding and improved proxy calibrations. We
20 used Pacific Ocean core-top sediments to generate new calibrations of the B/Ca proxy
21 for past carbonate system parameters in two upwelling/subpolar species of asymbiotic
22 planktic foraminifera (*Globigerina bulloides* and *Neogloboquadrina incompta*). Both
23 species show significant positive correlation of B/Ca with calcite saturation (Ω_{calcite})
24 and carbonate ion concentration ($[\text{CO}_3^{2-}]$) across a broad range of environmental
25 conditions. This suggests a calcification rate control on B/Ca incorporation (as Ω_{calcite}
26 regulates calcification rate), in agreement with recent inorganic calcite studies. This is
27 also consistent with a surface entrapment model of trace element incorporation into
28 CaCO_3 . In neither species is B/Ca significantly correlated with pH, suggesting that
29 pH does not directly regulate boron incorporation, and that calculation of pH directly
30 from foraminiferal B/Ca is not suitable. Correlations between B/Ca and $[\text{B}(\text{OH})_4^-]$,
31 $[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]$ and $[\text{B}(\text{OH})_4^-]/\text{DIC}$ are weaker than with Ω_{calcite} . Boron partition
32 coefficients ($K_D = [\text{B}/\text{Ca}]_{\text{solid}} / [\text{B}(\text{OH})_4^- / \text{HCO}_3^-]_{\text{seawater}}$) show little or no correlation
33 with $[\text{CO}_3^{2-}]$ or temperature and vary widely, providing no support for application of
34 K_D to calculate carbonate system parameters from B/Ca. We also discuss potential
35 effects of depth-related dissolution, temperature, and salinity on B/Ca. These

36 empirical calibrations linking foraminiferal calcite B/Ca with Ω_{calcite} provide a strong
37 tool for reconstructing the past ocean carbonate system and improve our
38 understanding of the proxy's geochemical basis.
39

40 **2. Introduction**

41

42 The global ocean acts as a major reservoir for atmospheric CO₂ and thus plays a
43 fundamental role in the climate system. Uptake of atmospheric CO₂ by the oceans
44 both in the past and today results in lower ocean pH and calcium carbonate saturation
45 (Ω_{calcite} and $\Omega_{\text{aragonite}}$), impacting many marine organisms that are sensitive to
46 fluctuations in these carbonate system parameters (Doney et al., 2009). In light of
47 accelerating anthropogenic CO₂ emissions and ocean acidification, there is a need for
48 proxies that can be used to reconstruct past ocean carbonate chemistry and provide
49 data sets for climate model testing. Constraining the marine carbonate system requires
50 quantitative knowledge of at least two of the six marine carbonate system parameters
51 (pH, [CO₃²⁻], [HCO₃⁻], [CO_{2aq}], total alkalinity (TA), dissolved inorganic carbon
52 (DIC) (Zeebe and Wolf-Gladrow, 2005)) as well as temperature, salinity, and
53 pressure, and allows insight into ocean-atmosphere carbon exchange, and in areas
54 where surface waters and the atmosphere are equilibrated, could allow reconstruction
55 of past atmospheric $p\text{CO}_2$.

56

57 While proxies for some carbonate system parameters have been developed and
58 applied (e.g. boron isotope ($\delta^{11}\text{B}$) in CaCO₃ for seawater pH reconstruction),
59 carbonate system proxies that can be applied at moderate or high resolution in down-
60 core studies are needed. The ratio of boron to calcium (B/Ca) in planktic
61 foraminiferal calcite has been suggested as a proxy for one of several related seawater

62 variables: either carbonate ion concentration ($[\text{CO}_3^{2-}]$ (Foster, 2008; Hendry et al.,
 63 2009)), the ratio of seawater borate to bicarbonate ($[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]$ (Palmer et al.,
 64 2010; Tripathi et al., 2009; Yu et al., 2007b)), or the ratio of borate to dissolved
 65 inorganic carbon ($[\text{B}(\text{OH})_4^-]/[\text{DIC}]$ (Allen and Hönisch, 2012; Allen et al., 2012)) (the
 66 latter two may serve as proxies for pH if total aqueous boron and DIC are known).
 67
 68 The relationship between B/Ca and $[\text{CO}_3^{2-}]$ is consistent with studies reporting a
 69 strong calcification rate control over B/Ca in inorganic calcite (Gabitov et al., 2014;
 70 Kaczmarek et al., 2016; Ruiz-Agudo et al., 2012; Uchikawa et al., 2015); some
 71 foraminiferal calcite data also suggest calcification rate control over B/Ca (Henehan
 72 et al., 2015; Naik and Naidu, 2014; Penman et al., 2014). Calcification rate is
 73 regulated by Ω_{calcite} (Zeebe and Wolf-Gladrow, 2005; $\Omega_{\text{calcite}} = ([\text{CO}_3^{2-}][\text{Ca}^{2+}])_{\text{in situ}}/K_{\text{sp}}$, where K_{sp} is $([\text{CO}_3^{2-}][\text{Ca}^{2+}])_{\text{saturation}}$); since $[\text{Ca}^{2+}]$ varies only slightly in the
 74 global ocean, variability in $[\text{CO}_3^{2-}]_{\text{in situ}}/[\text{CO}_3^{2-}]_{\text{saturation}}$ is the dominant control over
 75 Ω and calcification rate. Reconstructed Ω_{calcite} , pH or $[\text{CO}_3^{2-}]$ can be combined with
 76 another carbonate system variable and data on temperature, pressure, salinity and
 77 total P and Si content to reconstruct the entire carbonate system. An important
 78 analytical advantage of B/Ca over $\delta^{11}\text{B}$ as a carbonate-system proxy is its smaller
 79 sample size requirements and simpler sample preparation and analysis, which can be
 80 performed concurrently with analysis of other elemental ratios such as Mg/Ca (widely
 81 used for paleo-temperature reconstruction) and U/Ca and Li/Ca (other elements which
 82 may reflect the carbonate system), allowing higher-resolution records to be produced.
 83

84

85 The development and application of boron-based carbonate system proxies (B/Ca and
86 $\delta^{11}\text{B}$) is based on the pH control over the relative abundance of the two dissolved
87 aqueous boron species in seawater (borate ($\text{B}(\text{OH})_4^-$) and boric acid ($\text{B}(\text{OH})_3$)), of
88 which $\text{B}(\text{OH})_4^-$ dominates at higher pH (Hemming and Hanson, 1992). Because the
89 boron isotope ($\delta^{11}\text{B}$) composition of calcite agrees with the seawater $\text{B}(\text{OH})_4^-$ $\delta^{11}\text{B}$
90 composition, Hemming and Hanson (1992) suggested that the tetrahedral $\text{B}(\text{OH})_4^-$ is
91 adsorbed onto calcite surfaces and then dehydroxylated to form BO_3^{3-} during calcite
92 formation, ultimately substituting for CO_3^{2-} in the calcite lattice. The calcite B
93 concentration and $\delta^{11}\text{B}$ ultimately depends on the $\text{B}(\text{OH})_4^-$ concentration in seawater
94 (a function of pH), and potentially also on other factors. An equilibrium reaction and
95 partition coefficient (K_D) for boron incorporation were proposed by Hemming and
96 Hanson (1992):

97

99

$$100 \quad K_D = [\text{HBO}_3^{2-} / \text{CO}_3^{2-}]_{\text{solid}} / [\text{B}(\text{OH})_4^- / \text{HCO}_3^-]_{\text{seawater}} \quad (2)$$

101

102 This expression for K_D was later simplified, based on the stoichiometry of calcite

103 $[\text{CO}_3^{2-}] \approx [\text{Ca}^{2+}]$ (Yu et al., 2007b):

104

$$105 \quad K_D = [\text{B/Ca}]_{\text{solid}} / [\text{B}(\text{OH})_4^- / \text{HCO}_3^-]_{\text{seawater}} \quad (3)$$

106

107 Initial core-top calibrations of the B/Ca proxy in planktic foraminifera applied the
108 theoretical partition coefficient (K_D ; equation 3) to calculate pH or $[\text{CO}_3^{2-}]$, and found
109 a strong relationship of K_D with temperature (Foster, 2008; Yu et al., 2007b) (but
110 with opposite sign), and sometimes with $[\text{CO}_3^{2-}]$ (Foster, 2008) or growth rate (Ni et
111 al., 2007). However, lack of consensus about how to apply K_D , strong covariance of
112 carbonate system parameters with one another and with temperature, and an
113 incomplete understanding of the role of individual ion species on boron incorporation
114 created uncertainty regarding application of K_D with this proxy (Allen and Hönisch,
115 2012; Seki et al., 2010). Further, some of the K_D -based carbonate system
116 reconstructions (Foster, 2008; Tripathi et al., 2009; Yu et al., 2007b) yielded results for
117 some species that were later shown to be effectively independent of the measured
118 variations in B/Ca (Allen and Hönisch, 2012; Seki et al., 2010). Subsequent
119 calibration of the B/Ca proxy in cultured planktic foraminifera has shown strong
120 direct relationships between B/Ca and carbonate system parameters (Allen et al.,
121 2012, 2011). Accordingly, some researchers recommend that calibrations of this
122 proxy test and develop empirical calibrations of the B/Ca proxy directly with
123 environmental parameters, rather than using K_D (Allen et al., 2012; Allen and
124 Hönisch, 2012), like with other trace element proxies (e.g. Mg/Ca). We follow this
125 approach, and discuss mechanistic explanations for our results.

126

127 While laboratory culture studies have begun to establish B/Ca calibrations for
128 photosymbiont-bearing tropical or subtropical species of planktic foraminifera (Allen
129 et al., 2012, 2011), little B/Ca calibration work has been done in species common in
130 nutrient-rich upwelling zones and mid- and high-latitude areas. In addition, B/Ca has
131 been under-studied in asymbiotic species, whose carbonate chemistry is not affected
132 by symbiont photosynthesis and thus may be easier to interpret.

133

134 In this study, we present Pacific core-top calibrations of B/Ca in two asymbiotic
135 species common in subpolar, temperate, and upwelling zones, *Neogloboquadrina*
136 *incompta* (also known as *Neogloboquadrina pachyderma* (dextral)) and *Globigerina*
137 *bulloides*, and investigate controls on boron incorporation in these species in Pacific
138 Ocean samples. Because of the wide geographical distributions and range of habitats
139 of this study's samples (Fig. 1), we assign calcification depths appropriate for each
140 sample based on its Mg/Ca or $\delta^{18}\text{O}$ temperature or literature data, and then assign
141 water column carbonate chemistry data (based on the sample-specific calcification
142 depth) for establishing a B/Ca calibration. Robust calibrations for *N. incompta* and *G.*
143 *bulloides* will allow quantitative reconstructions of ocean carbonate chemistry in new
144 regions, allowing us to study past ocean acidification events and interactions between
145 seawater carbonate chemistry and climate.

146

147 **3. Methods**

148 3.1. Samples

149 Elemental and isotopic analyses were conducted on two species of planktic,
150 asymbiotic foraminifera from Pacific Ocean core-top samples (Fig. 1) representing a
151 range of carbonate chemistry and temperature conditions. *G. bulloides* is often found
152 in a near-surface to mixed layer habitat, and *N. incompta* is commonly found close to
153 the thermocline, but sometimes nearer to the surface (absolute depth ranges for both
154 species vary by region) (Field, 2004, Sautter & Thunell, 1991a). *N. incompta* from 31
155 sites and *G. bulloides* from 37 sites were analyzed (Table S1, S2).

