Reconstructing coral calcification fluid dissolved inorganic carbon chemistry from skeletal boron: An exploration of potential controls on coral aragonite B/Ca

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Abstract

The boron geochemistry of coral skeletons reflects the dissolved inorganic carbon (DIC) chemistry of the calcification fluid from which the skeletons precipitates and may be a valuable tool to investigate the effects of climate change on coral calcification. In this paper I calculate the predicted B/Ca of aragonite precipitating from seawater based fluids as a function of pH, [DIC] and [Ca2+]. I consider how different co-precipitating DIC species affect aragonite B/Ca and also estimate the impact of variations in the B(OH)4−/co-precipitating DIC aragonite partition coefficient (KD), which may be associated with changes in the DIC and Ca2+ chemistry of the calcification fluid. The coral skeletal B/Ca versus calcification fluid pH relationships reported previously can be reproduced by estimating B (OH)4− and co-precipitating DIC speciation as a function of pHCF and assuming that KD are constant i.e. unaffected by calcification fluid saturation state. Assuming that B(OH)4− co-precipitates with CO32−, then observed patterns can be
reproduced by a fluid with approximately constant [DIC] i.e. increasing pH\textsubscript{CF} concentrates CO\textsubscript{3}^{2-}, as a function of DIC speciation. Assuming that B(OH)\textsubscript{4}^- co-precipitates with HCO\textsubscript{3}^- only or CO\textsubscript{3}^{2-} + HCO\textsubscript{3}^- then the observed patterns can be reproduced if [DIC]\textsubscript{CF} and pH\textsubscript{CF} are positively related i.e. if DIC is increasingly concentrated in the calcification fluid at higher pH\textsubscript{CF} probably by CO\textsubscript{2} diffusion into the calcification site.

Keywords: Geochemistry, Geology, Oceanography

1. Introduction

The boron geochemistry of coral skeletons offers a potential method to reconstruct the dissolved inorganic carbon (DIC) chemistry of the coral calcification fluid (Allison et al., 2014) and to determine how it responds to environmental change. Coral biomineralisation underpins the production of the coral reef structure and understanding the controls on the calcification process is key to predicting the impacts of increasing seawater temperatures (Hoegh-Guldberg et al., 2007) and pCO\textsubscript{2} (ocean acidification, Caldeira and Wickett, 2003) on reef development.

Dissolved boron in seawater occurs primarily as boric acid, B(OH)\textsubscript{3}, and borate, B (OH)\textsubscript{4}^-, and speciation is controlled by ambient pH (Hemming and Hanson, 1992). Most reports suggest that B(OH)\textsubscript{4}^- is selectively incorporated into aragonite (Sen et al., 1994; Noireaux et al., 2015) substituting for CO\textsubscript{3}^{2-} in the lattice (Balan et al., 2016) and is depleted in \textsuperscript{11}B compared to B(OH)\textsubscript{3} (Klochko et al., 2006). Hence aragonite \textdelta\textsuperscript{11}B reflects the pH of the fluid from which it precipitates (Allison et al., 2010) while [B] (usually measured as B/Ca) reflects both fluid pH and the concentration of the DIC species competing with B(OH)\textsubscript{4}^- for inclusion in the carbonate (Allen et al., 2012).

Coral aragonite precipitates from an extracellular calcifying fluid enclosed in a semi-isolated space between the coral tissue and underlying skeleton (Clode and Marshall, 2002). The calcification fluid is derived from seawater (Tambutté et al., 2012) but corals actively increase its pH above that of seawater (Al-Horani et al., 2003; Venn et al., 2011; Venn et al., 2012) altering the fluid DIC chemistry. To date there has been no direct comparison of coral skeletal \textdelta\textsuperscript{11}B and calcifying fluid pH to confirm that skeletal \textdelta\textsuperscript{11}B records actual calcifying fluid pH. Fluid pH can be estimated by direct observation of pH sensitive dyes at the calcification site. The mean pH of dye-based observations in the light and dark of the branching coral Stylophora pistillata (Venn et al., 2011) is in good agreement with fluid pH estimates derived from skeletal \textdelta\textsuperscript{11}B of different individuals of the same coral species cultured at present day seawater pCO\textsubscript{2} (Krief et al., 2010), when corrected for the typical ratio of light:dark calcification rates (Gattuso et al., 1999). Positive trends are observed between seawater pH and calcification fluid pH when fluid pH is either inferred from skeletal \textdelta\textsuperscript{11}B (Honisch et al., 2004; Reynaud et al., 2004) or...
directly measured (Venn et al., 2012). These collective observations suggest that skeletal δ¹¹B reflects calcification fluid pH changes.

Increasing calcification fluid pH shifts the fluid DIC equilibrium in favour of carbonate (CO₃²⁻) at the expense of CO₂ and bicarbonate (HCO₃⁻) and creates a concentration gradient facilitating the diffusion of CO₂ from the overlying coral tissue into the fluid (Erez, 1978). This CO₂ can react to form more HCO₃⁻ and CO₃²⁻, thereby increasing calcification fluid DIC. Preliminary application of the skeletal B/Ca – calcification fluid DIC proxy suggested that [DIC] at the coral calcification site is increased above that of seawater and that bicarbonate contributes to the DIC pool used for calcification (Allison et al., 2014). The B (OH)₄⁻:aragonite partition coefficient utilized in this study was estimated from the B/Ca analysis of a secondary aragonite cement in a fossil coral coupled with alkalinity measurements of pore fluid and δ¹¹B of the cement (indicating pore fluid pH). Recent inorganic aragonite precipitation studies indicate that the borate: aragonite partition coefficient can be highly variable (Mavromatis et al., 2015; Holcomb et al., 2016) and is probably affected by the saturation state of the precipitating fluid (Holcomb et al., 2016). This complicates the interpretation of coral skeletal [B].

