B/Ca in coccoliths and relationship to calcification vesicle pH and dissolved inorganic carbon concentrations

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Electronic Annex 1: Model simulations of B isotopic composition of coccoliths

1) Stable isotopes of B and their inclusion in the model

Since the model of B uptake in coccolithophorids differs significantly from models used for organisms like foraminifera or corals which calcify from a seawater reservoir, model predictions of the B isotopic composition of the coccoliths may offer a test of the relevance of the model and illustrate the potential for future paired measurements of B/Ca and B isotopes in the coccolith to more tightly constrain chemical conditions in the coccolith vesicle.

Boron has two stable isotopes, ^{11}B and ^{10}B, which are fractionated between the borate and boric acid present in seawater. The δ^{11}B of boric acid is 19 to 35 permil higher than that of borate, with the exact value of the fractionation factor ($\alpha_{4\text{-}3}$, expression of fractionation between $B(OH)_3$ and $B(OH)_4^-$, equivalent to $1/^{11\text{-}10}K_B$) still under discussion. The $^{11\text{-}10}K_B$ was originally estimated at 1.0194 (Kakihana et al., 1977) but subsequent theoretical and experimental work suggests a value in the range of 1.025 to 1.035 (Liu and Tossell, 2005; Oi, 2000; Rustad et al., 2010; Sonoda et al., 2000; Zeebe, 2005). We use the intermediate value of 1.0272 (Klochko et al., 2006) in our calculations. Whereas absolute values of modeled δ^{11}B are clearly dependent on the choice of $^{11\text{-}10}K_{B,}$ the main trends of B isotope variation in the model are independent of the exact choice of $^{11\text{-}10}K_{B.}$ The isotopic composition of B is tracked throughout the model calculations described in the main text. We illustrate in figures the isotopic composition of borate in the coccolith vesicle. The B isotopic composition of coccoliths is expected to be identical to that of borate in the coccolith vesicle, since borate is the form of B incorporated into the calcite (Hemming et al., 1998; Hemming and Hanson, 1992; Hemming et al., 1995; Rae et al., 2011).

2) Model predictions for B isotopes in coccoliths

Because boric acid is the main form of B acquired by cells in our model, the boron isotopic composition of borate (and coccoliths) is always enriched relative to seawater borate. In the first of our model experiments (described in main text, section 4.2), we maintain a constant coccolith vesicle pH (either 8.3, 8.0, or 7.8) and DIC. As described previously, in each case, as seawater pH increases, there is reduced cellular uptake of boric acid resulting in reduced borate in the coccolith vesicle and a lower B/Ca of the coccolith. Borate in the coccolith vesicle, and therefore B in coccoliths, always has a higher δ^{11}B value than seawater borate (Figure EA-1-1b). At higher coccolith vesicle pH values, the borate in the coccolith vesicle is increasingly offset to higher δ^{11}B values because a higher fraction of the vesicle boric acid is converted to borate. The slope in plots of δ^{11}B vs. seawater pH is the same for all cases because the variable seawater pH causes a change in the δ^{11}B of seawater boric acid, which is inherited by the coccolith vesicle.