156
157 Core-top samples came from a combination of different surface-preserving core
158 types, including multicores, box-cores, gravity and piston cores, and push cores
159 obtained by ROV (Remotely Operated Vehicle), and were collected from water
160 depths between 250 m and 3900 m (Table S1, S2; Fig. 2). All samples were from the
161 upper 9 cm of the sediment, and most (54 of the 68) were from the upper 5 cm,
162 indicating that the samples most likely represent late Holocene sediments. Samples
163 were confirmed to be of Holocene age either by previous age determination by other
164 investigators or verified using the $\delta^{18}\text{O}$ values of *N. incompta* and *G. bulloides* (Table
165 S1, S2).

166 3.2. Sample preparation

167 For each core-top sample, ~80 *N. incompta* tests in the 125-250 μm size fraction or
168 ~40 *G. bulloides* tests in the 250-355 μm size fraction (seven samples were from a

169 wider size range due to limited abundance, but only three of these were used in the
170 calibration, and do not represent outliers in the data; Table S1) were picked for a total
171 weight of ~200-350 µg per sample. Mean weight per shell of pooled shells in each
172 sample was determined using a Sartorius Microbalance scale. The samples were
173 crushed and cleaned following the methods of Martin and Lea (2002) (revised from
174 Boyle and Keigwin, 1985). Sample cleaning consisted of multiple ultrasonication
175 steps in boron-clean MilliQ water and methanol, a reductive and oxidative step, and
176 additional rinses with boron-clean MilliQ water. A reductive cleaning step was
177 included because it has been shown that this step is important for removal of Mg
178 associated with remnant organic matter and adsorbed phases (Bian and Martin, 2010).
179 These methods have been shown by Yu et al. (2007a) to yield results equivalent to
180 those without the reductive step (Barker et al., 2003), though the reductive step results
181 in some preferential Mg loss (about 15%, which can be corrected for following
182 Regenberg et al. (2006) and Rosenthal et al. (2004) – not corrected here). All sample
183 handling following crushing was done in a laminar flow fume hood, and samples
184 were kept closed whenever possible to avoid boron contamination from air filters.

185 *3.3. Elemental analysis*

186 All analyses (¹¹B, ²⁴Mg, ⁴³Ca, ²³⁸U, ²⁷Al, ⁵⁵Mn and ⁵⁶Fe) were conducted concurrently
187 by Inductively Coupled Mass Spectrometer (ICP-MS, Finnigan Element XR) at
188 UCSC using the procedure described in Brown et al. (2011) based on established
189 techniques (Al-Ammar et al., 2000; Rosenthal et al., 1999). The cleaned tests were
190 transferred to acid-cleaned plasticware on the day of analysis and dissolved in 400 µL

191 of 0.075 HNO₃ (Optima grade). A small number of early analytical runs were free-
192 aspirated using a Teflon spray-chamber, but the vast majority of analyses used a
193 peristaltic pump and a cyclonic quartz spray chamber. These results were comparable,
194 but the latter pumping technique had a more stable calcium signal. Ammonia gas
195 injected into the spray chamber at 5 mL/min reduced the memory effects common in
196 boron analysis. Instrument boron blanks were reduced using washout and uptake
197 times of 30 s and 40 s, respectively.

198

199 In-run blanks for all elements of interest were measured on the same 0.075N nitric
200 acid solution used for sample dissolution. To monitor intra-run variability, a liquid
201 consistency standard (B/Ca = 60.14 µmol/mol, [Ca] = 100 ppm) and a solid
202 foraminiferal consistency standard (composed of crushed and mixed *Pullenia*
203 *obliquiloculata* (>500 µm) from core-top PLDS-77BX; B/Ca = 51.5 µmol/mol) were
204 used. To account for possible matrix effects due to varying [Ca] and
205 Element/Calcium (El/Ca) in the samples, we used a set of five liquid calibration
206 standards of varying El/Ca diluted to four calcium concentrations ranging from 20-
207 150 ppm to generate calibration equations for each element before each day's
208 analysis. However, matrix effects (differing [Ca] for the same El/Ca) were small
209 (calibration equations for different [Ca] with the same El/Ca were not significantly
210 different), and so element daily calibrations combined El/Ca results at differing [Ca]
211 into a single calibration equation. We corrected for drift and mass bias using the
212 liquid consistency standard. When foraminiferal abundance permitted, we performed

213 duplicate analyses of foraminifera by splitting crushed samples before cleaning (56%
214 of *N. incompta* samples, 43% of *G. bulloides* samples). The boron blank during
215 analysis was ~9% of the liquid consistency standard B value (blanks for all other
216 elements were lower) and was subtracted from the signal; the blank remained
217 relatively stable during a typical run. Replicate analysis of the solid foraminiferal
218 consistency standard yielded reproducibility of $\pm 7\%$ ($3.5 \mu\text{mol/mol}$; 1σ) for B/Ca and
219 $\pm 9\%$ (0.19 mmol/mol ; 1σ) for Mg/Ca between runs; this standard is used to confirm
220 long-term stability of the liquid standards and to provide the most conservative error
221 bars on the foraminiferal El/Ca data. The between-run reproducibility (based on
222 measurement of the liquid consistency standard and blanks after every 5 samples;
223 $n=139$) was $\pm 1.2\%$ (1σ) for B/Ca and $\pm 0.3\%$ for Mg/Ca, and the in-run
224 reproducibility was $\pm 1.3\%$ (1σ) for B/Ca and $\pm 0.4\%$ for Mg/Ca.

225 3.4. Stable isotopes

226 Carbon and oxygen stable isotope ratios were measured for all core-top samples of
227 both species in the same size fractions used for elemental analysis. Depending on
228 shell weight, 4-18 tests were pooled per sample, and replicate analyses were
229 conducted for approximately half the samples. Samples were analyzed at UCSC using
230 an IRMS (MAT-256) with a Kiel auto-carbonate device, or, for 14 samples, using a
231 Prism model IRMS with a dual inlet carbonate device. Analytical precision based on
232 replicate measurements of the in-house carbonate standard Carrara Marble and NBS-
233 19 included with each analytical run was $\pm 0.06 \text{ ‰}$ for $\delta^{18}\text{O}$ and $\pm 0.03 \text{ ‰}$ for $\delta^{13}\text{C}$
234 (1σ).

235 3.5. Hydrographic data

236 Hydrographic data for most core-top sites were obtained from the 2009 World Ocean
237 Atlas (WOA09; water column temperature, salinity, and nutrient concentrations
238 ($[\text{PO}_4^{3-}]$ and $[\text{SiO}_3]$), http://www.nodc.noaa.gov/OC5/WOA09/pr_woa09.html) and
239 DIC (also known as TCO_2), total alkalinity (ALK) and anthropogenic CO_2 were
240 obtained from the Global Ocean Data Analysis Project (GLODAP, version 1.1; Key,
241 2004). Gridded output was produced using Ocean Data View's 3D interpolation tool
242 (Schlitzer, 2006) (Table S1, S2). For the coastal areas, we selected non-gridded
243 hydrographic data that is more geographically precise due to the greater spatial
244 variability of hydrographic conditions and because these areas are more heavily
245 represented in our dataset. Data sources for coastal sample areas in Southern
246 California and Washington State are the North American Carbon Program (2007 data;
247 Feely et al., 2008) and the Pacific Marine Environmental Lab (PMEL) West Coast
248 Carbon Cruise (2011 data; Patsavas et al., 2015), and data for one Canadian coastal
249 sample are from the 2010 Canadian Coastal Carbon Cruise (British Columbia, D.
250 Ianson, pers. comm.) (Table S1, S2).

251

252 After correcting DIC for anthropogenic CO_2 contribution (Sabine et al., 2004), we
253 used the hydrographic data to calculate pre-industrial carbonate system parameters
254 (pH , $[\text{CO}_3^{2-}]$, HCO_3^- , DIC, $\text{B}(\text{OH})_4^-$, and other derivative parameters; Table S1 and
255 S2) using the program $\text{CO}_2\text{sys.xls}$ version 2.1 (Pelletier et al., 2007), with K_1 and K_2
256 from Lueker et al., 2000, K_B and K_{HSO_4} from Dickson (1990), total B from Lee et al.,

257 (2010), and pH on the total scale. At each sample location, we determined bottom
258 water $\Delta[\text{CO}_3^{2-}]$ ($\Delta[\text{CO}_3^{2-}] = [\text{CO}_3^{2-}]_{\text{in-situ}} - [\text{CO}_3^{2-}]_{\text{saturation}}$) to evaluate potential post-
259 depositional effects on shell chemistry using gridded data from the WOA09
260 hydrographic and the GLODAP 1.1 carbonate chemistry datasets.

261 3.6. Calcification depths

262 One of the largest sources of uncertainty in relating foraminiferal shell chemistry to
263 water column conditions derives from the selection of calcification depths and the
264 corresponding temperature, salinity, and carbonate system parameters. Vertical
265 gradients in hydrographic parameters (including carbonate chemistry) are often steep,
266 such that selection of a depth some tens of meters shallower or deeper results in
267 significantly different calcification conditions. As this study uses samples from
268 diverse geographic and oceanographic conditions, we assigned a specific calcification
269 depth for each sample area and species.

270

271 Calcification depths were generally assigned based on temperatures reconstructed
272 from Mg/Ca for *G. bulloides* and from $\delta^{18}\text{O}$ for *N. incompta* (Table S1, S2). We
273 matched the proxy-derived calcification temperature to the local temperature profile
274 from hydrographic data to select calcification depth and depth-specific hydrographic
275 parameters. For *G. bulloides*, we applied the species-specific Mg/Ca temperature
276 calibration of Mashiotto et al. (1999); these calculated temperatures were generally
277 within 1°C of those calculated from other region-specific *G. bulloides* Mg/Ca-
278 temperature calibrations (Marr et al., 2011; McConnell and Thunell, 2005).

279

280 Although we measured Mg/Ca in *N. incompta*, existing calibration relationships for
281 *N. incompta* (von Langen et al., 2005) and *N. pachyderma* (sinistral) (Elderfield and
282 Ganssen, 2000; Nürnberg et al., 1996) resulted in calcification depths that were much
283 deeper than described for this species. Depth-related partial dissolution in low bottom
284 water $\Delta[\text{CO}_3^{2-}]$ may have lowered the Mg/Ca values of some *N. incompta* samples in
285 this dataset (see discussion, Section 5.7). Indeed, *N. incompta* Mg/Ca shows a
286 significant ($p < 0.01$) decreasing trend with bottom water depth (Fig. 2C). Though
287 techniques exist for correcting Mg/Ca for depth-related dissolution (Mekik et al.,
288 2007; Regenberg et al., 2006), the required species-specific calibrations are not
289 available for *N. incompta*.

290

291 Therefore, for *N. incompta*, we used $\delta^{18}\text{O}$ temperatures to select calcification depths
292 ($\delta^{18}\text{O}$ is uncorrelated with core-top depth); when $\delta^{18}\text{O}$ -based calcification
293 temperatures were compared with local hydrographic profiles, they generally yielded
294 water temperatures in agreement with regionally-determined calcification depths
295 estimated from plankton tow and sediment trap studies. We used a *N. incompta*-
296 specific $\delta^{18}\text{O}$ -temperature calibration (von Langen et al., 2000, as in Bemis et al.
297 2002), and to select local water $\delta^{18}\text{O}$, we used the global sea surface $\delta^{18}\text{O}$ database
298 (Schmidt et al., 1999) (subtracting 0.04‰ from surface water values to account for *N.*
299 *incompta*'s subsurface calcification), or for Southern California core-tops, we applied
300 the local salinity- $\delta^{18}\text{O}$ relationship of Bemis et al. (2002) to calculate water $\delta^{18}\text{O}$ at a

301 typical calcification depth (Sautter and Thunell, 1991b). *N. incompta* $\delta^{18}\text{O}$ -based
302 calcification temperatures ranged between 7°-18°C for samples outside the equatorial
303 zone, and 13°-21°C for the eastern equatorial Pacific (3°N to 3°S).

