



Investigating controls on boron isotope ratios in shallow marine carbonates



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ABSTRACT

The boron isotope–pH proxy has been widely used to reconstruct past ocean pH values. In both planktic foraminifera and corals, species-specific calibrations are required in order to reconstruct absolute values of pH, due to the prevalence of so-called vital effects – physiological modification of the primary environmental signals by the calcifying organisms. Shallow marine abiotic carbonate (e.g. ooids and cements) could conceivably avoid any such calibration requirement, and therefore provide a potentially useful archive for reconstructions in deep (pre-Cenozoic) time. However, shallow marine abiotic carbonates could also be affected by local shifts in pH caused by microbial photosynthesis and respiration, something that has up to now not been fully tested. In this study, we present boron isotope measurements from shallow modern marine carbonates, from the Bahama Bank and Belize to investigate the potential of using shallow water carbonates as pH archives, and to explore the role of microbial processes in driving nominally ‘abiogenic’ carbonate deposition. For Bahama bank samples, our boron-based pH estimates derived from a range of carbonate types (i.e. ooids, peloids, hardground cements, carbonate mud, stromatolitic micrite and calcified filament micrite) are higher than the estimated modern mean-annual seawater pH values for this region. Furthermore, the majority (73%) of our marine carbonate-based pH estimates fall out of the range of the estimated pre-industrial seawater pH values for this region. In shallow sediment cores, we did not observe a correlation between measured pore water pH and boron-derived pH estimates, suggesting boron isotope variability is a depositional rather than early diagenetic signal. For Belize reef cements, conversely, the pH estimates are lower than likely *in situ* seawater pH at the time of cement formation. This study indicates the potential for complications when using shallow marine non-skeletal carbonates as marine pH archives. In addition, variability in $\delta^{11}\text{B}$ based pH estimates provides additional support for the idea that photosynthetic CO_2 uptake plays a significant role in driving carbonate precipitation in a wide range of shallow water carbonates.

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1. Introduction

Determination of ocean pH in the past can provide valuable insights into the geochemical evolution of the ocean and atmosphere. Paleo-pH records can be used to estimate atmospheric CO_2 concentrations (e.g. Foster, 2008), and to help evaluate the relationship between CO_2 concentrations and global climate (e.g. Anagnostou et al., 2016). At present, boron isotope ratios ($\delta^{11}\text{B}$) as recorded in marine carbonates are typically thought of as our best means for reconstructing past seawater pH values. The foundation

for the $\delta^{11}\text{B}$ -pH proxy is a large isotopic fractionation between the two predominant aqueous boron species (trigonal $\text{B}(\text{OH})_3$ and tetrahedral $\text{B}(\text{OH})_4^-$) and the pH dependence of their relative abundances. Only borate, the charged species, is thought to be incorporated into biogenic carbonates (e.g. Rae et al., 2011), and hence there is a predictable relationship between ocean pH and the $\delta^{11}\text{B}$ of CaCO_3 . This relationship can be summarized by Eq. (1):

$$\text{pH} = \text{p}K_{\text{B}}^* - \log \left(\frac{\delta^{11}\text{B}_{\text{Sol}} - \delta^{11}\text{B}_{\text{C}}}{\delta^{11}\text{B}_{\text{Sol}} - ({}^{11}\text{B}/{}^{10}\text{B})_{\text{B}} \times \delta^{11}\text{B}_{\text{C}} - 1000({}^{11}\text{B}/{}^{10}\text{B})_{\text{B}} - 1} \right) \quad (1)$$

where $\text{p}K_{\text{B}}^*$ is the dissociation constant for boric acid, $\delta^{11}\text{B}_{\text{Sol}}$ is the isotopic composition of the parent solution, $\delta^{11}\text{B}_{\text{C}}$ is the isotopic

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composition of the carbonate and $^{11-10}K_B$ is the boron isotope fractionation factor between boric acid and the borate ion. $^{11-10}K_B$ has been determined empirically as 1.0272 ± 0.0006 (Klochko et al., 2006) in artificial seawater and later corroborated within uncertainty as 1.026 ± 0.001 (Nir et al., 2015). Although measurements of synthetic calcites to date do not adhere to this theoretical framework (e.g. Noireaux et al., 2015; Sanyal et al., 2000), inorganically precipitated aragonites appear to faithfully record the $\delta^{11}B$ of ambient $B(OH)_4^-$ ion (Noireaux et al., 2015). This suggests that modern aragonitic carbonates should adhere to the theoretical basis of the boron isotope pH proxy laid out in Eq. (1), and therefore could constitute a promising archive for paleo applications.