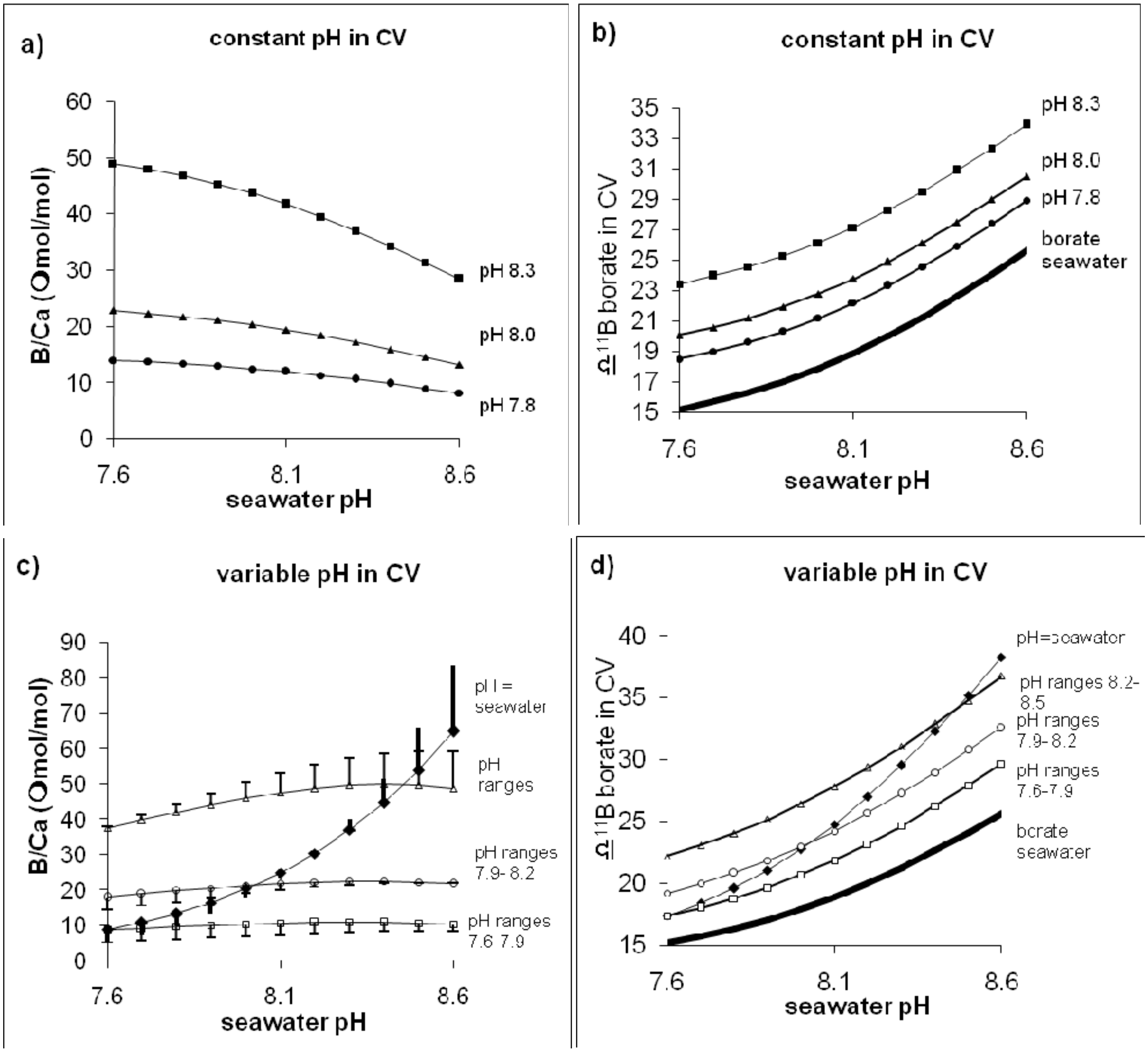

Figure EA-1-1. Modeled variations in coccolith B/Ca and boron isotopic composition of borate in the coccolith vesicle. a) and b) Case for constant pH and DIC of 2200 µmol kg^{-1} in the coccolith vesicle. Three pH values are indicated: pH = 8.3 (filled squares), pH = 8.0 (open triangles) and pH=7.8 (solid circles). In b) the bold black curve provides the isotopic composition of the extracellular borate in seawater. c) and d) Case for variable pH and constant DIC of 2200 µmol kg^{-1} in the coccolith vesicle. Solid diamond indicates coccolith vesicle pH identical to seawater pH (i.e. ranging from 7.6 to 8.6). Cases of attenuated covariation of C.V. pH with seawater pH are shown for C.V. pH 8.2-8.5 (open triangles), pH 7.9-8.2 (open circles) and pH 7.6 to 7.9 (open squares**).** In c) the vertical error bars show the difference between B/Ca expected for K_D of 0.0005 and the B/Ca that results if the K_D varied by +/- 35% over the coccolith vesicle pH range from 7.6 to 8.6, as described in the section 4.1.6 of the text. The model calculations were done assuming seawater speciation constants for boron and carbonate system given by (Dickson et al., 2007), for salinity of 35 and temperature of 20ºC and pH on total scale.