304

305 However, in a small number of samples (n=6 for *N. incompta*, n=8 for *G. bulloides*),
306 both Mg/Ca and $\delta^{18}\text{O}$ calcification temperatures ($\pm 2^\circ\text{C}$) provided depths well outside
307 of the range of species- and region-specific literature values for calcification depth. In
308 those cases, we applied literature-based, region- and species-based calcification
309 depths (these previous studies determined calcification depths using plankton tows
310 and sediment traps, and some of these studies used Mg/Ca or $\delta^{18}\text{O}$ to determine
311 calcification depth; Table S1, S2), which compared well with nearby geochemically-
312 derived calcification depths. The calcification depths we used (whether from Mg/Ca,
313 $\delta^{18}\text{O}$, or selected from the literature) agree with those determined for the appropriate
314 regions in Pacific Ocean studies (Bolton and Marr, 2013; Field, 2004; Marr et al.,
315 2011; McConnell and Thunell, 2005; Pak and Kennett, 2002; Reynolds and Thunell,
316 1985; Sautter and Thunell, 1991a; Ujiie and Ujiie, 2000).

317 3.7. Data treatment

318 We evaluated the relationship between B/Ca and calcification depth water parameters
319 using the Pearson correlation coefficient of B/Ca with each parameter, a Student's t-
320 test, and a bivariate least squares regression (generated using PAST software;
321 (Hammer et al., 2001)). We also evaluated the correlation of calcification depth water

parameters with each other (Table S3) and of trace element data with each other (Table 4; (Hammer et al., 2001)). Parameters evaluated at calcification depth are temperature, salinity, $[\text{PO}_4^{3-}]$, alkalinity, DIC, pH, $[\text{CO}_3^{2-}]$, $\text{B}(\text{OH})_4^-$, Ω_{calcite} , and the ratio of $\text{B}(\text{OH})_4^-$ to HCO_3^- , DIC, and $[\text{CO}_3^{2-}]$, as well as bottom water $\Delta[\text{CO}_3^{2-}]$.

4. Results

4.1. Sample selection and trace element data quality assessment

Twenty-seven *G. bulloides* and twenty-four *N. incompta* samples were used for the core-top calibration based on the availability of water column carbonate chemistry data, sample age, and the quality of the El/Ca data (i.e. uncontaminated as determined by deviation of samples' U, Mn, Fe or Al values from other samples in the same region). B/Ca data show little or no significant correlation with the other elements measured, and Mg/Ca in *G. bulloides* is not significantly correlated with any other element (Table S4). Five additional *G. bulloides* samples that belong to a distinct morphotype of *G. bulloides* (referred to as “encrusted *G. bulloides*” due to an outer calcite crust) and had suitable water data were also used here. We present two calibrations for *G. bulloides*: one for only the non-encrusted *G. bulloides* (Section 5.4), and one including both encrusted (5) and non-encrusted (27) *G. bulloides* (Section 5.6). All foraminiferal geochemical data collected for this study are shown in Tables S1 and S2.

4.2. Core-top B/Ca

344 The samples used in this study span a broad range of hydrographic conditions,
 345 including temperature (~9-27 °C), salinity (~31.5-35.5), pH (~7.9 – 8.2), Ω_{calcite} (2.5-
 346 5.5), and $[\text{CO}_3^{2-}]$ (106-220 $\mu\text{mol/kg}$).
 347
 348 Core-top *N. incompta* B/Ca values (Fig. 3, S1, Table S1, S3) are significantly
 349 correlated ($p < 0.001$) with calcification depth-specific Ω_{calcite} ($r^2 = 0.83$), $[\text{CO}_3^{2-}]$ ($r^2 =$
 350 0.82), $[\text{B}(\text{OH})_4^-]$ ($r^2 = 0.77$), $[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]$ ($r^2 = 0.73$), $[\text{B}(\text{OH})_4^-/\text{DIC}]$ ($r^2 = 0.73$),
 351 salinity ($r^2 = 0.55$), and temperature ($r^2 = 0.52$). Core-top *G. bulloides* B/Ca values
 352 (Fig. 3, S1, Table S2, S3) are significantly correlated ($p < 0.001$) with calcification
 353 depth-specific Ω_{calcite} ($r^2 = 0.83$), $[\text{CO}_3^{2-}]$ ($r^2 = 0.81$), $[\text{B}(\text{OH})_4^-]$ ($r^2 = 0.69$), $[\text{B}(\text{OH})_4^-$
 354 $/\text{HCO}_3^-]$ ($r^2 = 0.69$), $[\text{B}(\text{OH})_4^-/\text{DIC}]$ ($r^2 = 0.67$), salinity ($r^2 = 0.50$), and temperature
 355 ($r^2 = 0.82$). Many of these variables are autocorrelated, as discussed below. In neither
 356 species is B/Ca correlated with DIC or PO_4^{3-} . In some regions, correlations between
 357 B/Ca and pH and temperature can be observed, but with very different, region-
 358 specific slopes (Fig. 4B,C,E,F), while regional correlations of B/Ca with Ω_{calcite} have
 359 similar slopes (Fig. 4A,D).
 360
 361 Though we measured U/Ca, and past studies show it may also have a relationship
 362 with carbonate chemistry (Russell et al., 2004), this relationship is inconsistent in
 363 both species studied (Table S4) and does not agree with previous studies, likely
 364 because U/Ca is more susceptible to redox-related post-depositional alteration than

365 many other commonly measured trace elements (Morford and Emerson,
 366 1999). Therefore, we do not treat the U/Ca data in this study.
 367
 368 We find large intraspecies differences in B/Ca values; *N. incompta* B/Ca values range
 369 from 43-78 $\mu\text{mol/mol}$, and *G. bulloides* B/Ca values range from 23-61 $\mu\text{mol/mol}$. In
 370 regressions of B/Ca and Ω_{calcite} , *N. incompta* has a steeper slope and higher B/Ca
 371 values than *G. bulloides* (Fig. 3A), showing that *N. incompta* has a higher carbonate
 372 chemistry sensitivity than *G. bulloides*. Such sensitivity and interspecies differences
 373 are also seen in other planktic foraminifera species (Allen et al., 2012; Foster, 2008;
 374 Yu et al., 2007b).
 375
 376 Calculated K_D values (Equation 3) range between 1.4 to 2.0 for *N. incompta* (mean =
 377 1.7 ± 0.2 (1σ)), and 0.7 to 1.2 for *G. bulloides* (mean 1.0 ± 0.1 (1σ); Fig. 5, Table S1,
 378 S2). K_D is uncorrelated (*N. incompta*) or weakly correlated with temperature (*G.*
 379 *bulloides*, $r^2 = 0.48$), and is not significantly correlated with $[\text{CO}_3^{2-}]$ in either species.
 380 Neither bottom water depth nor bottom water $\Delta[\text{CO}_3^{2-}]$ are correlated with B/Ca in
 381 either species (Fig. 2A, B), indicating that B/Ca in these samples is not affected by
 382 depth-related dissolution.

383

384 5. Discussion

385 5.1 Hydrographic context - decoupled variables

386 Previous studies of planktic foraminiferal and inorganic calcite have proposed that
387 B/Ca in calcite is controlled by one of several related carbonate system variables:
388 either pH, $[\text{CO}_3^{2-}]$, $[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]$, $[\text{B}(\text{OH})_4^-]/[\text{DIC}]$, or calcification rate (which
389 can be indicated by Ω_{calcite}), and potentially temperature and/or salinity as well (see
390 introduction). Some of these potential controlling variables are highly correlated with
391 one another in our study (i.e. Ω_{calcite} , $[\text{CO}_3^{2-}]$, $[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]$, and $[\text{B}(\text{OH})_4^-]$
392 $/[\text{DIC}]$), making their potential effects on B/Ca harder to distinguish based purely on
393 this study's empirical results. However, others are uncorrelated (e.g. pH, temperature,
394 and salinity; Table S3A,B) from other carbonate system variables (e.g. those listed
395 above), unlike commonly seen in typical ocean conditions or prior studies (as
396 discussed below). The partial decoupling of carbonate system variables, temperature
397 and salinity in this cross-Pacific dataset allows us to begin to separate the effects of
398 these normally tightly-correlated parameters on planktic foraminiferal B/Ca.

399

400 When our hydrographic and carbonate system data across the entire Pacific basin are
401 combined, correlation between many parameters is weak or insignificant. For
402 example, at *N. incompta* core-top sites, temperature and pH are uncorrelated ($r^2 =$
403 0.00), and Ω_{calcite} is not strongly correlated with temperature or pH ($r^2 = 0.39$, $r^2 =$
404 0.56, respectively); at *G. bulloides* sites, temperature and pH are not significantly
405 correlated ($r^2 = 0.17$), and Ω_{calcite} is uncorrelated with pH ($r^2 = 0.01$), though Ω_{calcite} is
406 correlated with temperature ($r^2 = 0.75$) (Table S3A,B). This frequent lack of

407 correlation of hydrographic parameters contrasts with some previous B/Ca core-top
408 calibration studies (Foster, 2008; Yu et al., 2013, 2007), where strong correlation ($r^2 \geq$
409 0.7) of temperature and $[\text{CO}_3^{2-}]$ is common (*G. bulloides*, *N. pachyderma*, *G. ruber*,
410 *G. sacculifer*), and very strong correlation of pH and $[\text{CO}_3^{2-}]$ is seen in some cases (r^2
411 > 0.95 ; *G. sacculifer*, *N. dutertrei*), making it difficult to distinguish the effects of pH,
412 temperature, and Ω_{calcite} (or $[\text{CO}_3^{2-}]$) on B/Ca.

413

414 These initially surprising relationships result from the diverse range of hydrographic
415 settings in this study (e.g. coastal and equatorial upwelling areas, high-latitude coastal
416 sites, open-ocean and oligotrophic settings). Although hydrographic parameters tend
417 to co-vary within some Pacific regions (Fig. S2), each region's relationships are
418 unique, resulting in lack of correlation of these parameters when combined. In
419 addition, our study uses some samples from coastal upwelling regions, where the
420 relationships between carbonate system and other hydrographic parameters differ
421 from those in the open ocean, contributing further to the lack of correlation in the
422 combined dataset. Some carbonate system parameters in this study are highly
423 correlated (Ω_{calcite} , $[\text{CO}_3^{2-}]$, $[\text{B}(\text{OH})_4^-]$, $[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]$, and $[\text{B}(\text{OH})_4^-]/[\text{DIC}]$), so
424 it is not possible to independently evaluate their potential effects on B/Ca with our
425 data alone. However, other hydrographic parameters (pH, temperature, and Ω_{calcite})
426 are not inter-correlated across the whole Pacific dataset, allowing us to investigate
427 the relationships between these parameters and B/Ca.

428 5.2 Controls on B/Ca

429 5.2.1 Carbonate system and calcification rate

430 In the Pacific Ocean core-top samples used in this study, B/Ca in *N. incompta* and *G.*
431 *bulloides* is significantly positively correlated with calcification depth Ω_{calcite} , $[\text{CO}_3^{2-}]$,
432 $[\text{B}(\text{OH})_4^-]$, $[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]$, and $[\text{B}(\text{OH})_4^-/\text{DIC}]$ (in order of decreasing r^2 ; Fig. 3);
433 these parameters are highly correlated with one another (Table S3). The correlation of
434 B/Ca with Ω_{calcite} is seen in a variety of regions (e.g. the upwelling-influenced
435 Southern California, the Eastern Equatorial Pacific, and the Gulf of California; Fig.
436 4), suggesting a common control for both species, and that these relationships are
437 robust across a wide range of Pacific Ocean hydrographic settings. The strong
438 empirical correlation of B/Ca with carbonate system parameters can be used to
439 reconstruct the carbonate system in the geologic past.

