Factors affecting B/Ca ratios in synthetic aragonite

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ABSTRACT

Measurements of B/Ca ratios in marine carbonates have been suggested to record seawater carbonate chemistry, however experimental calibration of such proxies based on inorganic partitioning remains limited. Here we conducted a series of synthetic aragonite precipitation experiments to evaluate the factors influencing the partitioning of B/Ca between aragonite and seawater. Our results indicate that the B/Ca ratio of synthetic aragonites depends primarily on the relative concentrations of borate and carbonate ions in the solution from which the aragonite precipitates; not on bicarbonate concentration as has been previously suggested. The influence of temperature was not significant over the range investigated (20–40 °C), however, partitioning may be influenced by saturation state (and/or growth rate). Based on our experimental results, we suggest that aragonite B/Ca ratios can be utilized as a proxy of $[CO_3^{2-}]$. Boron isotopic composition ($\delta^{11}B$) is an established pH proxy, thus B/Ca and $\delta^{11}B$ together allow the full carbonate chemistry of the solution from which the aragonite precipitated to be calculated. To the extent that aragonite precipitation by marine organisms is affected by seawater chemistry, B/Ca may also prove useful in reconstructing seawater chemistry. A simplified boron purification protocol based on amberlite resin and the organic buffer TRIS is also described.
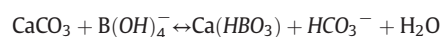
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1. Introduction

Boron concentrations and boron isotopic compositions in marine carbonates are potential archives of past seawater pH and carbonate chemistry (e.g. Sanyal et al., 1996; Pelejero et al., 2005; Pearson and Palmer, 1999; Douville et al., 2010; Rae et al., 2011; Henehan et al., 2013; Penman et al., 2013). In seawater, boron is typically present in two forms, boric acid ($B(OH)_3$) and borate ($B(OH)_4^-$), the relative abundances of which depend largely on pH (e.g. Culberson and Pytkowicz, 1968; Dickson, 1990; Klochko et al., 2006). The $B(OH)_4^-$ ion is thought to be the primary form of boron incorporated into calcium carbonate (e.g. Sen et al., 1994; Hemming et al., 1995), thus offering the potential to use B/Ca ratios to estimate pH and/or carbonate chemistry (e.g. Yu et al., 2007). However, there is uncertainty as to how boron incorporation may depend upon concentrations of different dissolved inorganic carbon (DIC) species (e.g. Hemming et al., 1995; Uchikawa et al., 2015). In addition, there are suggestions that $B(OH)_3$ may also be incorporated, especially in calcite (e.g. Xiao et al., 2008; Klochko et al., 2009; Rollion-Bard et al., 2011; Mavromatis et al., 2015; Uchikawa et al., 2015), thus potentially complicating the interpretation of B/Ca ratios.

Various relationships have been used to explore the range of possible factors controlling B incorporation in both synthetic (e.g. Mavromatis et al., 2015; Uchikawa et al., 2015) and biogenic carbonates (e.g. Ni et al., 2007; Yu et al., 2007; Yu and Elderfield, 2007; Foster, 2008; Douville et al., 2010; Allen et al., 2011; Rae et al., 2011; Tripati et al., 2011; Allen et al., 2012; Allison et al., 2014; Babila et al., 2014; Henehan et al., 2015). Here we consider several of the relationships proposed by previous studies: $B(OH)_4^-/CO_3^{2-}$, $B(OH)_4^-/HCO_3^-$, $B(OH)_4^-/(CO_3^{2-} + HCO_3^-)$, B/HCO_3^-, $B/(CO_3^{2-} + HCO_3^-)$, $B(OH)_4^-/\Delta CO_3^{2-}$ (where ΔCO_3^{2-} is the difference between the actual $[CO_3^{2-}]$ and the $[CO_3^{2-}]$ at which the solution would be saturated with respect to aragonite, $\Omega_{Arag} = 1$). In addition to various empirical relationships, we also consider potential balanced exchange reactions with the following expressions for the distribution coefficient:
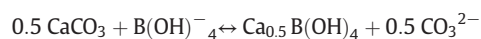
Reaction (1) (Hemming and Hanson, 1992):

$$CaCO_3 + B(OH)_4^- \leftrightarrow Ca(HBO_3) + HCO_3^- + H_2O$$

$$K_D = \frac{\left[HBO_3^{2-}/CO_3^{2-} \right]_{CaCO_3}}{\left[B(OH)_4^-/HCO_3^- \right]_{solution}} \tag{1}$$

Reaction (2):

$$0.5\ CaCO_3 + B(OH)^-_4 \leftrightarrow Ca_{0.5}B(OH)_4 + 0.5\ CO_3^{2-}$$

$$K_D = \frac{[B(OH)_4^- / [CO_3^{2-}]^{0.5}]_{CaCO_3}}{[B(OH)_4^- / [CO_3^{2-}]^{0.5}]_{solution}} \qquad (2)$$