If the pH of the coccolith vesicle varies to be equal to seawater pH, then borate in the coccolith vesicle will increase because the proportional change in vesicular borate with increasing pH is greater than the proportional decrease in ambient boric acid. This leads to a steep rise in B/Ca of coccoliths with increasing seawater pH, (as shown in main text Figure 4c), and steepens the slope of coccolith $\delta^{11}B$ vs seawater pH, compared to the slope for constant CV pH (Figure EA-1-1d). In the other cases, where coccolith vesicle pH covaries with that of seawater, but to a lesser extent, then the trend of decreasing boric acid uptake is offset by the increasing fraction as borate inside the cell, and the slope of $\delta^{11}B$ with increasing seawater pH is intermediate between the case of constant CV pH and the case of identical variations in seawater and CV pH (Figure EA-1-1d). This is because of the combined effects of increasing $\delta^{11}B$ of external boric acid and internal borate.

3) Potential for paired measurements of coccolith $\delta^{11}B$ and B/Ca to constrain conditions in the coccolith vesicle

Since the B isotopic composition is independent of the DIC concentration and responds only to pH, combined measurements of B/Ca and the B isotopic composition of coccoliths could more tightly constrain the chemical conditions in the coccolith vesicle. In section 4.3.1 of the main text we noted that for a given seawater pH, the various strains of *E. huxleyi* defined distinct high and low B/Ca populations, which could be explained by either differences in coccolith vesicle pH or DIC. In the case of variable pH in the coccolith vesicle, there would be substantial differences in the $\delta^{11}B$ of borate in the coccolith vesicle among the different strains, which should be reflected in the $\delta^{11}B$ of the coccoliths (Figure EA-1-2). Alternatively, if the different B/Ca arise from variable DIC but constant pH in the CV, then $\delta^{11}B$ of coccoliths would be uniform for all strains (Figure EA-1-2). The absolute $\delta^{11}B$ would depend on the particular pH of the CV.