440

441 The relationships between Ω_{calcite} (and $[\text{CO}_3^{2-}]$, which covaries with Ω_{calcite}) and B/Ca
442 are similarly strong (Fig. 3). Recent studies provide both experimental (Gabitov et al.,
443 2014; Kaczmarek et al., 2016; Ruiz-Agudo et al., 2012; Uchikawa et al., 2015) and
444 theoretical (Watson, 2004) evidence for the regulation of B/Ca by calcification rate
445 (which can be expressed using Ω_{calcite}). Since $[\text{Ca}^{2+}]$ is quasi-conservative, Ω_{calcite} can
446 be approximated as $\Omega_{\text{calcite}} \approx [\text{CO}_3^{2-}]_{\text{measured}} / [\text{CO}_3^{2-}]_{\text{saturation}}$ (Sarmiento and Gruber,
447 2006), and Ω_{calcite} can be used to calculate $[\text{CO}_3^{2-}]$ (or vice versa) on timescales $< \sim 1$
448 Ma (the residence time of $[\text{Ca}^{2+}]$ in seawater).

449

450 Previous core-top calibration studies of B/Ca in various species of planktic
 451 foraminifera have focused more on linking B/Ca to $[\text{CO}_3^{2-}]$ than to Ω_{calcite} , so we
 452 compare our $[\text{CO}_3^{2-}]$ results to those studies. The absolute B/Ca values measured for
 453 *N. incompta* and *G. bulloides* in this study agree with the B/Ca ranges reported by
 454 previous studies of these species in the North Atlantic (Yu et al., 2013, 2007b) (Fig.
 455 3) and Antarctica (Hendry et al., 2009) using core-top sediments and sediment traps.
 456 The reported correlation of B/Ca with $[\text{CO}_3^{2-}]$ however has generally been weak
 457 except in the case of *Globorotalia inflata* (Allen and Hönisch, 2012; Yu et al.,
 458 2007b). This often weak correlation of B/Ca with $[\text{CO}_3^{2-}]$ reported in the published
 459 studies may be explained in part by their narrow range in $[\text{CO}_3^{2-}]$ (e.g. $\sim 40 \mu\text{mol/kg}$ in
 460 Yu et al., 2007, 2013 compared with ~ 85 (*N. incompta*) or $100 \mu\text{mol/kg}$ (*G. bulloides*)
 461 in this study). The assignment of a constant calcification depth (e.g. 50 m) in these
 462 published studies instead of the use of varying, temperature-proxy-based calcification
 463 depths (as in this study) may have obscured the foraminiferal calcification conditions,
 464 and therefore also partially explain their often weak correlation of B/Ca with $[\text{CO}_3^{2-}]$.
 465
 466 Our study finds weaker relationships between B/Ca and $[\text{B}(\text{OH})_4^-]$, $[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]$
 467] and $[\text{B}(\text{OH})_4^-]/\text{DIC}$ than with Ω_{calcite} (Figure 3, Table S3). These parameters are
 468 related by chemical equilibria to Ω_{calcite} and so are highly correlated with Ω_{calcite} ($r^2 \geq$
 469 0.9; Table S3), so it is possible that the relationship of these variables to B/Ca could
 470 reflect their correlation with Ω_{calcite} more than a primary influence on B/Ca.
 471

472 In neither species is B/Ca significantly correlated with pH ($p < 0.001$; Fig. 3), nor is
 473 pH correlated with other carbonate system or $[B(OH)_4^-]$ -related parameters for *G.*
 474 *bulloides* (though they are correlated in *N. incompta*; Table S3). The lack of
 475 correlation between B/Ca and pH in this study and other studies of core-top planktic
 476 foraminifera (Foster, 2008; Yu et al., 2013, 2007b) and in inorganic calcite
 477 (Uchikawa et al., 2015) strongly suggests that although pH controls the speciation of
 478 boron between borate and boric acid, other factors control the amount of boron
 479 incorporated into planktic foraminifera and inorganic calcite.
 480
 481 In contrast to our findings, a study of B/Ca in cultured planktic foraminifera
 482 hypothesized that Ω_{calcite} variations do not affect B/Ca (Allen et al., 2012). While
 483 Allen et al. (2012) had two pairs of samples that evaluated changes in Ω_{calcite}
 484 independently of pH (samples 4&5, and 8&9, which both had varying Ω_{calcite} , and
 485 constant (samples 4&5) pH or somewhat stable pH (samples 8&9)), the two sample
 486 pairs showed different effects. Samples 8&9 were intended to evaluate Ω_{calcite} changes
 487 independently of pH (pH, however, differed by 0.14 units between the two samples,
 488 and other carbonate system variables differed dramatically) and showed quite low
 489 B/Ca values occurring with dramatically elevated Ω_{calcite} (and vice versa; Ω_{calcite} 2.2
 490 and 11.6, with measured B/Ca of 144 and 72.3 $\mu\text{mol/mol}$, respectively). Conversely,
 491 samples 4&5 showed an opposite effect: pH was constant between these two samples
 492 (though Ω_{calcite} between the two samples differed less than between samples 8&9, and
 493 some variations in temperature and salinity were present), and samples 4&5 showed

494 higher B/Ca occurring with higher Ω_{calcite} (and vice versa; Ω_{calcite} 5.4 and 4.5, with
495 measured B/Ca of 92.9 and 84.3 $\mu\text{mol/mol}$, respectively). These conflicting results
496 (which could be in part due to the unusual water chemistry conditions, designed to
497 vary some parameters more independently) left unresolved the question of how Ω_{calcite}
498 affects planktic foraminiferal B/Ca. Our study, which shows a consistent, strong
499 correlation between B/Ca and Ω_{calcite} but not pH (Fig. 3), can add some clarity by
500 strongly suggesting that pH is not a controlling variable on B/Ca, but rather Ω_{calcite} or
501 one of its correlated variables.

502

503 This hypothesis is supported by Marshall et al., (2013) and Osborne et al., (2016)
504 found a pronounced effect of $[\text{CO}_3^{2-}]$ on calcification efficiency in planktic
505 foraminifera, and other investigators have hypothesized a calcification rate control on
506 B/Ca based on down-core B/Ca data in foraminiferal calcite (Henehan et al., 2015;
507 Naik and Naidu, 2014; Penman et al., 2014). Experimental studies have demonstrated
508 that calcification rate is the primary control on the concentration of boron in inorganic
509 calcite (Gabitov et al., 2014; Kaczmarek et al., 2016; Ruiz-Agudo et al., 2012;
510 Uchikawa et al., 2015), and discuss a mechanistic explanation for higher B/Ca values
511 with faster calcification. These studies invoke a surface/growth entrapment model
512 (SEMO; Watson, 2004) or a surface kinetic model (DePaolo, 2011), in which faster
513 crystal growth (i.e. calcification rate) results in more boron being trapped in newly
514 formed calcite surfaces because less time is available for boron to escape via
515 diffusion or re-dissolution. The SEMO has been used to explain the incorporation of

516 both B and Sr into calcite (Kaczmarek et al., 2016; Tang et al., 2008), and so may
517 represent an important step toward a unified model for the incorporation of minor and
518 trace elements into calcite.

519

520 5.2.2. Temperature and salinity effects on B/Ca

521 Our study finds a positive relationship between B/Ca and temperature ($r^2 = 0.82$ for
522 *G. bulloides*, $r^2 = 0.52$ for *N. incompta*; Fig. 3F and Table S3). However, a large
523 portion of this relationship is likely spurious, particularly for *G. bulloides*, since
524 temperature and Ω_{calcite} are correlated at our study sites ($r^2 = 0.75$ for *G. bulloides*, r^2
525 $= 0.39$ for *N. incompta*). No significant temperature effect was observed in cultured
526 *Globigerinoides ruber*, *Globigerinoides sacculifer*, and *Orbulina universa* (Allen et
527 al., (2012)). Inorganic calcite precipitation experiments independently exploring
528 temperature effects on B/Ca are contradictory. Mavromatis et al., (2015) found no
529 significant B/Ca difference between calcite precipitated at 5° and 25°C when other
530 variables were stable, whereas Kaczmarek et al., (2016) observed decreasing B/Ca
531 from 12°C to 32°C at constant calcification rate. This suggests that if a positive
532 temperature effect on B/Ca exists (as posited by some earlier studies on planktic
533 foraminifera (Foster, 2008; Yu et al., 2007b)), it is weak, and may be overprinted by
534 the dominant effect of calcification rate (reflected by Ω_{calcite}).

535

536 Weak correlations of B/Ca with salinity are of only slightly larger magnitude than the
537 correlations between salinity and carbonate chemistry variables; Table S3), and

538 suggest that salinity may have only a weak effect on B/Ca, as also shown in three
539 species of cultured planktic foraminifera (Allen et al., 2012). B/Ca is uncorrelated
540 with $[\text{PO}_4^{3-}]$ in our study, unlike in Henehan et al., 2015, likely due to the absence of
541 photosymbionts in these species and their effects on carbonate chemistry.

542 *5.3 Insights from geographic region sample groups*

543 By dividing the results into several Pacific geographic regions, we see that some
544 water variables are much more tightly correlated in these regions than in the overall
545 dataset (e.g. $[\text{CO}_3^{2-}]$ and pH; Fig. S2). This allows us to evaluate which variables have
546 a relationship with B/Ca that may be simply an artefact of the regional relationship of
547 water parameters.

548

549 While B/Ca and pH are correlated in several regions (Fig. 4B,E), no significant
550 correlation between B/Ca and pH is seen in the cross-Pacific dataset (Fig. 3). The
551 B/Ca-pH regression lines in some regions differ dramatically (Fig. 4B,E), whereas the
552 relationship of B/Ca with Ω_{calcite} is similar across various regions (Fig. 4A,D). This
553 implies that these regional B/Ca-pH correlations are an artefact of the regional
554 correlation of many carbonate system parameters and environmental parameters with
555 one another (Fig. S2). The consistently strong B/Ca- Ω_{calcite} relationship, both
556 regionally and across the Pacific, supports a mechanistic relationship between B/Ca
557 and Ω_{calcite} .

558

559 5.4 B/Ca calibration

560 Based on the strong empirical relationship between B/Ca and Ω_{calcite} that is present
561 both regionally and across the Pacific, we report linear regressions of core-top B/Ca
562 with Ω_{calcite} for *N. incompta*:

563

564
$$\text{B/Ca} = \Omega_{\text{calcite}} * 18.51 (\pm 1.75) - 2.59 (\pm 6.13) \quad (4)$$

565

566 and *G. bulloides*:

567

568
$$\text{B/Ca} = \Omega_{\text{calcite}} * 13.85 (\pm 1.25) - 13.94 (\pm 5.02) \quad (5)$$

569

570 where B/Ca is in $\mu\text{mol/mol}$, Ω_{calcite} is unitless, and the $\pm$ term represents the errors in
571 each constant. This Ω_{calcite} calibration and the following $[\text{CO}_3^{2-}]$ calibration exclude
572 the five encrusted *G. bulloides* samples; alternate calibration equations which include
573 the encrusted *G. bulloides* are provided in section 5.6.