In this paper I explore how variations in calcification fluid DIC, [Ca²⁺] and pH affect skeletal B/Ca. Both boron and DIC speciation are pH dependent while variations in fluid DIC affect the saturation state of the fluid. I calculate the predicted B/Ca of aragonite precipitating from seawater based fluids with DIC, B and Ca²⁺ chemistries which are comparable to those of coral calcification fluids. Most coral datasets do not exhibit significant correlations between calcification fluid pH (inferred from δ¹¹B) and skeletal B/Ca (Fig. 1) and it is timely to consider why this is. It is unclear which dissolved inorganic carbon (DIC) species is/are involved in aragonite precipitation. CO₃²⁻ is predominantly incorporated in the crystal lattice (Von Euw et al., 2017) but HCO₃⁻ may also be involved in mineral precipitation (Wolthers et al., 2012; Mass et al., 2013; Von Euw et al., 2017). I consider how different co-precipitating DIC species affect aragonite B/Ca and also estimate the impact of variations in the B(OH)₄⁻/co-precipitating DIC aragonite partition coefficient, which may be associated with changes in the DIC and Ca²⁺ chemistry of the calcification fluid.

2. Methods

2.1. Impacts of coral processes on calcification fluid DIC chemistry

The key processes affecting calcification fluid DIC chemistry and their effects are summarized in Fig. 2. All pH values are reported on the total scale and the subscript CF denotes the DIC characteristics of the calcification fluid. Corals
increase pH_{CF} above that of seawater e.g. using the antiporter Ca-ATPase (Ip et al., 1991; Marshall, 1996) which pumps Ca^{2+} into the calcification site in exchange for 2H^{+}. H^{+} extrusion increases the total alkalinity of the fluid but does not affect DIC. Total alkalinity is defined as the number of moles of hydrogen equivalent to the excess of proton acceptors over proton donors in the fluid (Zeebe and Wolf-Gladrow, 2001) so proton extrusion increases total alkalinity and decreases [H^{+}] in a 1:1 mol ratio. Increasing pH_{CF} favours the reaction of CO_{2} and H_{2}O to form HCO_{3}^{-} and H^{+} and facilitates the diffusion of CO_{2} into the calcification site. This increases fluid [DIC] but does not affect total alkalinity. Bicarbonate anion

**Fig. 1.** Published relationships between coral calcification pH_{CF} (inferred from δ^{11}B) and skeletal B/Ca. Data sources are: 1 = Honisch et al. (2004); 2 = Allison et al. (2010), 3 = Dissard et al. (2012) and 4 = Allison et al. (2014). All data are corrected to the pH total scale. None of the datasets exhibit significant correlations between pH_{CF} and B/Ca with the exception of Acropora sp. corals cultured over a range of seawater pCO_{2} (Honisch et al., 2004).

**Fig. 2.** (a) The key processes affecting coral calcification fluid DIC chemistry and (b) their effects on seawater DIC, total alkalinity and pH_{CF}. 

transporters (BATs) convey HCO$_3^-$ into the calcification fluid, likely in exchange for Cl$^-$ (Zoccola et al., 2015). This increases total alkalinity and DIC in a 1:1 mol ratio and ultimately decreases pH$_{CF}$. Aragonite precipitation removes DIC and total alkalinity from the calcification fluid in a 1:2 mole ratio (one mole of the CO$_3^{2-}$ ion ultimately incorporated in the aragonite contains one mole of carbon but is doubly charged so contributes 2 moles to total alkalinity) and also decreases pH$_{CF}$.

2.2. Calcification fluid chemistry and precipitation scenarios

I calculate the DIC chemistry of a seawater based calcification fluid and the B/Ca of aragonite precipitated from it under a range of different scenarios (summarised in Table 1) as a function of pH$_{CF}$. The details of the scenarios are as follows:

2.2.1. Co-precipitating DIC species

I assume that either CO$_3^{2-}$ only, HCO$_3^-$ only, or both CO$_3^{2-}$ and HCO$_3^-$ co-precipitate with B(OH)$_4^-$ in the aragonite (Table 1, scenario 1).

Table 1. Summary of scenarios used to estimate coral calcification fluid chemistry and aragonite B/Ca.

| Scenario | Detail of different scenarios |
|----------|------------------------------|
| 1. Co-precipitating DIC species | a) B(OH)$_4^-$ co-precipitates with CO$_3^{2-}$<br>b) B(OH)$_4^-$ co-precipitates with HCO$_3^-$<br>c) B(OH)$_4^-$ co-precipitates with CO$_3^{2-}$ + HCO$_3^-$ |
| 2. DIC$_{CF}$ | a) DIC$_{CF}$ equals that of seawater (low DIC)<br>b) DIC$_{CF}$ is higher than that of seawater (high DIC) |
| 3. Seawater pCO$_2$ | a) Seawater DIC is in equilibrium with 400 μatm CO$_2$<br>b) Seawater DIC is in equilibrium with 800 μatm CO$_2$ |
| 4. B(OH)$_4^-$/co-precipitating DIC K$_D$ | a) variable<br>b) constant |
| 5. [Ca$^{2+}$]$_{CF}$ | a) [Ca$^{2+}$]$_{CF}$ covaries with proton extrusion<br>b) [Ca$^{2+}$]$_{CF}$ is unaffected by proton extrusion |
2.2.2. DIC\textsubscript{CF} and seawater pCO\textsubscript{2}

