



Influence of solution chemistry on the boron content in inorganic calcite grown in artificial seawater

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Received 29 March 2017; accepted in revised form 31 August 2017; available online 14 September 2017

Abstract

The ratio of boron to calcium (B/Ca) in marine biogenic carbonates has been proposed as a proxy for properties of seawater carbonate chemistry. Applying this proxy to planktic foraminifera residing in the surface seawater largely in equilibrium with the atmosphere may provide a valuable handle on past atmospheric CO₂ concentrations. However, precise controls on B/Ca in planktic foraminifera remain enigmatic because it has been shown to depend on multiple physicochemical seawater properties. To help establish a firm inorganic basis for interpreting the B/Ca records, we examined the effect of a suite of chemical parameters ([Ca²⁺], pH, [DIC], salinity and [PO₄³⁻]) on B/Ca in inorganic calcite precipitated in artificial seawater. These parameters were primarily varied individually while keeping all others constant, but we also tested the influence of pH and [DIC] at a constant calcite precipitation rate (*R*) by concurrent [Ca²⁺] adjustments. In the simple [Ca²⁺], pH and [DIC] experiments, both *R* and B/Ca increased with these parameters. In the pH-[Ca²⁺] and [DIC]-[Ca²⁺] experiments at constant *R*, on the other hand, B/Ca was invariant at different pH and decreased with [DIC], respectively. These patterns agree with the behavior of solution [B_{Total}/DIC] ratio such that, at a fixed [B_{Total}], it is independent of pH but decreases with [DIC]. Based on these results, *R* and [B_{Total}/DIC] ratio appear to be the primary controls on B/Ca in inorganic calcite, suggesting that both B(OH)₄⁻ and B(OH)₃ are possibly involved in B incorporation. Moreover, B/Ca modestly increased with salinity and [PO₄³⁻]. Inorganic calcite precipitated at higher *R* and in the presence of oxyanions such as SO₄²⁻ and PO₄³⁻ in growth solutions often undergoes surface roughening due to formation of crystallographic defects, vacancies and, occasionally, amorphous/hydrous CaCO₃. These non-lattice sites may provide additional space for B, particularly B(OH)₃. Consequently, besides the macroscopic influence of *R* and bulk solution chemistry, molecular-scale processes associated with calcite nucleation can be an important consideration for B incorporation, especially in complex ionic solutions. Lastly, the covariance of B/Ca with [DIC] and salinity observed here qualitatively agrees with those in planktic foraminifera. It follows that their impact on foraminiferal B/Ca is partly inorganically driven, which may explain why the effect is evident across different species.

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Keywords: Boron; B/Ca; Boron isotopes; Inorganic calcite; Paleo-proxy; Foraminifera; Vital effects; Paleoclimatology; Ocean acidification

1. INTRODUCTION

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Marine carbonates (CaCO₃) are known to incorporate various elements dissolved in seawater. These elements may occupy non-lattice sites or fully substitute for Ca²⁺

<https://doi.org/10.1016/j.gca.2017.09.016>

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or CO_3^{2-} positions in the CaCO_3 lattice, thereby influencing the fundamental mineral properties such as solubility (Morse and Mackenzie, 1990; Morse et al., 2007). Their incorporation typically depends on the physicochemical state of seawater. Hence, quantification of trace elements in carbonate fossils (e.g., foraminiferal tests) has become an indispensable practice in paleoceanography for probing Earth's geochemical, climatic and environmental history (see reviews by Lea, 1999; Henderson, 2002; Katz et al., 2010).

Boron (B) is one such element that has gained much interest in recent years, despite its low concentrations of ~ 100 ppm at most in biogenic CaCO_3 (Vengosh et al., 1991; Hemming and Hanson, 1992). This stems from the prospect that B abundance in CaCO_3 (measured as the B/Ca ratio) could be a useful proxy for ocean carbonate chemistry and, to a greater extent, from the use of B isotopes ($\delta^{11}\text{B}$) as a pH proxy. The paleoceanographic utility of these B-based proxies is rooted in the B speciation in seawater and a proposed model of B incorporation into CaCO_3 . Dissolved B in seawater mainly exists as boric acid ($\text{B}(\text{OH})_3$) and borate ion ($\text{B}(\text{OH})_4^-$), and their relative concentration within the total dissolved B ($[\text{B}_{\text{Total}}] \approx [\text{B}(\text{OH})_3] + [\text{B}(\text{OH})_4^-]$) depends on pH (Fig. 1a). Due to a constant isotopic offset, the $\delta^{11}\text{B}$ of both $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ also