574

575 For comparison with other studies, and because Ω_{calcite} and $[\text{CO}_3^{2-}]$ vary in tandem
576 and will provide equivalent results in studies with near-surface foraminifera and
577 stable seawater $[\text{Ca}^{2+}]$ (e.g. the past 1 Ma), we also report linear fits of core-top data
578 with $[\text{CO}_3^{2-}]$ for *N. incompta*:

579

580
$$\text{B/Ca} = [\text{CO}_3^{2-}] * 0.420 (\pm 0.041) - 0.173 (\pm 6.05) \quad (6)$$

581

582 and *G. bulloides*:

583

584
$$B/Ca = [CO_3^{2-}] * 0.319 (\pm 0.031) - 12.69 (\pm 5.29) \quad (7)$$

585

586 where B/Ca is in $\mu\text{mol/mol}$ and $[CO_3^{2-}]$ is in $\mu\text{mol/kg}$; alternate calibration equations

587 which include the encrusted *G. bulloides* are provided in section 5.6.

588

589 A B/Ca study using cultured tropical planktic foraminifera (Allen et al., 2012)

590 generated B/Ca-B(OH)₄⁻/DIC calibration relationships based on theoretical

591 assumptions. Equations relating B/Ca to B(OH)₄⁻/DIC in the species *G. ruber*, *G.*

592 *sacculifer* and *O. universa* (Allen et al., 2012) show slopes that are much shallower

593 than those for *N. incompta* and *G. bulloides* in this study (see Fig. S1 and caption for

594 regressions), indicating a higher carbonate system sensitivity of *N. incompta* and *G.*

595 *bulloides* than the cultured tropical species. B/Ca values in this study's asymbiotic

596 subpolar/upwelling species (range: ~20-80 $\mu\text{mol/mol}$) are much lower than in the

597 symbiont-bearing tropical species cultured in Allen et al., (2012) (range: 80-220

598 $\mu\text{mol/mol}$), which is consistent with faster calcification by tropical, symbiont-bearing

599 foraminifera in high Ω_{calcite} , warm waters. According to the SEMO, rapid calcification

600 would allow less time for diffusion of boron out of the calcite surface layer than in

601 slower-calcifying subpolar/upwelling foraminifera. Hence the relation between B/Ca

602 and $\text{B(OH)}_4^-/\text{DIC}$ in our study and in published records is likely also related to
603 calcification rates.

604 5.5 The role of the partition coefficient K_D

605 K_D values in our study (Fig. 5) are comparable to those reported for North Atlantic *N.*
606 *pachyderma* and *G. bulloides* (Yu et al., 2013, 2007b) and are within the range of
607 other planktic species studied (Foster, 2008). However, we see large variations of K_D
608 for both species, and we find no correlation of K_D with $[\text{CO}_3^{2-}]$ (Fig. 5). K_D is
609 uncorrelated with temperature in *N. incompta*, and weakly correlated with
610 temperature in *G. bulloides*, which agrees with a lack of temperature dependence of
611 K_D in culture studies (Allen et al., 2012, 2011).

612

613 Some studies have generated calibrations of a constant boron partition coefficient
614 (K_D ; Equation 3) for inorganic calcite (Sanyal et al., 2000) and foraminiferal calcite
615 (Yu et al., 2013) to calculate carbonate system parameters. However, recent inorganic
616 calcite experiments find large variations in boron partition coefficients (Mavromatis
617 et al., 2015), and studies of cultured and core-top planktic foraminifera have found
618 that K_D varies widely between and within species (Foster, 2008; Yu et al., 2013,
619 2007b), likely due to non-equilibrium calcification conditions. This indicates that use
620 of a constant K_D is not appropriate.

621

622 Alternatively, some studies of the planktic foraminifera B/Ca carbonate system proxy
623 have generated calibrations of a variable K_D (with and without temperature

dependence for K_D). However, carbonate system reconstructions based on K_D are sometimes spurious (Foster, 2008; Tripathi et al., 2009), likely due to the covariance of K_D , temperature, and carbonate parameters (Allen and Hönisch, 2012). Application of K_D to B/Ca carbonate system calibrations has been shown (e.g. by Allen and Hönisch, 2012; Seki et al., 2010) to lead to a muted signal of B/Ca in proxy reconstructions (Tripathi et al., 2009; Yu et al., 2007b), and we conclude such applications should be avoided.

We also performed a test proposed by Allen and Hönisch (2012) in which an average of the sample populations' B/Ca values is used to generate an “artificial K_D ” value (by dividing average B/Ca for each species by $[B(OH)_4^-]/[HCO_3^-]$). If the true and “artificial” K_D relationships with environmental parameters (e.g. $[CO_3^{2-}]$ and temperature) were alike, this would indicate that the K_D calibration is independent of B/Ca variations and is driven by the denominator of K_D ($[B(OH)_4^-] / HCO_3^-]$) or another parameter. However, the true and “artificial” K_D relationships in this dataset are not alike for $[CO_3^{2-}]$ or temperature (Fig. 5), and so we conclude that our correlations are not driven by the K_D denominator or temperature, but rather by the variation of B/Ca with other carbonate system parameters, specifically calcification rate (indicated by Ω_{calcite}).

5.6 Encrusted *G. bulloides* morphotype

Some core-top *G. bulloides* samples (n=8) show distinct chemical and physical properties from the others (Fig. 3, S3, S4, Table S2), with higher $\delta^{18}O$ values (1.4‰

646 to 2.8 ‰), heavier shell weights (generally 15-30 µg), and a narrow Mg/Ca range
647 (1.1-1.5 mmol/mol, corresponding to temperatures of 7-10°C). These specimens are
648 thickly-calcified with a small aperture and appear to represent a different *G. bulloides*
649 morphotype (“encrusted *G. bulloides*”) and potentially a different *G. bulloides*
650 genotype (Darling et al., 2003). The encrusted *G. bulloides* morphotype has been
651 found previously in the Pacific Ocean, including in Southern Californian, New
652 Zealand, and Chilean waters (Field, 2004; Marr et al., 2011; Mohtadi et al., 2005;
653 Osborne et al., 2016; Sautter and Thunell, 1991b), and based on its Mg/Ca and $\delta^{18}\text{O}$
654 signature, it appears to calcify in colder, deeper waters than most non-encrusted *G.*
655 *bulloides*, as also suggested previously (Bemis et al., 2002; Sautter and Thunell,
656 1991b). Further background on the geochemistry and visual appearance (including
657 Scanning Electron Microscope (SEM) images; Fig. S4) of encrusted vs. non-
658 encrusted *G. bulloides* is provided in the supplemental information.

659

660 The B/Ca and Mg/Ca values of these encrusted *G. bulloides* are within the range of
661 the non-encrusted *G. bulloides* (Table S2, Fig. S3), making it appropriate to include
662 both the encrusted and non-encrusted *G. bulloides* in the B/Ca calibrations. Studies
663 based on regions or time-periods which clearly have only non-encrusted *G. bulloides*
664 (e.g. in the tropics and subtropics) may prefer to use calibrations that exclude the
665 encrusted *G. bulloides* (shown in Section 5.4). However, for studies in areas or time-
666 periods where/when both encrusted and non-encrusted *G. bulloides* occur (e.g. areas
667 where the proportion of the two types varies based on glacial-interglacial cycles or

seasonal hydrographic changes), it is important to use calibration equations that include the encrusted *G. bulloides*. Therefore, we report linear regressions of core-top data with Ω_{calcite} and $[\text{CO}_3^{2-}]$ that combine both non-encrusted (n=27) and encrusted (n=5) *G. bulloides*:

$$\text{B/Ca} = \Omega_{\text{calcite}} * 13.37 (\pm 1.304) - 11.31 (\pm 5.215) \quad (r^2 = 0.78) \quad (8)$$

$$\text{B/Ca} = [\text{CO}_3^{2-}] * 0.313 (\pm 0.031) - 11.127 (\pm 5.268) \quad (r^2 = 0.77) \quad (9)$$

where B/Ca is in $\mu\text{mol/mol}$, Ω_{calcite} is unitless, and $[\text{CO}_3^{2-}]$ is in $\mu\text{mol/kg}$.

5.7 Preservation of B/Ca and Mg/Ca signals in *N. incompta* and *G. bulloides*

We find no evidence that *N. incompta* or *G. bulloides* B/Ca values are affected by post-depositional dissolution, as their B/Ca values do not correlate with $\Delta[\text{CO}_3^{2-}]$ or core-top water depth (Fig. 2A,B). A dissolution effect on B/Ca in low saturation conditions has been observed in some studies and/or some species (Coadic et al., 2013; Hönisch and Hemming, 2004; Seki et al., 2010) but is absent in other studies (Foster, 2008; Hennehan et al., 2015; Wara et al., 2003). It is likely that, similar to Mg/Ca, susceptibility of B/Ca to post-depositional dissolution varies across different foraminifera species, as other work also suggests (Dai et al., 2016).

689 A depth-related dissolution effect on *N. incompta* Mg/Ca values is suggested by
690 correlation of *N. incompta* Mg/Ca with water depth and $\Delta[\text{CO}_3^{2-}]$ (Fig. 2C,D), and by
691 an average Mg/Ca temperature $7^\circ \pm 3^\circ\text{C}$ lower than the average $\delta^{18}\text{O}$ temperature
692 using the von Langen et al. (2005) Mg/Ca calibration, or 6°C lower using the Mg/Ca
693 calibration of Elderfield & Ganssen (2000), and 4°C for that of Nürnberg et al.
694 (1996). This implies that carbonate system reconstructions using *N. incompta* that
695 require reconstructed temperature need to use a different temperature proxy than
696 Mg/Ca unless the samples are from conditions with high bottom water $\Delta[\text{CO}_3^{2-}]$ (and
697 therefore not subject to alteration of Mg/Ca). By comparison, *G. bulloides* Mg/Ca-
698 derived temperatures are within $< 2^\circ\text{C}$ of $\delta^{18}\text{O}$ temperatures on average, and are
699 uncorrelated with water depth or $\Delta[\text{CO}_3^{2-}]$ (Fig. 2C,D). Our results agree with those
700 of Mekik et al., (2007), who found that Mg/Ca in *Neogloboquadrina dutertrei* from
701 the equatorial Pacific is lower in low $\Delta[\text{CO}_3^{2-}]$ waters, but that Mg/Ca in *G. bulloides*
702 did not vary with $\Delta[\text{CO}_3^{2-}]$.

703 *5.8 Study limitations and suggestions for future proxy application*

704 Empirical proxy calibrations using core-top foraminifera provide the most direct link
705 to down-core samples, as the samples reflect the complete foraminiferal life cycle in
706 natural marine environments and the effects of sinking in the water column and
707 residence in the sediment, which cultured or sediment trap foraminifera cannot show,
708 but are experienced by all down-core samples. However, core-top studies are limited
709 by uncertainty in the growth conditions of the foraminifera, particularly because of
710 the dearth of subsurface carbonate chemistry measurements in many regions, and

711 because it is unclear how earlier calcification conditions compare to today. Another
712 limitation arises from uncertainty in the depth habitat of foraminifera, which may be
713 reasonably well constrained using temperature proxies from foraminiferal calcite, but
714 requires high-quality local subsurface water data, and understanding of the potential
715 seasonality of foraminiferal growth.

716

717 The spatial and temporal resolution of open-ocean hydrographic data applied in this
718 calibration could be improved. For example, though the GLODAP (Key, 2004)
719 interpolated carbonate system data are the best available for many regions in this
720 study, their spatial resolution is sometimes low, and they are often not suitable for
721 coastal sites, so we were forced to omit eight samples from our calibrations for lack
722 of appropriate carbonate system data. Fortunately, because of their high spatial and
723 temporal resolution, the high-resolution regional water datasets we used for Southern
724 California, Washington State, and British Columbia (Feely et al., 2008; Patsavas et
725 al., 2015; D. Ianson, pers. comm.) are much more appropriate; such measurements are
726 needed for other regions. Further, calcification depths selected for some core-top
727 samples are poorly constrained, particularly for samples in which literature-based
728 depths were assigned when neither Mg/Ca nor $\delta^{18}\text{O}$ temperatures yielded calcification
729 depths in agreement with prior studies. Finally, further studies constraining post-
730 depositional effects (e.g. Mg/Ca dissolution) are needed for more species of
731 foraminifera to better determine calcification depths.