I assume that the [DIC\textsubscript{CF}] is either low or high and that the fluid is overlain or surrounded by coral tissues and/or ambient seawater in equilibrium with either 400 \textmu atm CO\textsubscript{2} or 800 \textmu atm CO\textsubscript{2}. I assume that [DIC\textsubscript{CF}] is either equivalent to that of seawater (the low DIC\textsubscript{CF} scenario) or is higher than this (the high DIC\textsubscript{CF} scenario), Table 1. In the case that [DIC\textsubscript{CF}] is equivalent to that of seawater, I effectively calculate the DIC of the calcification fluid as a closed system. I do not infer that the fluid is closed to CO\textsubscript{2} diffusion but rather that additions of CO\textsubscript{2} to the calcification fluid by diffusion are balanced by loss of DIC to precipitation. This is supported by direct measurements of pH\textsubscript{CF} and [CO\textsubscript{3}\textsuperscript{2-}]\textsubscript{CF} which indicate that DIC\textsubscript{CF} is approximately constant and equal to that of ambient seawater (Cai et al., 2016). I assume that ambient seawater is in equilibrium with either 400 \textmu atm CO\textsubscript{2} (ambient seawater has pH 8 and [DIC] = 1796 \mu mol kg\textsuperscript{-1}) or 800 \textmu atm CO\textsubscript{2} (ambient seawater has pH 7.74 and [DIC] = 1911 \mu mol kg\textsuperscript{-1}). This doubling of seawater pCO\textsubscript{2} indicates how DIC\textsubscript{CF} is affected if the [CO\textsubscript{2}] of the coral tissue and body compartments is higher than that of ambient seawater (Cai et al., 2016). In the high DIC scenario, I assume that diffusion of CO\textsubscript{2} into the calcification fluid increases [DIC\textsubscript{CF}] approximately twofold above that of seawater at typical coral calcification fluid pH and at a seawater pCO\textsubscript{2} of 400 \textmu atm CO\textsubscript{2}. The transport rate of CO\textsubscript{2} across a membrane can be expressed by Fick's first law of diffusion as:

\[
\text{Flux} = -P \cdot A \cdot \Delta C_w
\]  

Where P = the membrane permeability, A = the diffusional area and \Delta C\textsubscript{w} the difference of CO\textsubscript{2} concentrations in the water phase immediately adjacent to the two sides of the membrane (Endeward et al., 2014). Assuming that P and A remain constant, the flux of CO\textsubscript{2} into the calcification fluid is controlled by the CO\textsubscript{2} concentration difference between the calcification fluid and the overlying coral tissue. I estimate this concentration difference assuming that the [CO\textsubscript{2}] of the overlying tissue is the same as ambient seawater (11.3 \mu mol kg\textsuperscript{-1} and 22.6 \mu mol kg\textsuperscript{-1} in the 400 and 800 \mu atm CO\textsubscript{2} scenarios respectively) and that the [CO\textsubscript{2}] of the calcification fluid reflects that of ambient seawater brought to pH\textsubscript{CF} (Fig. 3a,b). I arbitrarily assume that CO\textsubscript{2} diffusion doubles the [DIC\textsubscript{CF}] at pH 8.5 (the typical mean coral calcification fluid pH, Allison et al., 2014) in the 400 \mu atm CO\textsubscript{2} scenario (i.e. adding 1796 \mu mol kg\textsuperscript{-1} to the DIC\textsubscript{CF}) and scale the addition of DIC to the calcification fluid over the full pH range at 400 and 800 \mu atm CO\textsubscript{2} as a linear function of \Delta C\textsubscript{w}. This calculation is shown in detail in Appendix 1. I assume that additional H\textsuperscript{+} extrusion compensates for the pH decrease associated with the ingress of CO\textsubscript{2} so that pH\textsubscript{CF} is unaffected by this CO\textsubscript{2} invasion. I calculate the final [DIC\textsubscript{CF}] as the [DIC\textsubscript{seawater}] plus CO\textsubscript{2} added by diffusion (Fig. 3c).
I estimate the concentrations of DIC species and total alkalinity in the calcification fluid by setting pH$_{CF}$ and [DIC]$_{CF}$ and calculating all other carbonate system parameters with CO2sys version 2.0 (Pierrot et al., 2006) using the equilibrium constants for carbonic acid from Mehrbach et al. (1973), refit by Dickson and Millero (1987) and for KH$_2$SO$_4$ from Dickson (1990). Total fluid boron was set to 416 μmol kg$^{-1}$ (Uppstrom, 1974). I assume constant temperature (25 °C) and salinity (35).

2.2.3. B(OH)$_4^-$/co-precipitating DIC aragonite $K_D$

To estimate the B(OH)$_4^-$/co-precipitating DIC aragonite partition coefficients (hereafter abbreviated to $K_D$) to apply in the calculations I combine data from two studies that measured boron partitioning in inorganic aragonite at ~25 °C.
(Mavromatis et al., 2015; Holcomb et al., 2016). I exclude data collected from experiments conducted in the presence of buffers. I calculate the $\text{B(OH)}_4^−/\text{DIC}_{\text{co-precipitating}}$ ratios of the precipitation fluids and combine these with the B/Ca of the precipitated aragonites to estimate $K_D$. Aragonite precipitation rate is typically positively correlated with the precipitation fluid saturation (Burton and Walter, 1987), an indication of the concentrations of solute ions in solution, and trace element partitioning may be affected by mineral precipitation rate (Watson, 1994; Elderfield et al., 1996). I plot the $K_D$ against the saturation of the precipitating fluid defined as $\Omega_{\text{aragonite}} ([\text{Ca}^{2+}] [\text{CO}_3^{2−}] / K^{*}_{\text{sparagonite}})$ for scenario 1a, $[\text{Ca}^{2+}] [\text{HCO}_3^{−}]$ for scenario 1b and $[\text{Ca}^{2+}] [\text{CO}_3^{2−} + \text{HCO}_3^{−}]$ for scenario 1c. The experiments of Mavromatis et al. (2015) and Holcomb et al. (2016) were conducted in 0.1–0.2 M NaCl solutions and seawater respectively. I have not corrected solute concentrations to activities. I have used stoichiometric equilibrium constants (conventionally denoted as $K^*$), which correct for ionic strength and utilize ion concentrations rather than activities, for all calculations. There are no obvious offsets between the data of Holcomb et al. (2016) and Mavromatis et al. (2015) and all 3 partition coefficients are linearly positively correlated with fluid saturation (Fig. 4) according to the relationships:

$$K_D \text{B(OH)}_4^−/\text{CO}_3^{2−} = 1.48 \times 10^{-3} \Omega - 1.30 \times 10^{-3} (r^2 = 0.86) \quad (2)$$

$$K_D \text{B(OH)}_4^−/\text{HCO}_3^{−} = 1.85 \times 10^{2} [\text{Ca}^{2+}] [\text{HCO}_3^{−}] + 4.01 \times 10^{-3} (r^2 = 0.89) \quad (3)$$

$$K_D \text{B(OH)}_4^−/(\text{CO}_3^{2−} + \text{HCO}_3^{−}) = 2.28 \times 10^{2} [\text{Ca}^{2+}] [\text{CO}_3^{2−} + \text{HCO}_3^{−}] + 3.81 \times 10^{-3} (r^2 = 0.87) \quad (4)$$