Reaction (3):
$$3\ CaCO_3 + 2\ B(OH)_4^- \leftrightarrow Ca_3(BO_3)_2 + CO_2 + 2\ HCO_3^- + 3\ H_2O$$

$$K_D = \frac{[[BO_3^{3-}]^2 / [CO_3^{2-}]^3]_{CaCO_3}}{[[B(OH)_4^-]^2 / [CO_2][HCO_3^-]^2]_{solution}} \qquad (3)$$

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

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

We conducted a series of experiments to explore how carbonate chemistry, organic additives, temperature, and boron concentration may influence B/Ca ratios in aragonite formed from seawater-like solutions. Manipulation of pH, DIC, and Ca^{2+} are among the mechanisms potentially driving biogenic calcification, thus our experiments focused on manipulating these variables. In addition to these inorganic variables, there are also a wide range of organic molecules produced by calcifying organisms which may influence calcification (e.g. Mass et al., 2013). We chose to test one specific mechanism by which organic molecules could influence B/Ca, that of buffering pH. In seawater, the two dominant pH buffers are DIC and B species, thus variations in pH (such as might occur adjacent to a growing aragonite crystal) would directly affect DIC and B speciation. By adding an additional buffering agent (such as 2-amino-2-hydroxymethyl-propane-1,3-diol (TRIS) or 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES)), pH could in theory be more stable adjacent to the growing crystal which could alter the relationship between B/Ca and bulk solution chemistry. In addition to biological processes affecting elemental ratios, there is also a potential for some of the compounds used to study crystal growth to influence elemental incorporation. Calcein is among the molecules commonly used to mark growing crystals in living organisms (e.g. Venn et al., 2013), and the influence of calcein on the incorporation of a number of elements has been tested (Dissard et al., 2009), though no information is thus-far available as the effect of calcein on B/Ca, thus it was tested here.

2. Methods

2.1. Aragonite precipitation

Aragonite was precipitated from seawater (0.2 μm filtered to remove living organisms) using several different approaches adapted from existing methods (Kinsman and Holland, 1969; Kitano et al., 1978; Gaetani and Cohen, 2006; Holcomb et al., 2009; Gabitov et al., 2011; Wang et al., 2013). The range of experimental protocols used was intended to precipitate aragonite under a wide range of solution chemistries in order to encompass the likely compositional range of biologically mediated solutions and thus more fully evaluate the factors that affect boron incorporation during bio-calcification. Detailed descriptions of the protocols used for each of the 65 experiments are provided in the Supplementary materials (see section S1 and Table S1 for more details). Briefly, all experiments were carried out in plastic containers held within constant temperature water baths. Two general types of experiments were conducted: degassing (Fig. 1B) and pumping (Fig. 1A) experiments. Degassing experiments were carried out by dissolving $CaCO_3$ in seawater at ~1 atm pCO_2 with the addition of $MgCl_2$, $SrCO_3$ (to maintain seawater like Mg/Ca and Sr/Ca ratios) and various additives (TRIS, HEPES, calcein, boron, $CaCl_2$, etc. depending upon the experiment). As CO_2 degassed in these experiments, Ω_{Arag} increased until aragonite began to precipitate. Degassing experiments were bubbled at controlled rates with air or air/CO_2 mixes during precipitation to stabilize pH. Pumping experiments were conducted by adding seawater containing $CaCO_3$ (dissolved by bubbling with CO_2) or concentrated seawater (evaporated to achieve 2× normal salinity = 2× sw) and a $NaHCO_3$ or Na_2CO_3 or NaOH or mixture there-of solution (here after referred to as NaX solution) to seawater using a syringe pump. The simultaneous injection of 2× sw and NaX solutions allowed carbonate chemistry to be modified while maintaining salinity ~constant. Pumping rates were varied over the course of each experiment to stabilize pH during precipitation. Some of these experiments were additionally bubbled with air or air/CO_2 mixtures, and some contained additional additives. All experiments were stirred continuously.

The evolution of solution chemistry during precipitation differed among experiments. In general, in pumping experiments an initial pH and alkalinity was established, precipitation then removed CO_3^{2-} thus reducing DIC (or equivalently total inorganic carbon) and alkalinity, while pumping of the NaX solution added DIC and alkalinity, thus allowing carbonate chemistry to be maintained nearly constant during precipitation. In degassing experiments, though pH was maintained nearly constant, DIC, and alkalinity both declined during precipitation due to the precipitate removing DIC and alkalinity and bubbling removing DIC. To illustrate the relationships between different solution chemistry parameters potentially relevant for B/Ca, Fig. 2 shows various chemical parameters plotted versus pH_T for our experiments, as well as the values expected for seawater at different DIC concentrations.

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

2.2. Precipitate characterization

2.2.1. Mineralogy

The mineralogy of most experiments was characterized by XRD (see Supplemental materials section S4) and/or Raman spectroscopy (DeCarlo et al., 2015; and Supplemental materials S4). Some experiments contained phases other than aragonite and were generally