732

733 Core-top calibration studies also experience both limitations and advantages due to
734 their age range. The Holocene age of samples used in this study's calibrations means
735 that the foraminifera pooled in one core-top sample may have been produced over
736 periods from decades to thousands of years. This has the advantage that short-term
737 seasonal or climate variations may be dampened in the B/Ca values. However, the
738 time averaging of the pooled foraminifera in core-top samples does not exactly mirror
739 the temporal range of the modern water data used in this study, as these
740 measurements represent episodic, non-continuous recent water column
741 measurements. In addition, while water data derived from GLODAP/WOA and
742 interpolated using ODV's 3D interpolation tool are the best data available, the data's
743 time frames averaged differ for each site, and represent a potential source of error.
744 This results in some uncertainty about how earlier core-top calcification conditions
745 compare to the modern measurements of water conditions.
746
747 We caution that if embarking on a down-core record from regions not thoroughly
748 treated in this study, one should first assess the modern carbonate chemistry and
749 modern planktic foraminiferal B/Ca from the region to confirm that the relationships
750 found in this study apply. For example, B/Ca- Ω_{calcite} relationships are less well
751 constrained for coastal waters near Chile, New Zealand, and the southeast Pacific;
752 these regions require further study and data to improve applications of this proxy.
753 However, we observed robust regional B/Ca- Ω_{calcite} relationships in Southern

754 California, the Gulf of California, and the Eastern Equatorial Pacific); our calibrations
755 may be applied there to reconstruct past Ω_{calcite} or $[\text{CO}_3^{2-}]$.

756

757 **6. Conclusions**

758 Core-top calibration of B/Ca in Pacific Ocean *N. incompta* and *G. bulloides*
759 (subpolar/upwelling asymbiotic planktic foraminifera species) shows a strong
760 significant correlation with seawater calcite saturation (Ω_{calcite}) and carbonate ion
761 concentration ($[\text{CO}_3^{2-}]$) across diverse environmental conditions. As Ω_{calcite} is a direct
762 regulator and indicator of calcite precipitation rate, this suggests that precipitation rate
763 regulates the incorporation of boron into planktic foraminiferal calcite in these
764 species. This agrees with several recent studies of inorganically-precipitated calcite
765 which show a strong control of precipitation rate on B/Ca, and agrees with the
766 mechanistic explanation of trace element incorporation into CaCO_3 described in the
767 surface entrapment model (SEMO; Watson, 2004).

768

769 Though we find significant correlations of B/Ca with seawater $[\text{B}(\text{OH})_4^-]$, $[\text{B}(\text{OH})_4^-]$
770 $/\text{HCO}_3^-]$, and $[\text{B}(\text{OH})_4^-/\text{DIC}]$, these are weaker than the correlation of B/Ca with
771 Ω_{calcite} . Given the experimental and theoretical evidence for a calcification rate control
772 over B/Ca, it is likely that the relationship between these parameters and B/Ca is due
773 to their correlation with Ω_{calcite} . B/Ca is not significantly correlated with pH in either
774 species, suggesting that while pH controls the speciation of boron and inorganic
775 carbon in seawater, other factors regulate the amount of boron taken up into planktic

776 foraminiferal carbonates; thus, planktic foraminiferal B/Ca should not be used to
777 reconstruct pH directly. B/Ca in *N. incompta* and *G. bulloides* shows no evidence of
778 being impacted by dissolution in low $\Delta[\text{CO}_3^{2-}]$ bottom waters.

779

780 This study finds little or no correlation of the boron partition coefficient K_D with
781 $[\text{CO}_3^{2-}]$ or temperature. Like studies of cultured planktic foraminifera (Allen et al.,
782 2012, 2011), our results suggest that application of a calibrated K_D (whether constant
783 or variable) is not suitable for calculating carbonate system parameters for the Pacific
784 Ocean using these species, or perhaps generally. Instead, our results provide the first
785 empirical calibration directly relating B/Ca to Ω_{calcite} (or $[\text{CO}_3^{2-}]$) in core-top planktic
786 foraminifera, which agrees with new mechanistic understanding of boron
787 incorporation into carbonates, and can be used to reconstruct the past carbonate
788 system to study past climate and ocean acidification events.

789

790

791 **7. Acknowledgements**

792 We thank the Oregon State University core repository, the Monterey Bay Aquarium
793 Research Institute (MBARI), A. Christina Ravelo, and Juan-Carlos Herguera for
794 providing core-top samples. We thank Richard Feely (NOAA) for water data from
795 two western North American carbonate cruises, Debbie Ianson (Fisheries and Oceans
796 Canada) for unpublished water data for a British Columbia sample, Rob Franks, Dyke
797 Andreasen for analytical guidance, and Rachel Brown Reid and Linda Anderson for

798 guidance in boron methods. Christina Ravelo and Paul Koch provided insightful
799 comments on previous drafts. Constructive comments from Kate Hendry, Robert
800 Thunell, one anonymous reviewer, and the editor Heather Stoll, improved the
801 manuscript. Funding for this research was provided by a NSF CAREER grant OCE-
802 0449732 to AP, a UCSC Institute of Marine Science Packard Ocean Science &
803 Technology Endowment Award to A.P. and N.Q.K., and UCOP Research Grants
804 Program Office Coastal Environmental Quality Initiative (CEQI) to A.P., A.R. and
805 D.P.. N.Q.K. was supported by a Ford Foundation Diversity Predoctoral Fellowship.
806

807 **8. Figure captions**

808 **Figure 1**

809 Maps showing the location of core-top samples and B/Ca results. Maps A, B, C show
810 *G. bulloides* locations and B/Ca values (see color bar for scale, which differs from *N.*
811 *incompta* scale); inset B shows Southern California and Gulf of California samples,
812 and inset C shows Galapagos samples. Maps D, E, F show *N. incompta* locations and
813 B/Ca values (note that the color bar scale differs from *G. bulloides*); inset E shows
814 Southern California samples, and inset F shows Galapagos samples. Created using
815 Ocean Data View software.

816

817 **Figure 2**

818 Core-top B/Ca versus sediment-water interface depth (here referred to as core-top
819 water depth) (A) and bottom water $\Delta[\text{CO}_3^{2-}]$ (B), and core-top Mg/Ca versus core-top
820 water depth (C) and bottom water $\Delta[\text{CO}_3^{2-}]$ (D). *N. incompta* (blue diamonds) and *G.*
821 *bulloides* (red circles); r^2 is shown where a significant correlation is found ($p < 0.01$),
822 with text color indicating species. B/Ca and Mg/Ca error bars reflect one standard
823 deviation of the solid foraminiferal standard (see methods), which represents a more
824 conservative error than the liquid consistency standard. In panels B and D, samples
825 with $\Delta[\text{CO}_3^{2-}]$ values greater than 20 $\mu\text{mol/kg}$ have been omitted due to a non-linear
826 relationship between the higher and lower $\Delta[\text{CO}_3^{2-}]$ values (samples with high
827 $\Delta[\text{CO}_3^{2-}]$ are not from undersaturated conditions, and so are not susceptible to
828 dissolution effects on trace elements). B/Ca is uncorrelated with sample water depth

829 and $\Delta[\text{CO}_3^{2-}]$ for both species (A and B), implying that in these species, B/Ca is not
830 affected by depth-related dissolution. For *G. bulloides*, a lack of correlation of Mg/Ca
831 with water depth and $\Delta[\text{CO}_3^{2-}]$ suggests that this species does not experience depth-
832 related Mg/Ca dissolution. However, *N. incompta* Mg/Ca is significantly ($p=0.004$)
833 correlated with sample water depth (C) and $\Delta[\text{CO}_3^{2-}]$ (D), and appears to be affected
834 by depth-related dissolution based on calculated temperatures.

835

836 **Figure 3**

837 Variation of B/Ca with environmental parameters at the assigned calcification depth
838 in two species of core-top planktic foraminifera (*N. incompta* and *G. bulloides*) from
839 across the Pacific. *N. incompta* data generated in this study are shown in blue
840 diamonds with error bars, *G. bulloides* data generated in this study are shown in red
841 circles with error bars. The encrusted morphotype of *G. bulloides* is shown in green
842 triangles, and is shown in one version of regressions. North Atlantic *N. pachyderma*
843 (sinistral) data from Yu et al. (2013) are shown in empty gray diamonds, and North
844 Atlantic *G. bulloides* data from Yu et al. (2007) are shown in empty gray circles. In
845 each panel, a bivariate least squares regression of B/Ca to the water parameter is
846 shown for each species if the parameters are significantly correlated ($p<0.001$); see
847 also Table S3 for further r^2 and p values. B/Ca error bars reflect one standard
848 deviation of the solid foraminiferal standard ($\pm 3.5 \mu\text{mol/mol}$; see methods), which
849 represents a more conservative error than the liquid consistency standard, and
850 horizontal error bars reflect spatial errors of GLODAP or coastal data.

851

852 **Figure 4**

853 Regional geographic variation of B/Ca in *N. incompta* (left panels) and *G. bulloides*
854 (right panels) with environmental parameters at calcification depth. Regressions are
855 shown for regions only when the correlations are significant ($p < 0.01$) (e.g. Southern
856 California, Eastern Equatorial Pacific, Gulf of California, and in some cases,
857 Southeast Pacific). Note that symbol types and colors differ from those in other
858 figures. North Atlantic data are shown in empty gray symbols for comparison (Yu et
859 al., 2007, 2013). Floating error bars shown in panels A and D reflect one B/Ca
860 standard deviation of the solid foraminiferal standard ($\pm 3.5 \mu\text{mol/mol}$), which
861 represents a more conservative error than the liquid consistency standard, and apply
862 to panels B-F as well.

863

864 **Figure 5**

865 Relationship of K_D (equation 3) with temperature (A) and $[\text{CO}_3^{2-}]$ (B) for *N. incompta*
866 (blue diamonds) and *G. bulloides* (red circles). Encrusted *G. bulloides* are shown in
867 green triangles, but excluded from K_D calculations. North Atlantic data are shown in
868 empty gray symbols for comparison (Yu et al., 2007, 2013). The correlations of K_D
869 with temperature and $[\text{CO}_3^{2-}]$ are not significant ($p < 0.01$) except in the case of the *G.*
870 *bulloides* K_D –temperature relationship (Table S3), and all are weaker than those of
871 the B/Ca relationships with temperature and $[\text{CO}_3^{2-}]$. To illustrate the direct influence
872 of B/Ca on this study's carbonate system calibrations, we show an artificial K_D

873 relationship generated using average values of B/Ca for each species (41 $\mu\text{mol/mol}$
874 for *N. incompta*, 61 $\mu\text{mol/mol}$ for *G. bulloides*); blue Xs show *N. incompta* artificial
875 K_D with constant B/Ca, and red crosses show *G. bulloides* artificial K_D with constant
876 B/Ca. The artificial K_D relationships are different from those obtained using the
877 individual measured B/Ca data, indicating that B/Ca does have a significant influence
878 on these calibrations, unlike in some previous studies.