Fig. 4. $\text{B(OH)}_4^−/\text{co-precipitating DIC}$ aragonite partition coefficients (calculated from Mavromatis et al., 2015 and Holcomb et al., 2016) assuming that $\text{B(OH)}_4^−$ co-precipitates with (a) $\text{CO}_3^{2−}$ only, (b) $\text{HCO}_3^{−}$ only and (c) $\text{CO}_3^{2−} + \text{HCO}_3^{−}$, as a function of the saturation of the precipitating fluid defined as (a) $\Omega_{\text{aragonite}}$, (b) $[\text{Ca}^{2+}] [\text{HCO}_3^{−}]$ and (c) $[\text{Ca}^{2+}] [\text{CO}_3^{2−} + \text{HCO}_3^{−}]$, all concentrations in mol kg$^{-1}$. The lower half of each figure is an expanded view of the boxed section in the upper figure. The partition coefficients determined from analysis of an inorganic cement in a fossil coral (Allison et al., 2014) are also shown.
The incorporation of boron in aragonite is not fully understood but this observation is consistent with the growth entrapment model (e.g. Watson, 1994) which suggests that trace elements are captured as impurities at the crystal surface before they can diffuse back into the surrounding fluid. B/Ca incorporation in calcite is positively correlated with crystal extension (Gabitov et al., 2014) and precipitation rate (Uchikawa et al., 2015). $K_D \text{B(OH)}_4^-/\text{CO}_3^{2-}$ is also positively correlated with precipitation rate in aragonite but $K_D \text{B(OH)}_4^-/\text{HCO}_3^-$ and $K_D \text{B(OH)}_4^-/(\text{CO}_3^{2-} + \text{HCO}_3^-)$ do not show this relationship (Holcomb et al., 2016), although precipitation rate is not necessarily a good indication of crystal extension rate. In the growth entrapment model, maximum entrapment is reached at high crystal growth rates and $K_D$ becomes independent of crystal growth rate. This may just be occurring at the highest fluid saturation states in Fig. 4.

In calculating aragonite B/Ca I assume that $K_D$ are either dependent on fluid saturation state or are constant (scenarios 4a and b, Table 1). In the first case I am inferring that higher fluid saturation stimulates high crystal extension rates leading to relatively high B incorporation. In the second case I am assuming that high fluid saturation does not affect crystal extension rate. Coral calcification rates are positively correlated with the saturation states of the calcification fluid (Allison et al., 2014) and seawater (Gattuso et al., 1998). However it does not automatically follow that the growth rates of coral skeletal crystals increase at high saturation states. In the massive Porites spp. corals, typically used for palaeoenvironmental reconstruction, linear extension of the skeleton occurs by the deposition of centres of calcification or centres of rapid accretion (Nothdurft and Webb, 2007) which are aligned perpendicular to the plane of the skeleton surface. Fasciculi, composed of bundles of acicular aragonite crystals radiate out from these centres and are aligned perpendicular to the centres and approximately parallel to the skeleton surface. These make up the bulk of the skeleton (Allison, 1996). Fast coral calcification rates could reflect rapid extension of fasciculi crystals but could equally well be explained by constant extension rates of a larger volume of fasciculi crystals.

In the case that B(OH)$_4^-$/co-precipitating DIC $K_D$ is dependent on fluid saturation state (scenario 4a) I calculate calcification fluid saturation as $[\text{Ca}^{2+}]_{\text{CF}}[\text{CO}_3^{2-}]_{\text{CF}}/K^*_\text{sparagonite}$ for scenario 1a, $[\text{Ca}^{2+}]_{\text{CF}}[\text{HCO}_3^-]_{\text{CF}}$ for scenario 1b and $[\text{Ca}^{2+}]_{\text{CF}}[\text{HCO}_3^- + \text{CO}_3^{2-}]_{\text{CF}}$ for scenario 1c and then calculate $K_D$ from Eqs. (2)–(4) (Fig. 5). In the case that $K_D$ is independent of fluid saturation, I calculate the saturation state for a typical coral fluid based on direct measurements of $[\text{CO}_3^{2-}]_{\text{CF}}$ at pH$_{\text{CF}} = 8.55$ (pH = 8.7 NBS scale, Cai et al., 2016), broadly comparable to the mean pH$_{\text{CF}}$ derived from $\delta^{11}$B of massive Porites spp. field corals (Allison et al., 2014). I calculate $K_D$ of 0.00105, 0.00636 and 0.00669 for B(OH)$_4^-$/$\text{CO}_3^{2-}$, B (OH)$_4^-$/$\text{HCO}_3^-$ and B(OH)$_4^-$/(CO$_3^{2-} + \text{HCO}_3^-$) respectively. I apply these same $K_D$ to all scenarios in which I use a constant $K_D$, irrespective of [co-precipitating DIC]$_{\text{CF}}$, [Ca$^{2+}$]$_{\text{CF}}$ or CO$_2$ atmosphere.
2.2.4. \([Ca^{2+}]_\text{CF}\)

\([Ca^{2+}]_\text{CF}\) affects the saturation state of the calcification fluid and subsequently may influence the \(\text{B(OH)}_4^-\):aragonite partition coefficient (see section 2.2.3). I adopt 2 approaches to estimate \([Ca^{2+}]_\text{CF}\). In scenario 5a I assume that all proton extrusion from the calcification fluid is mediated by Ca-ATPase. This enzyme pumps 2\(H^+\) out of the fluid for every \(Ca^{2+}\) pumped in, thereby increasing fluid total alkalinity and \([Ca^{2+}]\) in a 2:1 mole ratio. I use the total alkalinity of the calcification fluid (calculated in the DICCF and seawater pCO\(_2\) section) to infer the activity of the enzyme and to calculate fluid \([Ca^{2+}]\) assuming that \([Ca^{2+}]\) of the fluid at pH 8 is that of ambient seawater (10 mmol kg\(^{-1}\)). Aragonite precipitation removes total alkalinity and \(Ca^{2+}\) in a 2:1 mole ratio so does not influence this approach. In scenario 5b I assume that proton extrusion is mediated by an alternative ATPase which does not affect fluid \([Ca^{2+}]\). Direct measurements of coral calcification fluids suggest that fluid \([Ca^{2+}]\) is similar to seawater (within 5%, Al-Horani et al., 2003) and in scenario 5b I assume a constant \([Ca^{2+}]_\text{CF}\) of 10 mmol kg\(^{-1}\).

