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Letter's

Evaluation of boron isotope ratio as a pH proxy in the deep sea coral *Desmophyllum dianthus*: Evidence of physiological pH adjustment

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ABSTRACT

The boron isotope ratio ($\delta^{11}B$) of foraminifers and tropical corals has been proposed to record seawater pH. To test the veracity and practicality of this potential paleo-pH proxy in deep sea corals, samples of skeletal material from twelve archived modern *Desmophyllum dianthus* (*D. dianthus*) corals from a depth range of 274–1470 m in the Atlantic, Pacific, and Southern Oceans, ambient pH range 7.57–8.05, were analyzed for $\delta^{11}B$. The $\delta^{11}B$ values for these corals, spanning a range from 23.56 to 27.88, are found to be related to seawater borate $\delta^{11}B$ by the linear regression: $\delta^{11}B_{coral}=(0.76\pm0.28)\ \delta^{11}B_{borate}+(14.67\pm4.19)$ (1 standard error (SE)). The *D. dianthus* $\delta^{11}B$ values are greater than those measured in tropical corals, and suggest substantial physiological modification of pH in the calcifying space by a value that is an inverse function of seawater pH. This mechanism partially compensates for the range of ocean pH and aragonite saturation at which this species grows, enhancing aragonite precipitation and suggesting an adaptation mechanism to low pH environments in intermediate and deep waters. Consistent with the findings of Trotter et al. (2011) for tropical surface corals, the data suggest an inverse correlation between the magnitude of a biologically driven pH offset recorded in the coral skeleton, and the seawater pH, described by the equation: $\Delta pH = pH$ recorded by coral $-$ seawater $pH = -(0.75\pm0.12)\ pH_w + (6.88\pm0.93)$ (1 SE). Error analysis based on 95% confidence interval(CI) and the standard deviation of the regression residuals suggests that the uncertainty of seawater pH reconstructed from $\delta^{11}B_{coral}$ is ±0.07 to 0.12 pH units. This study demonstrates the applicability of $\delta^{11}B$ in *D. dianthus* to record ambient seawater pH and holds promise for reconstructing oceanic pH distribution and history using fossil corals.

1. Introduction

It is now well documented that atmospheric carbon dioxide (pCO_2) varied with the growth and decay of polar ice sheets over the last 800 kyr (Luthi et al., 2008; Petit et al., 1999). In general, during periods of increasing atmospheric pCO_2, surface ocean pH decreases as a result of CO_2 uptake (Hönisch and Hemming, 2005). The driving mechanisms that cause atmospheric pCO_2 variations, and how they relate to the Earth's climate system, are not well constrained. Since the Industrial Revolution, however, atmospheric CO_2 has increased beyond the range of natural Pleistocene variations, displaying a sharp rise in the last ~50 years (Keeling, 1961; Luthi et al., 2008; Petit et al., 1999) mainly as a result of fossil fuel burning (Le Quére et al., 2009). Such an increase has resulted in substantial decrease in oceanic pH (Sabine et al., 2004), which has raised much concern for the physiological and ecological response of marine calcifying organisms (Gattuso and Hansson, 2011; Hoegh-Guldberg et al., 2007). Insights into these issues can be gained by developing paleo-proxies for aspects of the ocean carbonate system. One that has received much recent focus is the boron isotope ($\delta^{11}B$) proxy for seawater pH, as preserved in various biogenic carbonate archives (e.g. Hemming and Hönisch, 2007). An important step in the development of the $\delta^{11}B$ proxy is its calibration against pH using specimens of modern biocalcifying organisms that grew at locations where seawater pH is well quantified (e.g. Rae et al., 2011).

The biogenic carbonate $\delta^{11}B$ proxy has been explored and described in extensive detail elsewhere (Douville et al., 2010; Hemming and Hanson, 1992; Hönisch and Hemming, 2005; Klochko et al., 2006; Rae et al., 2011; Sanyal et al., 1996; Spivack et al., 1993; Trotter et al., 2011; Zeebe et al., 2001, 2003). At typical modern seawater pH, boron (B) exists mostly

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in the forms of boric acid ($B(OH)_3$) and borate ion ($B(OH)_4^-$) with a distinct isotopic fractionation between the two species such that boric acid is enriched in the heavier isotope (^{11}B) by 27.2‰ compared to borate ion (Klochko et al., 2006). The relative abundance of these two B species is pH dependent while total seawater B varies only on long time scales given its oceanic residence time of 10–14 million years (Lemarchand et al., 2000; Paris et al., 2010). Because the isotopic composition of total boron in seawater must be maintained as the relative abundance of the species changes with pH, the isotope ratio of each species must also change. Therefore the isotopic composition of each species for recent times in earth history depends entirely on pH.

On the basis of the similarity of the boron isotopic composition of all marine carbonates to that of seawater borate, boron is believed to be incorporated into biogenic and inorganic carbonates overwhelmingly as the borate species (Hemming and Hanson, 1992). Incorporation in this form results in the $\delta^{11}B$ of marine carbonates tracking the $\delta^{11}B$ of borate ion and thus being sensitive to pH variations, with a typical ~1‰ increase in $\delta^{11}B$ for a 0.1 unit increase in seawater pH. Boron isotope measurements in foraminiferal calcite and tropical coral aragonite have been used extensively as proxies of surface oceanic pH or pCO_2 (Douville et al., 2010; Hönisch and Hemming, 2005; Hönisch et al., 2009; Liu et al., 2009; Palmer and Pearson, 2003; Pelejero et al., 2005; Sanyal and Bijma, 1999; Wei et al., 2009). However, there have been only a few efforts to reconstruct the evolution of intermediate to deep ocean pH using this proxy (Hönisch et al., 2008; Rae et al., 2011; Sanyal et al., 1995; Yu et al., 2010). Successful demonstration of the utility of the boron isotope pH proxy in a new carbonate archive, Deep Sea Corals (DSC), would open a new window on deep ocean pH records.