879

880

933 **9. References**

- 934 Al-Ammar, A.S., Gupta, R.K., Barnes, R.M., 2000. Elimination of boron memory
935 effect in inductively coupled plasma-mass spectrometry by ammonia gas
936 injection into the spray chamber during analysis. *Spectrochimica Acta Part B* 55
937 629–635.
- 938 Allen, K.A., Hönisch, B., 2012. The planktic foraminiferal B/Ca proxy for seawater
939 carbonate chemistry: A critical evaluation. *Earth Planet. Sci. Lett.* 345–348,
940 203–211. doi:10.1016/j.epsl.2012.06.012
- 941 Allen, K.A., Hönisch, B., Eggins, S.M., Rosenthal, Y., 2012. Environmental controls
942 on B/Ca in calcite tests of the tropical planktic foraminifer species
943 *Globigerinoides ruber* and *Globigerinoides sacculifer*. *Earth Planet. Sci. Lett.*
944 351–352, 270–280. doi:10.1016/j.epsl.2012.07.004
- 945 Allen, K.A., Hönisch, B., Eggins, S.M., Yu, J., Spero, H.J., Elderfield, H., 2011.
946 Controls on boron incorporation in cultured tests of the planktic foraminifer
947 *Orbulina universa*. *Earth Planet. Sci. Lett.* 309, 291–301.
948 doi:10.1016/j.epsl.2011.07.010
- 949 Barker, S., Greaves, M.J., Elderfield, H., 2003. A study of cleaning procedures used
950 for foraminiferal Mg/Ca paleothermometry. *Geochemistry Geophys.*
951 *Geosystems* 4, 1–20. doi:10.1029/2003GC000559
- 952 Bemis, B.E., Spero, H.J., Thunell, R.C., 2002. Using species-specific
953 paleotemperature equations with foraminifera: a case study in the Southern
954 California Bight. *Mar. Micropaleontol.* 46, 405–430. doi:10.1016/s0377-

8398(02)00083-x

Bian, N., Martin, P.A., 2010. Investigating the fidelity of Mg/Ca and other elemental data from reductively cleaned planktonic foraminifera. *Paleoceanography* 25, PA2215. doi:10.1029/2009PA001796

Bolton, A., Marr, J.P., 2013. Trace element variability in crust-bearing and non crust-bearing *Neogloboquadrina incompta*, *P-D* intergrade and *Globoconella inflata* from the Southwest Pacific Ocean: Potential paleoceanographic implications. *Mar. Micropaleontol.* 100, 21–33. doi:10.1016/j.marmicro.2013.03.008

Boyle, E.A., Keigwin, L.D., 1985. Comparison of Atlantic and Pacific paleochemical records for the last 215,000 years: changes in deep ocean circulation and chemical inventories. *Earth Planet. Sci. Lett.* 76, 135–150. doi:10.1016/0012-821X(85)90154-2

Brown, R.E., Anderson, L.D., Thomas, E., Zachos, J.C., 2011. A core-top calibration of B/Ca in the benthic foraminifers *Nuttallides umbonifera* and *Oridorsalis umbonatus*: A proxy for Cenozoic bottom water carbonate saturation. *Earth Planet. Sci. Lett.* 310, 360–368. doi:10.1016/j.epsl.2011.08.023

Coadic, R., Bassinot, F., Dissard, D., Douville, E., Greaves, M., Michel, E., 2013. A core-top study of dissolution effect on B/Ca in *Globigerinoides sacculifer* from the tropical Atlantic: Potential bias for paleo-reconstruction of seawater carbonate chemistry. *Geochemistry, Geophys. Geosystems* 14, 1053–1068. doi:10.1029/2012GC004296

Dai, Y., Yu, J., Johnstone, H.J.H., 2016. Distinct responses of planktonic

977 foraminiferal B/Ca to dissolution on seafloor. *Geochem. Geophys. Geosyst.*
 978 1339–1348. doi:10.1002/2015GC006199.

979 Darling, K.F., Kucera, M., Wade, C.M., von Langen, P.J., Pak, D.K., 2003. Seasonal
 980 distribution of genetic types of planktonic foraminifer morphospecies in the
 981 Santa Barbara Channel and its paleoceanographic implications.
 982 *Paleoceanography* 18, 1–11. doi:10.1029/2001PA000723

983 DePaolo, D.J., 2011. Surface kinetic model for isotopic and trace element
 984 fractionation during precipitation of calcite from aqueous solutions. *Geochim.*
 985 *Cosmochim. Acta* 75, 1039–1056. doi:10.1016/j.gca.2010.11.020

986 Dickson, A.G., 1990. Thermodynamics of the dissociation of boric acid in synthetic
 987 seawater from 273.15 to 318.15 K. *Deep Sea Res.* 37, 755–766.

988 Doney, S.C., Fabry, V.J., Feely, R.A., Kleypas, J.A., 2009. Ocean Acidification: The
 989 Other CO₂ Problem. *Ann. Rev. Mar. Sci.* 1, 169–192.
 990 doi:10.1146/annurev.marine.010908.163834

991 Elderfield, H., Ganssen, G.M., 2000. Past temperature and delta18O of surface ocean
 992 waters inferred from foraminiferal Mg/Ca ratios. *Nature* 405, 442–5.
 993 doi:10.1038/35013033

994 Feely, R.A., Sabine, C.L., Hernández-Ayón, J.M., Ianson, D., Hales, B., 2008.
 995 Evidence for upwelling of corrosive “acidified” water onto the continental shelf.
 996 *Science* 320, 1490–1492. doi:10.1126/science.1155676

997 Field, D.B., 2004. Variability in vertical distributions of planktonic foraminifera in
 998 the California Current: Relationships to vertical ocean structure.

999 Paleocceanography 19, PA2014. doi:10.1029/2003PA000970

1000 Foster, G.L., 2008. Seawater pH, pCO₂ and [CO₃²⁻] variations in the Caribbean Sea
 1001 over the last 130 kyr: A boron isotope and B/Ca study of planktic foraminifera.
 1002 Earth Planet. Sci. Lett. 271, 254–266. doi:10.1016/j.epsl.2008.04.015

1003 Gabitov, R.I., Rollion-Bard, C., Tripathi, A.K., Sadekov, A., 2014. In situ study of
 1004 boron partitioning between calcite and fluid at different crystal growth rates.
 1005 Geochim. Cosmochim. Acta 137, 81–92. doi:10.1016/j.gca.2014.04.014

1006 Hammer, Ø., Harper, D.A.T., Ryan, P.D., 2001. PAST: Paleontological Statistics
 1007 Software Package for Education and Data Analysis. Palaeontologia Electronica
 1008 4(1): 9pp. Palaeontol. Electron. 4, 9.

1009 Hemming, N.G., Hanson, G.N., 1992. Boron isotopic composition and concentration
 1010 in modern marine carbonates. Geochim. Cosmochim. Acta 56, 537–543.

1011 Hendry, K., Rickaby, R.E.M., Meredith, M., Elderfield, H., 2009. Controls on stable
 1012 isotope and trace metal uptake in *Neogloboquadrina pachyderma* (sinistral) from
 1013 an Antarctic sea-ice environment. Earth Planet. Sci. Lett. 278, 67–77.
 1014 doi:10.1016/j.epsl.2008.11.026

1015 Hennehan, M.J., Foster, G.L., Rae, J.W.B., Prentice, K.C., Erez, J., Bostock, H.C.,
 1016 Marshall, B.J., Wilson, P.A., 2015. Evaluating the utility of B/Ca ratios in
 1017 planktic foraminifera as a proxy for the carbonate system: a case study of
 1018 *Globigerinoides ruber*. Geochemistry, Geophys. Geosystems 1–18.
 1019 doi:10.1002/2014GC005514

1020 Hönisch, B., Hemming, N.G., 2004. Ground-truthing the boron isotope-paleo-pH

1021 proxy in planktonic foraminifera shells: Partial dissolution and shell size effects.
 1022 Paleoceanography 19, 1–13. doi:10.1029/2004PA001026
 1023 Kaczmarek, K., Nehrke, G., Misra, S., Bijma, J., Elderfield, H., 2016. Investigating
 1024 the effects of growth rate and temperature on the B/Ca ratio and $\delta^{11}\text{B}$ during
 1025 inorganic calcite formation. Chem. Geol. 421, 81–92.
 1026 doi:10.1016/j.chemgeo.2015.12.002
 1027 Key, R.M., 2004. A global ocean carbon climatology: Results from Global Data
 1028 Analysis Project (GLODAP). Global Biogeochem. Cycles 18, 1–23.
 1029 doi:10.1029/2004GB002247
 1030 Lee, K., Kim, T.-W., Byrne, R.H., Millero, F.J., Feely, R.A., Liu, Y.-M., 2010. The
 1031 universal ratio of boron to chlorinity for the North Pacific and North Atlantic
 1032 oceans. Geochim. Cosmochim. Acta 74, 1801–1811.
 1033 doi:10.1016/j.gca.2009.12.027
 1034 Lueker, T.J., Dickson, A.G., Keeling, C.D., 2000. Ocean pCO₂ calculated from
 1035 dissolved inorganic carbon, alkalinity, and equations for K₁ and K₂: validation
 1036 based on laboratory measurements of CO₂ in gas and seawater at equilibrium.
 1037 Mar. Chem. 70, 105–119. doi:10.1016/S0304-4203(00)00022-0
 1038 Marr, J.P., Baker, J.A., Carter, L., Allan, A.S.R., Dunbar, G.B., Bostock, H.C., 2011.
 1039 Ecological and temperature controls on Mg/Ca ratios of *Globigerina bulloides*
 1040 from the southwest Pacific Ocean. Paleoceanography 26, 1–15.
 1041 doi:10.1029/2010PA002059
 1042 Marshall, B.J., Thunell, R.C., Henehan, M.J., Astor, Y., Wejnert, K.E., 2013.

1043 Planktonic foraminiferal area density as a proxy for carbonate ion concentration:
 1044 A calibration study using the Cariaco Basin ocean time series. *Paleoceanography*
 1045 28, 363–376. doi:10.1002/palo.20034
 1046 Martin, P.A., Lea, D.W., 2002. A simple evaluation of cleaning procedures on fossil
 1047 benthic foraminiferal Mg/Ca. *Geochemistry Geophys. Geosystems* 3, 1–8.
 1048 doi:10.1029/2001GC000280
 1049 Mashiotto, T.A., Lea, D.W., Spero, H.J., 1999. Glacial – interglacial changes in
 1050 Subantarctic sea surface temperature and $\delta^{18}\text{O}$ -water using foraminiferal Mg.
 1051 *Earth Planet. Sci. Lett.* 170, 417–432.
 1052 Mavromatis, V., Montouillout, V., Noireaux, J., Gaillardet, J., Schott, J., 2015.
 1053 Characterization of boron incorporation and speciation in calcite and aragonite
 1054 from co-precipitation experiments under controlled pH, temperature and
 1055 precipitation rate. *Geochim. Cosmochim. Acta* 150, 299–313.
 1056 doi:10.1016/j.gca.2014.10.024
 1057 McConnell, M.C., Thunell, R.C., 2005. Calibration of the planktonic foraminiferal
 1058 Mg/Ca paleothermometer: Sediment trap results from the Guaymas Basin, Gulf
 1059 of California. *Paleoceanography* 20, 1–18. doi:10.1029/2004PA001077
 1060 Mekik, F., François, R., Soon, M., 2007. A novel approach to dissolution correction
 1061 of Mg/Ca-based paleothermometry in the tropical Pacific. *Paleoceanography* 22,
 1062 1–12. doi:10.1029/2007PA001504
 1063 Mohtadi, M., Hebbeln, D., Marchant, M., 2005. Upwelling and productivity along the
 1064 Peru–Chile Current derived from faunal and isotopic compositions of planktic

1065 foraminifera in surface sediments. *Mar. Geol.* 216, 107–126.
 1066 doi:10.1016/j.margeo.2005.01.008

1067 Morford, J.L., Emerson, S., 1999. The geochemistry of redox sensitive trace metals in
 1068 sediments. *Geochim. Cosmochim. Acta* 63, 1735–1750.