2.2.5. Calculating aragonite B/Ca

I calculate the B/Ca of aragonite precipitated from the calcification fluid under the various scenarios. Aragonite B/Ca equates to aragonite \(\text{B(OH)}_4^-/\text{CO}_3^{2-}\) as \(C\) and \(C\) are equimolar in CaCO\(_3\). I assume that dissolved boron is transported into the calcification fluid in seawater and that the total \([B]\) of the fluid is the same as seawater i.e. 416 \(\mu\text{mol kg}^{-1}\) (Uppstrom, 1974). I assume this concentration is constant for all scenarios as aragonite precipitation has little effect on \([B]_\text{CF}\) due to the low \(\text{B(OH)}_4^-/\text{co-precipitating DIC}\) aragonite partition coefficients (Fig. 4). I estimate \([\text{B(OH)}_4^-]_\text{CF}\) using \(K_B = 2.527 \times 10^{-9}\) (Dickson, 1990) and calculate fluid \(\text{B(OH)}_4^-/\text{co-precipitating DIC}\). I multiply fluid \(\text{B(OH)}_4^-/\text{co-precipitating DIC}\) by \(K_D\) to calculate aragonite B/Ca.
3. Results and discussion

3.1. [DIC]_{CF}

$^{81}$B of *Porites* spp. field corals suggests that mean coral pH_{CF} is $\sim$8.5 (Allison et al., 2014). Here I assume that [DIC]_{CF} is either comparable to that of seawater or is doubled by CO$_2$ diffusion at pH_{CF} = 8.5 and 400 $\mu$atm CO$_2$. It is probable that these calculations reproduce the approximate DIC chemistry of the coral calcification fluid. Covariation of pH_{CF} and DIC_{CF} suggests that [DIC]_{CF} is broadly similar to that of seawater (Cai et al., 2016). While coral uptake of $^{45}$Ca and $^{14}$C in dual labelling experiments suggesting that the majority of skeletal carbon is derived from CO$_2$ which diffuses into the calcification site rather than from seawater (Erez, 1978).

In scenarios where [DIC]_{CF} increases above that of seawater I describe the CO$_2$ concentration gradient ($\Delta_{CW}$) between the coral tissue and the calcification fluid assuming that the [CO$_2$] of the overlying tissue is the same as ambient seawater and that fluid [CO$_2$] reflects that of ambient seawater brought to pH_{CF}. The [CO$_2$] of a fluid brought to pH_{CF} is exponentially related to pH_{CF} i.e. at high pH_{CF} fluid [CO$_2$] becomes progressively smaller (Fig. 3a,b). Any increase in $\Delta_{CW}$ at high pH_{CF} is also progressively smaller and fluid [DIC] eventually begins to plateau. The final [DIC]_{CF} ranges from 1796 $\mu$mol kg$^{-1}$ and 1911 $\mu$mol kg$^{-1}$ (the low DIC scenarios) to $\sim$4100 $\mu$mol kg$^{-1}$ and $\sim$6600 $\mu$mol kg$^{-1}$ at pH_{CF} 9 for the 400 and 800 $\mu$atm CO$_2$ high DIC scenarios respectively (Fig. 3c). [DIC]_{CF} is higher at 800 $\mu$atm CO$_2$ as the larger $\Delta_{CW}$ facilitates more CO$_2$ diffusion into the calcification fluid.

3.2. [Ca$^{2+}$]_{CF}

I estimate the [Ca$^{2+}$]_{CF} assuming that either Ca-ATPase is responsible for all proton extrusion (resulting in pumping of Ca$^{2+}$ into the calcification site) or that other, non-Ca pumping, enzymes fulfil this role (resulting in no change to [Ca$^{2+}$]_{CF}). In the first scenario [Ca$^{2+}$]_{CF} increases by 5% and 6% above that of seawater at 400 and 800 $\mu$atm CO$_2$ respectively at low DIC and by 23% and 42% respectively at high DIC (Fig. 3d). The concentration increase is higher in the high DIC scenarios because increased Ca-ATPase activity is required to attain pH_{CF} when more CO$_2$ diffuses into the calcification fluid. Similarly [Ca$^{2+}$]_{CF} increases more at 800 $\mu$atm CO$_2$ than at 400 $\mu$atm CO$_2$ reflecting the higher Ca-ATPase activity to reach pH $\sim$7.7.

3.3. Fluid B(OH)$_4^-$/[co-precipitating DIC]

Concentrations of individual co-precipitating DIC species under the different scenarios are illustrated in Fig. 6. In the low DIC scenarios I treat the calcification fluid as a closed system and the concentrations of co-precipitating DIC species are
dependent on pH$_{\text{CF}}$. [CO$_3^{2-}$]$_{\text{CF}}$ is positively correlated with pH$_{\text{CF}}$. [HCO$_3^{-}$]$_{\text{CF}}$ is negatively correlated and [CO$_3^{2-}$ + HCO$_3^{-}$]$_{\text{CF}}$ is almost constant (Fig. 6a,b solid lines). The high DIC scenarios (when CO$_2$ invasion increases [DIC]$_{\text{CF}}$ above that of seawater) are associated with higher [co-precipitating DIC]$_{\text{CF}}$ than the low DIC at comparable pH$_{\text{CF}}$. However while both [CO$_3^{2-}$]$_{\text{CF}}$ and [CO$_3^{2-}$ + HCO$_3^{-}$]$_{\text{CF}}$ are positively correlated with pH$_{\text{CF}}$, [HCO$_3^{-}$]$_{\text{CF}}$ increases to a maximum at $\sim$ pH 8.3–8.5 and then begins to decrease again (Fig. 5a,b dotted lines). Above this pH$_{\text{CF}}$, any further increase in [DIC]$_{\text{CF}}$ is relatively small (Fig. 3c) and the decrease in proportional abundance of HCO$_3^{-}$ as pH$_{\text{CF}}$ increases outweighs any increase in total [DIC]$_{\text{CF}}$.