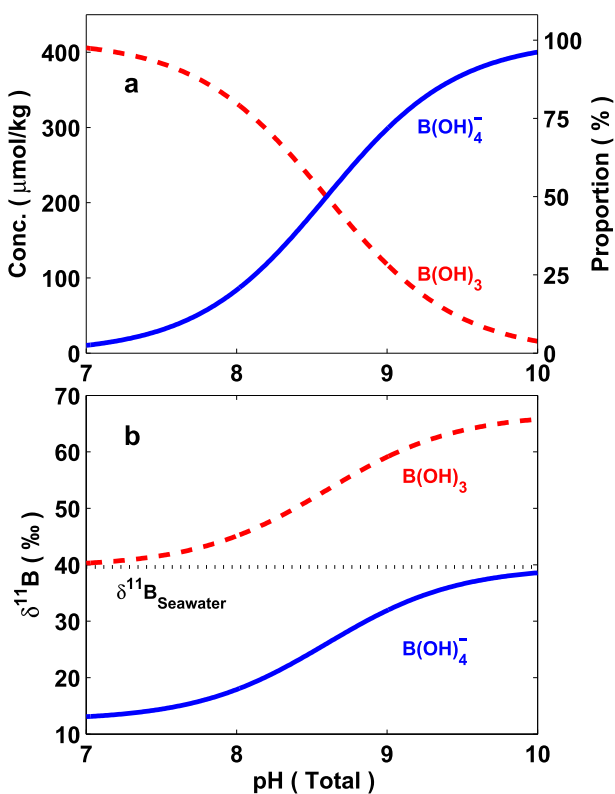


Fig. 1. pH-induced shift in the distribution (Panel a) and isotopic composition (Panel b) of $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ at $T = 25$ °C and $S = 35$ psu. The system presented here is constrained for modern seawater condition of $[\text{B}_{\text{Total}}] = 416$ $\mu\text{mol/kg}$ and $\delta^{11}\text{B}_{\text{Seawater}} = +39.61$ ‰ using $pK_B^* = 8.60$ and $^{11-10}\alpha_{\text{B3-B4}} = 1.0272$ (Dickson et al., 2007; Foster et al., 2010; Klochko et al., 2006).

change predictably with pH (Zeebe and Wolf-Gladrow, 2001; Klochko et al., 2006; Foster et al., 2010; Foster and Rae, 2016; see Fig. 1b). Based on broad similarity between the $\delta^{11}\text{B}$ of modern marine CaCO_3 and that of seawater $\text{B}(\text{OH})_4^-$ (Vengosh et al., 1991; Hemming and Hanson, 1992), it was proposed that, as opposed to the neutral $\text{B}(\text{OH})_3$, the charged $\text{B}(\text{OH})_4^-$ is ultimately substituted with CO_3^{2-} in the CaCO_3 lattice (Hemming and Hanson, 1992; Hemming et al., 1995) as follows:



for which a distribution coefficient K_D based on measurable terms (Yu et al., 2007) can be expressed as:

$$K_D = (\text{B/Ca})_{\text{CaCO}_3} / [\text{B}(\text{OH})_4^- / \text{HCO}_3^-]_{\text{Solution}} \quad (2)$$

Although there are some complications (see a review by Foster and Rae, 2016), a growing number of successive studies, by and large, continue to show reasonable covariance between the $\delta^{11}\text{B}$ of CaCO_3 of various origins and the $\delta^{11}\text{B}$ of $\text{B}(\text{OH})_4^-$ and thereby pH (e.g., Henehan et al., 2016; Rae et al., 2011; Hönisch et al., 2004; Reynaud et al., 2004; Trotter et al., 2011; Penman et al., 2013; Farmer et al., 2015, 2016; Sanyal et al., 2000).

Because B abundance in CaCO_3 increases with $[\text{B}(\text{OH})_4^-]$ (Kitano et al., 1978), a straightforward interpretation of Eq. (1) implies, as is the case for $\delta^{11}\text{B}$, B/Ca in CaCO_3 should analogously depend on pH due to the interplay between $[\text{B}(\text{OH})_4^-]$ and pH (Fig. 1a). Indeed, the pH dependence was confirmed in inorganic calcite (Sanyal et al., 2000; He et al., 2013) and cultured planktic foraminifers (*Orbulina universa*, *Globigerinoides ruber* and *Globigerinoides sacculifer*) (Sanyal et al., 1996; Allen et al., 2011, 2012; Henehan et al., 2015; Holland et al., 2017; Haynes et al., 2017). However, new data from recent inorganic experiments have revealed a more complicated picture. For instance, our research group demonstrated that B/Ca in inorganic calcite increases not only with pH but also with [DIC] (dissolved inorganic carbon, where $[\text{DIC}] = [\text{CO}_{2(\text{aq})}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$) and $[\text{Ca}^{2+}]$ (Uchikawa et al., 2015). Elevating pH, [DIC] and $[\text{Ca}^{2+}]$ all leads to higher saturation and generally more rapid precipitation. Hence, these results collectively point to kinetic effects associated with calcite precipitation rate (denoted as R), which is consistent with independent experimental results by others (Gabitov et al., 2014; Mavromatis et al., 2015; Kaczmarek et al., 2016). In that study, we additionally grew calcite at two pH values while holding R constant by concurrent $[\text{Ca}^{2+}]$ adjustments. The pH dependence was not observed in this case, as the samples yielded virtually identical B/Ca despite the difference in pH (and thus $[\text{B}(\text{OH})_4^-]$). This raised a concern that the pH dependence is not necessarily governed by $[\text{B}(\text{OH})_4^-]$, thereby challenging our perception of how the B/Ca proxy should work from a theoretical standpoint (Eq. (1)). However, because we used simple $\text{NaCl-CaCl}_2\text{-B}(\text{OH})_3\text{-Na}_2\text{CO}_3$ solutions, whether the results would be directly applicable to calcite precipitated in seawater is still an open question.

We address that issue in this study by performing a new round of calcite precipitation experiments. To close the gap of solution matrix between our experiments and natural

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