The boron isotope-pH proxy has been widely applied to foraminiferal calcite to infer past ocean pH and atmospheric CO_2 concentrations over the Cenozoic (e.g. Anagnostou et al., 2016). These applications are supported by the close agreement between boron-derived estimates of atmospheric pCO_2 and values from ice cores (Foster, 2008; Henehan et al., 2013; Hönlisch et al., 2009). Importantly, though, these studies rely on the use of appropriate species-specific calibration equations for extant species of foraminifera. Before the evolution of modern foraminiferal species, and when deep sea drill cores are not available, deeper time boron isotope work has focused on shallow marine abiotic carbonates (e.g. micrite from micritic mudstone, dolomicrite and peloids or 'micritized calcispheres'), often targeted to avoid admixture of biogenic material that might have different vital effects (e.g. the Permian–Triassic; Clarkson et al., 2015). However, there are several issues that may cloud reconstruction from micrite. Foremost, micritic mud in the modern day is commonly derived from altered biogenic carbonates, even if this is not visually discernible (e.g. Gischler et al., 2013; Macintyre and Reid, 1995; Reid et al., 1992). This provides the potential for variations in the geochemistry of carbonate mud to primarily reflect the composition of contributing biota, each with their own $\delta^{11}B$ vital effects, rather than variation in the environment. It has also been argued that cyanobacterially-mediated carbonates could be a major source of micrite and peloids (e.g. Berkovová and Munnecke, 2010; Kazmierczak et al., 1996; Pratt, 2001). More broadly, the microenvironment chemistries that produce authigenic abiotic carbonates can be modified by the syntrophic interactions of microbes (e.g. Diaz et al., 2013), raising the potential for disequilibrium in the carbonic acid system relative to surface waters to be predominantly reflected in the geochemistry of these common abiogenic shallow water carbonates. The corollary of this is that B isotopes could provide a novel and potentially very sensitive tool to track microbial influence on shallow water carbonate production, a topic that has been extensively debated (e.g. Diaz et al., 2013; Morse and Mackenzie, 1990).

In this study, we present boron isotope measurements in a wide range of modern shallow marine non-skeletal carbonates from the Bahamas and Belize and compare the back-calculated pH values with local Holocene pH estimates, to test the reliability of using $\delta^{11}B$ in such shallow marine carbonates to infer seawater pH. In the Bahamas, we focused on sediments near the Darby Research Station (Little Darby Island and Lee Stocking Island). Core-top and down-core samples (maximum depth ≈ 17 cm) of predominately aragonitic ooids and peloids, core-top oolitic hardground cements, core-top carbonate mud (often called micrite in the geological record despite coarsening during recrystallization) and stromatolitic micrite were collected for analysis. In addition, sediments from a nearby salt pond, red algae (*Neogoniolithon strictum*) from Darby Island and calcified cyanobacteria filament micrite from

Highborne Cay were collected. Finally, botryoidal aragonitic cements from within a Holocene reef limestone from Belize were also analyzed. We discuss the implications of our findings for deep time pH and paleoclimate reconstructions and models of shallow marine carbonate formation.

2. Methods

2.1. Sample selection

Most of our shallow marine carbonates were collected from Little Darby Island and Lee Stocking Island in the Bahamas, close to sampling sites of previous works (Burdige and Zimmerman, 2002; Gischler et al., 2013; Romaniello et al., 2013). Carbonates in this region have been extensively studied and they are often used as a modern analogue for ancient carbonate banks (e.g. Romaniello et al., 2013; Swart et al., 2009). Sediments in this area of the Bahamas are mainly oolite and peloid sands, grapestones and hardgrounds. The dominant mineral phase in local carbonates is aragonite (70–90 wt.%), with high-Mg calcite the second-most-abundant mineral (10–30 wt.%) (Burdige and Zimmerman, 2002; Hu and Burdige, 2007). Radiocarbon dating shows the ooid and peloids shoals across the Bahamas Archipelago have been accumulating for the past 1000–2800 yr (Duguid et al., 2010). Ooids typically have an older inner cortical layer several thousand years old, an outer cortex formed in the last several hundred years and outermost layers formed generally from 200 yr ago to the present (Duguid et al., 2010). Superficial ooids and peloids are abundant outside of active shoals, in part due to extensive micritization of ooids (Reid and Macintyre, 1998).

Sample names and their GPS locations are listed in Table 1 and plotted in Fig. 1. Ooid and peloid sands were measured from eight core-top samples (Cave, Musha, Rudder, Core 1: 0–2 cm, Core 3: 0–2 cm, Core 4: 0–1 cm, Core 6: 0–1 cm and Core 7: 0–1 cm), three down-core samples (Core 1, Core 6 and Core 7) and one salt pond sample (Core 2: 3–5 cm). Core 1 is located in the intertidal zone with a water depth of ~ 1 m during high tide. Core 3 is located within a *Thalassia testudinum* (turtle grass) meadow at a water depth of 2–3 m—this area is proximal to an active ooid shoal but is not currently active due to grass stabilization and is rich in peloids. Cores 4 and 6 were sampled from near Lee Stocking Island, also within a turtle grass bed at a water depth of 7–10 m. Core 7 has no sea grass cover, but was sampled close to Core 4 and Core 6, with a water depth of 7–10 m. The Cave, Musha and Rudder sample sites are all located in the subtidal zone and in active shoals. Core 2 captures the most extreme environment in the sample set, as it was collected from Anaconda Salt pond located in Little Darby Island. Except for Core 1, which gets exposed during low tide, our cores are well below the lowest low tide mark. Hardgrounds were collected in just one sample (a core-top) from Little Darby Island close to Core 3. Carbonate sediments were obtained from Little Darby lagoon, close to where Core 3 was collected. Lagoonal settings such as this are the only facies on the bank top that retain a high portion of fine-grained carbonates, despite extensive production of fine-grained aragonite by benthic green algae in this region. Stromatolites were collected from Lee Stocking Island. Red algae *Neogoniolithon strictum* (composed of high-Mg calcite), were collected from the west side of Darby Island. Thrombolitic microbialites were sampled from Highborne Cay. The calcified filaments in the microbialites transition into micritic cements in the fully lithified samples (Planavsky et al., 2009; Stolz et al., 2009). Finally, we also analyzed two samples of botryoidal cements from a reef slope cavity off Belize (Fig. 2a, b) that had been previously analyzed for $\delta^{13}C$, $\delta^{18}O$ and $\delta^{14}C$ (Ginsburg and James, 1976; Grammer et al., 1993).

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