B(OH)$_3$ and B(OH)$_4^{-}$ speciation are illustrated in Fig. 7 and calcification fluid B (OH)$_3$/co-precipitating DIC ratios are illustrated in Fig. 6c,d. B(OH)$_3$/HCO$_3^{-}$ and B(OH)$_4^{-}$/([CO$_3^{2-}$ + HCO$_3^{-}$]$_{\text{CF}}$) are positively correlated with pH$_{\text{CF}}$ in both the low and high DIC scenarios. As pH$_{\text{CF}}$ increases the increase in [B(OH)$_3$] (driven by the effect of pH on boron speciation) is larger than any increase in [HCO$_3^{-}$]$_{\text{CF}}$ and [CO$_3^{2-}$ + HCO$_3^{-}$]$_{\text{CF}}$. In contrast, fluid B(OH)$_3$/[CO$_3^{2-}$] is inversely correlated with pH$_{\text{CF}}$ at both low and high DIC. Here the proportional increase in [CO$_3^{2-}$]$_{\text{CF}}$.
at higher pH$_{CF}$ is larger than any increase in [B(OH)$_4$]$^{-}$.$\text{CF}$. The high DIC scenarios generate lower B(OH)$_4$$^{-}$/co-precipitating DIC than the low DIC scenarios at comparable pH because [co-precipitating DIC]$_{CF}$ are higher in the high DIC scenarios. Likewise, [co-precipitating DIC] are higher at 800 $\mu$atm seawater pCO$_2$ than at 400 $\mu$atm seawater pCO$_2$ for comparable pH$_{CF}$ yielding lower B(OH)$_4$$^{-}$/ [co-precipitating DIC] ratios at 800 $\mu$atm seawater pCO$_2$ (Fig. 6c,d).

3.4. Aragonite B/Ca

I calculate the B/Ca of aragonite precipitating from the fluids using the B(OH)$_4$$^{-}$/co-precipitating DIC fluid compositions (Fig. 6c,d) and calculated K$_D$ (Fig. 5) defined under the different scenarios. I consider a maximum of 48 scenarios (3 co-precipitating scenarios x 2 DIC scenarios x 2CO$_2$ atmospheres x 2 [Ca$^{2+}$] scenarios x 2 K$_D$ scenarios, Table 1). 30 of these are illustrated in Fig. 8. I do not reproduce the data that combine variable [Ca$^{2+}$]$_{CF}$ (scenario 5a) with a constant K$_D$ (scenario 4b) as in setting a constant K$_D$ I do not require [Ca$^{2+}$]$_{CF}$ to estimate calcification fluid saturation state. The constant and variable [Ca$^{2+}$]$_{CF}$ scenarios generate broadly similar patterns in skeletal B/Ca. I illustrate the impact of this change at 400 $\mu$atm seawater pCO$_2$ but calculate expected aragonite B/Ca at 800 $\mu$atm seawater pCO$_2$ using variable [Ca$^{2+}$]$_{CF}$ only.

3.4.1. Impact of K$_D$

Fig. 8a–f indicates aragonite B/Ca assuming that K$_D$ does not vary in response to calcification fluid saturation state. Patterns in calcification fluid B(OH)$_4$$^{-}$/co-precipitating DIC (Fig. 6c,d) are essentially preserved in aragonite B/Ca. Aragonite B/Ca is inversely correlated with pH$_{CF}$ if B(OH)$_4$$^{-}$ co-precipitates with CO$_3^{2-}$ and is positively correlated with pH$_{CF}$ if B(OH)$_4$$^{-}$ co-precipitates with HCO$_3^{-}$ or (CO$_3^{2-}$ + HCO$_3^{-}$). Higher [co-precipitating DIC]$_{CF}$ serves to dilute the calcification fluid B(OH)$_4$$^{-}$ and generates lower skeletal B/Ca. For this reason the high DIC
scenarios always generate lower skeletal B/Ca compared to the low DIC scenarios at comparable pH_{CF}.

Assuming that K_D varies in response to calcification fluid saturation state then these patterns change significantly (Fig. 8g–o). K_D is positively correlated with fluid saturation state for all co-precipitating DIC species (Fig. 4). In the case that B(OH)_4^- co-precipitates with CO_3^{2-}, [CO_3^{2-}]_{CF} is always relatively high at high pH_{CF} resulting in high K_D and enhanced B(OH)_4^- incorporation in the precipitating aragonite. Although fluid B(OH)_4^-/[CO_3^{2-}]_{CF} decreases at high pH (Fig. 6c), the increased B(OH)_4^- incorporation at high fluid saturation state overrides this dilution of fluid B(OH)_4^- by CO_3^{2-}. Put simply, over the pH_{CF} range 8 to 9 at 400 μatm seawater pCO_2, B(OH)_4^-/CO_3^{2-} decreases by x0.7 and x0.3 in the low and high DIC scenarios respectively (Fig. 6c) but K_D increases x8 and x22 (assuming a variable [Ca^{2+}]_{CF}) over the same pH range (Fig. 5b). So in the case that B(OH)_4^- co-precipitates with CO_3^{2-} and K_D is variable, aragonite B/Ca and pH_{CF} are always positively correlated (Fig. 8g,j,m). Higher aragonite B/Ca are generated in the high DIC scenarios than their low DIC counterparts for comparable pH_{CF} because the increase in K_D (promoting B(OH)_4^- incorporation in the aragonite) outweighs any B(OH)_4^- dilution by increased fluid [CO_3^{2-}].