1069 Naik, S.S., Naidu, P.D., 2014. Boron/calcium ratios in *Globigerinoides ruber* from the
 1070 Arabian Sea: Implications for controls on boron incorporation. *Mar.*
 1071 *Micropaleontol.* 107, 1–7. doi:10.1016/j.marmicro.2014.01.004

1072 Ni, Y., Foster, G.L., Bailey, T., Elliott, T., Schmidt, D.N., Pearson, P., Haley, B.,
 1073 Coath, C., 2007. A core top assessment of proxies for the ocean carbonate
 1074 system in surface-dwelling foraminifers. *Paleoceanography* 22, 1–14.
 1075 doi:10.1029/2006PA001337

1076 Nürnberg, D., Bijma, J., Hemleben, C., 1996. Assessing the reliability of magnesium
 1077 in foraminiferal as a proxy for water mass temperatures calcite. *Geochim.*
 1078 *Cosmochim. Acta* 60, 803–814.

1079 Osborne, E.B., Thunell, R.C., Marshall, B.J., Holm, J.A., Tappa, E.J., Benitez-
 1080 Nelson, C., Cai, W.-J., Chen, B., 2016. Calcification of the planktonic
 1081 foraminifera *Globigerina bulloides* and carbonate ion concentration: Results
 1082 from the Santa Barbara Basin. *Paleoceanography* 31, 1–20.
 1083 doi:10.1002/2016PA002933.Received

1084 Pak, D.K., Kennett, J.P., 2002. A Foraminiferal Isotopic Proxy for Upper Water Mass
 1085 Stratification. *J. Foraminifer. Res.* 32, 319–327.

1086 Palmer, M.R., Brummer, G.J.A., Cooper, M.J., Elderfield, H., Greaves, M.J.,

1087 Reichart, G.-J., Schouten, S., Yu, J., 2010. Multi-proxy reconstruction of surface
 1088 water pCO₂ in the northern Arabian Sea since 29ka. *Earth Planet. Sci. Lett.* 295,
 1089 49–57. doi:10.1016/j.epsl.2010.03.023

1090 Patsavas, M.C., Byrne, R.H., Wanninkhof, R., Feely, R.A., Cai, W.-J., 2015. Internal
 1091 consistency of marine carbonate system measurements and assessments of
 1092 aragonite saturation state: Insights from two U.S. coastal cruises. *Mar. Chem.*
 1093 176, 9–20. doi:10.1016/j.marchem.2015.06.022

1094 Pelletier, G., Lewis, E., Wallace, D., 2007. CO₂sys.xls: a calculator for the CO₂
 1095 system in seawater for Microsoft Excel/VBA.

1096 Penman, D.E., Zeebe, R.E., Thomas, E., Zachos, J.C., Hönisch, B., Zeebe, R.E.,
 1097 Thomas, E., Zachos, J.C., 2014. Rapid and sustained surface ocean acidification
 1098 during the Paleocene-Eocene Thermal Maximum. *Paleoceanography* 1–13.
 1099 doi:10.1002/2014PA002621

1100 Regenber, M., Nürnberg, D., Steph, S., Groeneveld, J., Garbe-Schönberg, D.,
 1101 Tiedemann, R., Dullo, W.-C., 2006. Assessing the effect of dissolution on
 1102 planktonic foraminiferal Mg/Ca ratios: Evidence from Caribbean core tops.
 1103 *Geochemistry, Geophys. Geosystems* 7, 1–23. doi:10.1029/2005GC001019

1104 Reynolds, L.A., Thunell, R.C., 1985. Seasonal succession of planktonic foraminifera
 1105 in the subpolar North Pacific. *J. Foraminifer. Res.* 15, 282–301.

1106 Rosenthal, Y., Field, M.P., Sherrell, R.M., 1999. Precise determination of
 1107 element/calcium ratios in calcareous samples using sector field inductively
 1108 coupled plasma mass spectrometry. *Anal. Chem.* 71, 3248–53.

1109 doi:10.1021/ac981410x
 1110 Rosenthal, Y., Perron-Cashman, S., Lear, C.H., Bard, E., Barker, S., Billups, K.,
 1111 Bryan, M., Delaney, M.L., Dwyer, G.S., Elderfield, H., German, C.R., Greaves,
 1112 M.J., Lea, D.W., Marchitto, T.M., Pak, D.K., Paradis, G.L., Russell, A.D.,
 1113 Schneider, R.R., Scheiderich, K., Stott, L.D., Tachikawa, K., Tappa, E., Thunell,
 1114 R.C., Wara, M.W., Weldeab, S., Wilson, P.A., 2004. Interlaboratory comparison
 1115 study of Mg/Ca and Sr/Ca measurements in planktonic foraminifera for
 1116 paleoceanographic research. *Geochemistry, Geophys. Geosystems* 5, 1–29.
 1117 doi:10.1029/2003GC000650
 1118 Ruiz-Agudo, E., Putnis, C.V., Kowacz, M., Ortega-Huertas, M., Putnis, A., 2012.
 1119 Boron incorporation into calcite during growth: Implications for the use of boron
 1120 in carbonates as a pH proxy. *Earth Planet. Sci. Lett.* 345–348, 9–17.
 1121 doi:10.1016/j.epsl.2012.06.032
 1122 Russell, A.D., Hönisch, B., Spero, H.J., Lea, D.W., 2004. Effects of seawater
 1123 carbonate ion concentration and temperature on shell U, Mg, and Sr in cultured
 1124 planktonic foraminifera. *Geochim. Cosmochim. Acta* 68, 4347–4361.
 1125 doi:10.1016/j.gca.2004.03.013
 1126 Sabine, C.L., Feely, R.A., Gruber, N., Key, R.M., Lee, K., Bullister, J.L.,
 1127 Wanninkhof, R., Wong, C.S., Wallace, D.W.R., Tilbrook, B., Millero, F.J.,
 1128 Peng, T.-H., Kozyr, A., Ono, T., Rios, A.F., 2004. The Oceanic Sink for
 1129 Anthropogenic CO₂. *Science* (80-.). 305, 367–371.
 1130 doi:10.1126/science.1097403

1131 Sanyal, A., Nugent, M., Reeder, R.J., Bijma, J., 2000. Seawater pH control on the
 1132 boron isotopic composition of calcite: Evidence from inorganic calcite
 1133 precipitation experiments. *Geochim. Cosmochim. Acta* 64, 1551–1555.
 1134 Sarmiento, J.L., Gruber, N., 2006. Ocean biogeochemical dynamics. Princeton
 1135 University.
 1136 Sautter, L.R., Thunell, R.C., 1991a. Planktonic foraminiferal response to upwelling
 1137 and seasonal hydrographic conditions: sediment trap results from San Pedro
 1138 Basin, Southern California Bight. *J. Foraminifer. Res.* 21, 347–363.
 1139 Sautter, L.R., Thunell, R.C., 1991b. Seasonal variability in the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of
 1140 planktonic foraminifera from an upwelling environment: sediment trap results
 1141 from the San Pedro Basin, Southern California Bight. *Paleoceanography* 6, 307–
 1142 334.
 1143 Schlitzer, R., 2006. Ocean Data View [WWW Document]. [http://odv.awi-](http://odv.awi-bremerhaven.de)
 1144 [bremerhaven.de](http://odv.awi-bremerhaven.de).
 1145 Schmidt, G.A., Bigg, G.R., Rohling, E.J., 1999. Global Seawater Oxygen-18
 1146 Database - v1.21. <http://data.giss.nasa.gov/o18data/>.
 1147 Seki, O., Foster, G.L., Schmidt, D.N., Mackensen, A., Kawamura, K., Pancost, R.D.,
 1148 2010. Alkenone and boron-based Pliocene $p\text{CO}_2$ records. *Earth Planet. Sci. Lett.*
 1149 292, 201–211. doi:10.1016/j.epsl.2010.01.037
 1150 Tang, J., Köhler, S.J., Dietzel, M., 2008. $\text{Sr}^{2+}/\text{Ca}^{2+}$ and $^{44}\text{Ca}/^{40}\text{Ca}$ fractionation
 1151 during inorganic calcite formation: I. Sr incorporation. *Geochim. Cosmochim.*
 1152 *Acta* 72, 3718–3732. doi:10.1016/j.gca.2008.05.031

1153 Tripathi, A.K., Roberts, C.D., Eagle, R.A., 2009. Coupling of CO₂ and ice sheet
 1154 stability over major climate transitions of the last 20 million years. *Science* 326,
 1155 1394–7. doi:10.1126/science.1178296

1156 Uchikawa, J., Penman, D.E., Zachos, J.C., Zeebe, R.E., 2015. Experimental evidence
 1157 for kinetic effects on B/Ca in synthetic calcite: Implications for potential
 1158 B(OH)₄⁻ and B(OH)₃ incorporation. *Geochim. Cosmochim. Acta* 150, 171–
 1159 191. doi:10.1016/j.gca.2014.11.022

1160 Ujiie, Y., Ujiie, H., 2000. Distribution and oceanographic relationships of modern
 1161 planktonic foraminifera in the Ryuku Arc region, northwest Pacific Ocean. *J.*
 1162 *Foraminifer. Res.* 30, 336–360.

1163 von Langen, P.J., Lea, D.W., Spero, H.J., 2000. Effects of temperature on oxygen
 1164 isotope and Mg/Ca values in *Neogloboquadrina pachyderma* shells determined
 1165 by live culturing. *Eos Trans. AGU* 81.

1166 von Langen, P.J., Pak, D.K., Spero, H.J., Lea, D.W., 2005. Effects of temperature on
 1167 Mg/Ca in neogloboquadrinid shells determined by live culturing. *Geochemistry,*
 1168 *Geophys. Geosystems* 6, 1–11. doi:10.1029/2005GC000989

1169 Wara, M.W., Delaney, M.L., Bullen, T.D., Ravelo, A.C., 2003. Possible roles of pH,
 1170 temperature, and partial dissolution in determining boron concentration and
 1171 isotopic composition in planktonic foraminifera. *Paleoceanography* 18, 24.
 1172 doi:10.1029/2002PA000797

1173 Watson, E.B., 2004. A conceptual model for near-surface kinetic controls on the
 1174 trace- element and stable isotope composition of abiogenic calcite crystals.

1175 Geochim. Cosmochim. Acta 68, 1473–1488. doi:10.1016/j.gca.2003.10.003
 1176 Yu, J., Elderfield, H., Greaves, M.J., Day, J., 2007a. Preferential dissolution of
 1177 benthic foraminiferal calcite during laboratory reductive cleaning. Geochemistry
 1178 Geophys. Geosystems 8, 1–17. doi:10.1029/2006GC001571
 1179 Yu, J., Elderfield, H., Hönisch, B., 2007b. B/Ca in planktonic foraminifera as a proxy
 1180 for surface seawater pH. Paleoceanography 22, 1–17.
 1181 doi:10.1029/2006PA001347
 1182 Yu, J., Thornalley, D.J.R., Rae, J.W.B., McCave, N.I., 2013. Calibration and
 1183 application of B/Ca , Cd/Ca , and $\delta^{11}\text{B}$ in *Neogloboquadrina pachyderma*
 1184 (sinistral) to constrain CO₂ uptake in the subpolar North Atlantic during the last
 1185 deglaciation. Paleoceanography 28, 237–252. doi:10.1002/palo.20024
 1186 Zeebe, R.E., Wolf-Gladrow, D.A., 2005. CO₂ in Seawater: Equilibrium, Kinetics,
 1187 Isotopes, Elsevier O. ed. Elsevier, Amsterdam.
 1188

Figure 1

Figure 2

Figure 3

- *G. bulloides*
- ◆ *N. incompta*
- ▲ Encrusted *G. bulloides*
- ◇ Yu et al. 2013, *N. pachyderma*
- Yu et al. 2007, *G. bulloides*

Figure 4

Figure 5