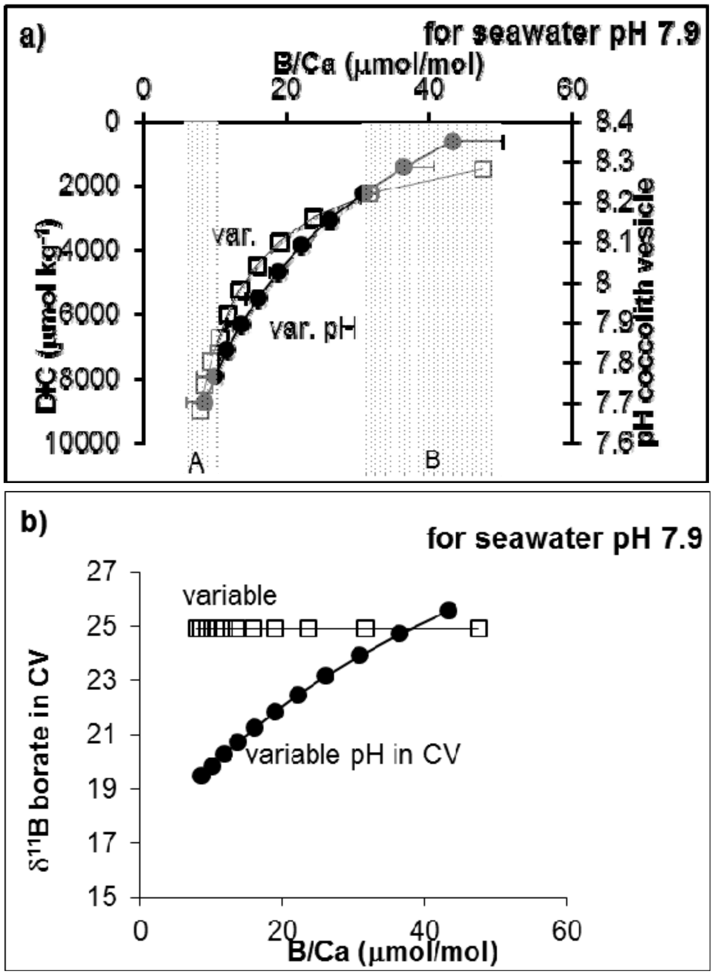

Figure EA-1-2. a) For the case of constant seawater pH of 7.9, estimate of the degree of variation in coccolith vesicle pH or DIC (in µmol kg^{-1}) which would be required to produce the range from low B/Ca (zone A, coinciding with values found in *E. huxleyi* RCC1212 and *C. braarudii*) to high B/Ca (zone B, coinciding with values found in *E. huxleyi* RCC1256 and RCC1238). Filled circles exhibit modeled variation for variable pH at a constant coccolith vesicle DIC of 2200 µmol kg^{-1}, open squares exhibit modeled variation for DIC (in µmol kg^{-1}) assuming a constant coccolith vesicle pH of 8.3. b) Modeled B isotopic composition for both scenarios described in panel a), if the variations in coccolith B/Ca among different strains at pH 7.9 are due entirely to changes in coccolith vesicle DIC (open square) or to changes in coccolith vesicle pH (solid circle). pH on total scale.

The rapidly growing strain of *C. braarudii* (2009) exhibited increasing B/Ca with increasing seawater pH, which could be accounted for by large changes in coccolith vesicle pH or by a large decrease in coccolith vesicle DIC concentration with increasing seawater pH (as described in section 4.1.3 of the main text). These two scenarios would be readily distinguished by B isotopic determinations since the case of the variable pH would entail a much larger variation in the δ^{11}B of borate in the coccolith vesicle than the case of constant pH and variable DIC in the coccolith vesicle (Figure EA-1-3).

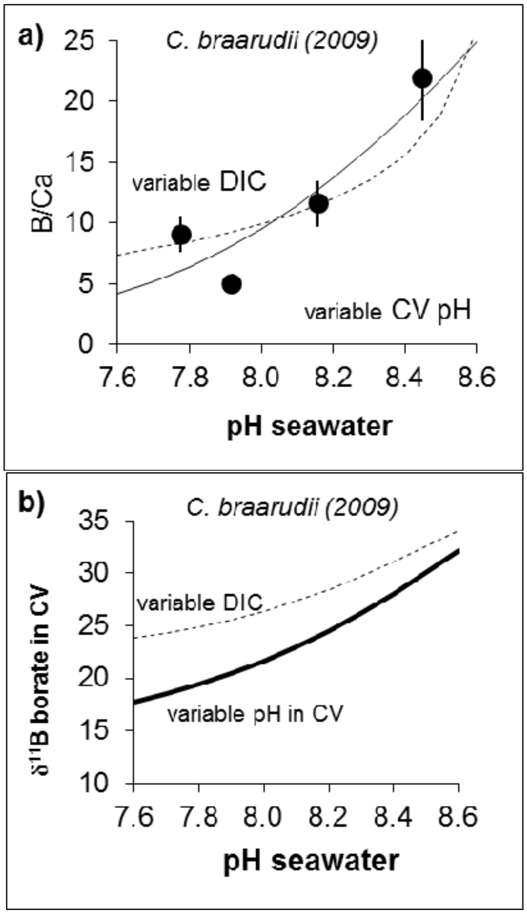

Figure EA-1-3. Comparison of B/Ca measurements in *C. braarudii* coccoliths grown at different seawater pH in 2009, and the modeled B/Ca and B isotopic composition of coccoliths. Solid line shows model for variable coccolith vesicle pH and DIC (pH of coccolith vesicle increasing from 7.7 to 8.2 as seawater pH increases, and coccolith vesicle DIC varying to maintain constant carbonate ion concentration of 200 μmol kg^{-1}). Dashed line shows model for constant coccolith vesicle pH of 8.35 and DIC decreasing with increasing seawater pH from 11000 to 1800 μmol/L. a) B/Ca, all in μmol/mol. For culture data, for simplicity a single error estimate from the 2 r.s.e. analytical uncertainty is shown. . b) Modeled variation in boron isotopic composition. Culture pH converted to total pH scale.

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