Variable K_D have a more subtle effect on aragonite B/Ca if B(OH)_4^- co-precipitates with either HCO_3^- only or CO_3^{2-} + HCO_3^- . Assuming that B(OH)_4^- co-precipitates with HCO_3^-, then at low DIC both [HCO_3^-]_{CF} and K_D are
relatively high at low pH\textsubscript{CF} and relatively low at high pH\textsubscript{CF} (Fig. 6a,b and Fig. 5 respectively). As pH\textsubscript{CF} increases, the proportional increase in fluid B(OH)\textsubscript{4}\textsuperscript{-}/HCO\textsubscript{3}\textsuperscript{-} (Fig. 6c,d) exceeds the proportional decrease in K\textsubscript{D} and aragonite B/Ca and pH\textsubscript{CF} are positively correlated (Fig. 8i,l,o). This pattern is maintained at high DIC although in this case the proportional increase in K\textsubscript{D} (driven by higher [HCO\textsubscript{3}\textsuperscript{-}]\textsubscript{CF} compared to the low DIC scenario) is outweighed by the proportional decrease in fluid B(OH)\textsubscript{4}\textsuperscript{-}/HCO\textsubscript{3}\textsuperscript{-} (driven by increased [HCO\textsubscript{3}\textsuperscript{-}]\textsubscript{CF}). Thus the high DIC scenarios generate lower aragonite B/Ca than the low DIC scenarios at comparable pH\textsubscript{CF}. Predicted aragonite B/Ca is broadly similar if B(OH)\textsubscript{4}\textsuperscript{-} co-precipitates with both CO\textsubscript{3}\textsuperscript{2-} + HCO\textsubscript{3}\textsuperscript{-} as HCO\textsubscript{3}\textsuperscript{-} is usually the dominant DIC species over the range of pH\textsubscript{CF}. Once again aragonite B/Ca is positively correlated with pH\textsubscript{CF} in all scenarios and high DIC scenarios generate lower aragonite B/Ca than their low DIC counterparts (Fig. 8h,k,n).

3.4.2. Impact of [Ca\textsuperscript{2+}]\textsubscript{CF}

The constant and variable [Ca\textsuperscript{2+}]\textsubscript{CF} scenarios generate broadly similar patterns in skeletal B/Ca (i.e. compare Fig. 8g–i with Fig. 8j–l respectively). [Ca\textsuperscript{2+}]\textsubscript{CF} are higher under the variable [Ca\textsuperscript{2+}] scenarios compared to constant [Ca\textsuperscript{2+}]\textsubscript{CF}, as proton extrusion by Ca-ATPase serves to increase [Ca\textsuperscript{2+}]\textsubscript{CF}. This causes small increases in fluid saturation state and therefore K\textsubscript{D} (Fig. 5a,b). These higher K\textsubscript{D} result in higher aragonite B/Ca but the effect is relatively subtle (compare Fig. 8g–i and j–l) as the proportional changes in [Ca\textsuperscript{2+}]\textsubscript{CF} over all scenarios are small compared to changes in [co-precipitating DIC]\textsubscript{CF}.

3.4.3. Impact of seawater pCO\textsubscript{2}

Seawater pCO\textsubscript{2} has a relatively minor impact on aragonite B/Ca. All [co-precipitating DIC]\textsubscript{CF} species are increased at 800 \textmu atm seawater pCO\textsubscript{2} compared to 400 \textmu atm seawater pCO\textsubscript{2} (Fig. 8). At constant K\textsubscript{D} these increases dilute the precipitating B(OH)\textsubscript{4}\textsuperscript{-} and decrease aragonite B/Ca. Over all co-precipitation scenarios, changes between predicted aragonite B/Ca at 400 and 800 \textmu atm seawater pCO\textsubscript{2} are almost imperceptible at low DIC and more significant at high DIC. When K\textsubscript{D} is variable, the increases in [co-precipitating DIC]\textsubscript{CF} generate higher K\textsubscript{D}. If B (OH)\textsubscript{4}\textsuperscript{-} co-precipitates with CO\textsubscript{3}\textsuperscript{2-}, then the effect of increasing K\textsubscript{D} outweighs the effect of decreased fluid B(OH)\textsubscript{4}\textsuperscript{-}/[CO\textsubscript{3}\textsuperscript{2-}] and aragonite B/Ca is higher at 800 \textmu atm compared to 400 \textmu atm seawater pCO\textsubscript{2}. If B(OH)\textsubscript{4}\textsuperscript{-} co-precipitates with HCO\textsubscript{3}\textsuperscript{-} or both CO\textsubscript{3}\textsuperscript{2-} + HCO\textsubscript{3}\textsuperscript{-} then the effect of decreased fluid B(OH)\textsubscript{4}\textsuperscript{-}/[co-precipitating DIC] outweighs the effect of increasing K\textsubscript{D} and aragonite B/Ca is lower at 800 \textmu atm compared to 400 \textmu atm seawater pCO\textsubscript{2}. Under all co-precipitation scenarios at variable K\textsubscript{D} changes between predicted aragonite B/Ca at 400 and 800 \textmu atm seawater pCO\textsubscript{2} are very subtle.
3.4.4. Additional factors to consider

Rayleigh fractionation can occur when aragonite precipitates from an isolated fluid reservoir (Elderfield et al., 1996). As the $K_D$ for all $\text{B(OH)}_4^−/\text{co-precipitating DIC}$ species are much smaller than 1, $\text{B(OH)}_4^−$ is preferentially discriminated against during aragonite formation. As precipitation proceeds, the $\text{B(OH)}_4^−/\text{co-precipitating DIC}$ of the fluid remaining in the reservoir, and of the aragonite precipitated from it, increases. The final $\text{B/Ca}$ of the precipitated aragonite reflects the proportion of the reservoir used in precipitation (Fig. 9). If Rayleigh fractionation occurs in the coral calcification fluid then skeletal $\text{B/Ca}$ will increase when a relatively large proportion of the fluid reservoir is precipitated. This is likely to occur at high fluid saturation states.

Partition coefficients are usually lower in aragonites precipitated on seeds compared to unseeded material (Fig. 4) and the coefficients utilised here may overestimate the calcification fluid DIC of coral aragonite (which precipitates on existing skeletal aragonite).