The boron isotope proxy applied to DSC offers several advantages compared to foraminifera: DSC are not only cosmopolitan in geographic distribution (Roberts et al., 2006), and of sufficient mass for precise U/Th dating (Cheng et al., 2000; Edwards et al., 2003; Goldstein et al., 2001; Schröder-Ritzrau et al., 2003), but they can also potentially provide single-individual snapshot records of climate-related oceanic variables with subdecadal resolution that only ice cores can rival (e.g. Adkins et al., 1998). In addition, most species are aragonitic and relatively rich in B (70–100 ppm; Douville et al., 2010), compared to ~10–20 ppm for calcitic forams (Rae et al., 2011) allowing analyses of $\delta^{11}B$ in small samples with high precision. Deep sea corals do not harbor symbiotic algae, hence they are not subject to physiological processes related to zooxanthellae activity that can contribute to pH-sensitive vital effects in other corals (Al-Horani et al., 2003) and in foraminifera (Zeebe et al., 2003). Although the majority of DSC grow in waters that are oversaturated with respect to aragonite (Guinotte et al., 2006), some can survive in conditions unfavorable to aragonite precipitation ($\Omega_{arag} < 1$, where $\Omega_{arag} = [Ca^{2+}][CO_3^{2-}]/K^*_{arag}$, and K^*_{arag} is the stoichiometric solubility product for aragonite). Therefore it is suspected that deep corals have mechanisms to elevate the aragonite saturation of the extracellular calcifying fluid (ECF) to induce carbonate precipitation, consistent with models for biocalcification in tropical corals (Adkins et al., 2003; Cohen and McConnaughey, 2003; McConnaughey, 1989a; Sinclair and Risk, 2006). Further modification of the pH of the physiologically controlled internal fluid reservoirs could be caused by respiration or other aspects of polyp metabolism or by variations in calcification rate (Adkins et al., 2003; Goreau, 1977; Krief et al., 2010; McConnaughey, 1989b). Regardless, foraminifera modeling studies have shown that the presence of such biological factors does not necessarily compromise the $\delta^{11}B$ pH proxy if their effect can be adequately characterized and is constant over a range of relevant pH (Zeebe et al., 2003). Generalizing from this case, physiological vital effects that shift the internal pH by a factor that is either constant or a function of external ambient seawater pH may be correctable and therefore preserve the signal of seawater pH in the $\delta^{11}B$ of the skeleton.

Here we present a calibration of the $\delta^{11}B$ proxy in globally distributed modern *Desmophyllum dianthus* (*D. dianthus*) coral specimens, against ambient pH at their growth locations. The relatively large size of these corals provides enough aragonite to allow the measurement of multiple geochemical proxies. A multi-proxy approach on individual corals growing at different locations in intermediate and deep waters could thereby reveal concomitant variations in chemical and physical properties in a single carbonate archive, a rare luxury. Our previous work on this species has demonstrated modern calibrations of P/Ca, Ba/Ca, and U/Ca ratios as proxies of seawater phosphate, barium, and carbonate ion (Anagnostou et al., 2011). The addition of a pH proxy would augment this suite of geochemical tools and, because of fundamental biogeochemical relationships among nutrients and carbonate system parameters, provide checks on paleoceanographic interpretations.

2. Materials and methods

2.1. Sample preparation and analytical approach

Corals were sampled from the National Museum of Natural History (Smithsonian Institution, Washington, D.C.) and from the National Institute for Water and Atmosphere (NIWA), Greta Point, Wellington, NZ (Fig. 1). Coral septa were separated mechanically and cleaned with a power dental saw to remove any surface crust material. Subsequently, the coral pieces were rinsed and ultrasonicated with distilled water several times, and any remaining tissue was removed with a brush. Next, the corals were dried in a laminar flow clean bench and crushed to <2 mm pieces. Informed by recent studies suggesting internal skeletal inhomogeneity in the DSC *Lophelia pertusa* (*L. pertusa*) (Blamart et al., 2007), sufficiently large skeletal samples (17–108 mg; Table 1) were excised to integrate any possible micro-structural heterogeneity in *D. dianthus* $\delta^{11}B$. Although we cannot prove that such heterogeneity was averaged in a completely consistent manner, the goal of this initial study is to test the potential of a $\delta^{11}B$-pH proxy method that is characterized by good subsampling

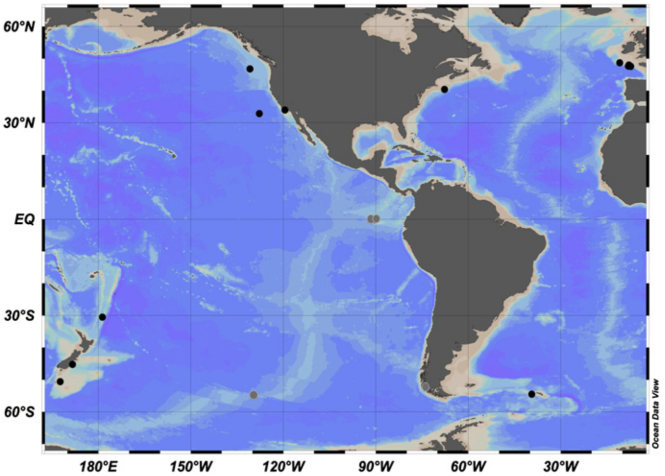

Fig. 1. Locations of the *D. dianthus* specimens used in this study. Grey circles represent samples for which reliable hydrographic data were not available and thus were not used in proxy calibration in proxy calibration.