In the scenario that ($\text{B(OH)}_4^−$ co-precipitates with $\text{CO}_3^{2−}$, in some instances the calcification fluid saturation states exceed the maximum state observed in the calculation of $K_D$ (Fig. 4). This occurs at pH 9 in the high DIC scenario at 400 μatm seawater pCO$_2$ and ≥pH 8.6 in the high DIC scenario at 800 μatm seawater pCO$_2$. I have assumed that $K_D$ is linearly correlated with calcification fluid saturation state and these high fluid saturation states generate $K_D$ (Fig. 5) that exceed the maximum values observed in Fig. 4. Under the growth entrapment model, $K_D$ approaches a constant value at high crystal extension rates (assumed to occur at high fluid saturation states) and in this case it is likely that I have overestimated aragonite $\text{B/Ca}$ at high pH$_{\text{CF}}$ in the high DIC scenario at 800 μatm seawater pCO$_2$.

![Fig. 9. Aragonite B/Ca as a function of the % of the fluid reservoir utilised during precipitation assuming that B(OH)$_4^−$ co-precipitates with CO$_3^{2−}$. The B(OH)$_4^−$/CO$_3^{2−}$ aragonite partition coefficient is arbitrarily set to 0.00105 when none of the reservoir is utilised.](http://dx.doi.org/10.1016/j.heliyon.2017.e00387)
3.5. Comparing modelled and observed coral skeletal B/Ca

The observed coral skeletal B/Ca from corals that grew under ambient CO₂ conditions (i.e. all the data from Fig. 1 with the exception of corals cultured under altered seawater pCO₂, Honisch et al., 2004) are superimposed onto the graphs in Fig. 8. I do not make any corrections for the different temperatures under which the corals grew. Temperature affects both DIC and boron speciation but the temperature range associated with the data represented in Fig. 1 is small (22–28 °C) and has a relatively minor effect on fluid B(OH)₄⁻/co-precipitating DIC (<15%). Temperature also has no observable effect on boron partitioning in aragonite above fluid pH of 8.3 (Mavromatis et al., 2015).

Given the assumptions made in the calculations, e.g. in setting [DIC]CF and constant K_D, I do not attempt to identify a scenario which duplicates the observed coral B/Ca values. However a comparison of the distribution of aragonite B/Ca that can be generated under the different scenarios is informative. Assuming that K_D varies in response to fluid saturation state then all co-precipitation scenarios suggest that pH_CF and aragonite B/Ca are positively correlated (Fig. 8g–o). Furthermore these scenarios generate relatively narrow ranges of potential B/Ca values (the area of each graph bounded by the low and high DIC scenario lines) irrespective of [DIC] and [Ca²⁺]. At high [co-precipitating DIC] the increase in K_D (promoting the incorporation of higher concentrations of B(OH)₄⁻ in the precipitating aragonite) counteracts the dilution of fluid B(OH)₄⁻ by high co-precipitating DIC_CF. In corals the observed skeletal B/Ca is relative constant regardless of inferred pH_CF (typically 8.3 to 8.8). This pattern cannot be reproduced by the variable K_D scenarios either separately or in combination. I conclude that the coral data cannot be well described by any of the scenarios employing variable K_D.

The scenarios utilizing constant K_D generate wider ranges of aragonite B/Ca that are comparable to the skeletal B/Ca versus pH_CF relationships observed in corals (Fig. 8a–f). The observation that coral data is best fitted assuming a constant K_D suggests that while coral calcification fluid saturation state may be critical in controlling calcification rate (Gattuso et al., 1999), it is unlikely to affect skeletal extension rate. Under the constant K_D scenarios skeletal B/Ca variations are driven by changes in pH_CF (affecting boron and DIC speciation) and [DIC]CF (affecting [co-precipitating DIC]CF).

Most datasets do not exhibit significant correlations between coral pH_CF and skeletal B/Ca (Fig. 1). In the case that B(OH)₄⁻ co-precipitates with CO₃²⁻, approximately constant skeletal B/Ca can be generated over a wide pH_CF range by a calcification fluid with approximately constant [DIC], as in the low DIC scenario modelled here. Increasing pH_CF shifts the DIC equilibrium (Fig. 6a) to increase [CO₃²⁻]CF which dilutes [B(OH)₄⁻]CF (Fig. 6c). In the case that B(OH)₄⁻
co-precipitates with HCO$_3^-$ only or CO$_3^{2-}$ + HCO$_3^-$ then constant [DIC]$_{CF}$ scenarios generate positive correlations between pH$_{CF}$ and skeletal B/Ca (Fig. 8b,c, e,f) which are inconsistent with the observed coral data. To generate approximately constant skeletal B/Ca over a wide pH$_{CF}$ range under these co-precipitation scenarios requires that [DIC]$_{CF}$ increases at higher pH$_{CF}$. Increasing pH$_{CF}$ serves to increase [DIC]$_{CF}$ probably by facilitating CO$_2$ diffusion into the calcification site.

4. Conclusions

Observed coral skeletal B/Ca versus pH$_{CF}$ relationships can be reproduced by estimating B(OH)$_4^-$ and co-precipitating DIC speciation as a function of pH$_{CF}$ and assuming that K$_D$ are constant i.e. unaffected by calcification fluid saturation state. Assuming that B(OH)$_4^-$ co-precipitates with CO$_3^{2-}$, then observed patterns can be reproduced by a fluid with approximately constant [DIC] i.e. increasing pH$_{CF}$ concentrates CO$_3^{2-}$, as a function of DIC speciation. Assuming that B(OH)$_4^-$ co-precipitates with HCO$_3^-$ or CO$_3^{2-}$ + HCO$_3^-$ then the observed patterns can be reproduced if [DIC]$_{CF}$ and pH$_{CF}$ are positively related i.e. if DIC is increasingly concentrated in the calcification fluid at higher pH$_{CF}$ probably by CO$_2$ diffusion into the calcification site.

Declarations

Author contribution statement

Nicola Allison: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Competing interest statement

The authors declare no conflict of interest.

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