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Effects of seawater-pH and biomineralization on the boron isotopic composition of deep-sea bamboo corals

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Abstract

The ocean is currently absorbing excess carbon from anthropogenic emissions, leading to reduced seawater-pH (termed 'ocean acidification'). Instrumental records of ocean acidification are unavailable from well-ventilated areas of the deep ocean, necessitating proxy records to improve spatio-temporal understanding on the rate and magnitude of deep ocean acidification. Here we investigate boron, carbon, and oxygen isotopes on live-collected deep-sea bamboo corals (genus *Keratoisis*) from a pH_{tot} range of 7.5–8.1. These analyses are used to explore the potential for using bamboo coral skeletons as archives of past deep-sea pH and to trace anthropogenic acidification in the subsurface North Atlantic Ocean (850–2000 m water depth). Boron isotope ratios of the most recently secreted calcite of bamboo coral skeletons are close to the calculated isotopic composition of borate anion in seawater ($\delta^{11}B_{borate}$) for North Atlantic corals, and 1–2‰ higher than $\delta^{11}B_{borate}$ for Pacific corals. Within individual coral skeletons, carbon and oxygen isotopes correlate positively and linearly, a feature associated with vital effects during coral calcification. $\delta^{11}B$ variability of 0.5–2‰ is observed within single specimens, which exceeds the expected anthropogenic trend in modern North Atlantic corals. $\delta^{11}B$ values are generally elevated in Pacific corals relative to $\delta^{11}B_{borate}$, which may reflect pH-driven physiological processes aiding coral calcification in environments unfavorable for calcite precipitation. Elevated $\delta^{11}B$ values are also observed proximal to the central axis in multiple Atlantic and Pacific specimens, relative to $\delta^{11}B_{borate}$, which might reflect ontogenetic variability in calcification rates. Although the observed boron isotope variability is too large to resolve the present anthropogenic ocean acidification signal at the studied depths in the North Atlantic (~0.03–0.07 pH units), pH changes $\geqslant$0.1 units might still be reconstructed using $\delta^{11}B$ measurements in bamboo corals.

1. INTRODUCTION

The ocean is the largest exchangeable carbon reservoir in the global carbon cycle and represents an important sink for anthropogenic carbon (C_{ant}) emissions (Gruber, 1998; Sabine et al., 2004; Khatiwala et al., 2009). The vast majority of the ocean's carbon is stored below the mixed layer in the intermediate and deep ocean, which are enriched in dissolved inorganic carbon (DIC) due to the active export of carbon from the surface ocean by physical and biological processes (e.g., Sigman et al., 2010). Emissions of anthropogenic carbon dioxide (CO_2) since the onset of the industrial era and air–sea gas exchange have resulted in a large input of C_{ant} to well-ventilated areas of the deep sea (Sabine et al., 2004; Wanninkhof et al., 2013). The net result of this C_{ant} pulse is a reduction in

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seawater pH termed 'ocean acidification' (e.g., Caldeira and Wickett, 2003; Feely et al., 2004; Doney et al., 2009).

Instrumental records of ocean acidification are limited in length and spatial coverage. Only three continuous time series of seawater carbonate system observations with >10 years of coverage are available for the surface ocean (Station ALOHA: Dore et al., 2009; BATS/Station S: Bates, 2007; ESOTC: González-Dávila et al., 2010). Similar records are not available for the intermediate and deep ocean; instead, pH changes must be inferred from back-calculated, tracer-based, or modeled estimates of C_{ant} inventories (Sabine et al., 2004; Khatiwala et al., 2009; Sabine and Tanhua, 2010). Paleoceanographic records extracted from surface corals using the boron isotope proxy can potentially supplement limited instrumental pH data for the surface ocean (Pelejero et al., 2005; Wei et al., 2009). In the intermediate and deep ocean, however, applications of boron proxies ($\delta^{11}B$, B/Ca) in epifaunal benthic foraminifera (e.g., Hönisch et al., 2008; Yu et al., 2010; Rae et al., 2011; Raitzsch et al., 2011) are better suited to longer timescales than the current anthropogenic perturbation, due to bioturbation and low accumulation rates of deep-sea sediments.

Deep-sea corals (DSC) potentially provide new opportunities to reveal deep-sea conditions from highly resolved records secreted over the lifespan of the coral (ranging from years to millennia, see review in Robinson et al., 2014). Previous studies have shown promise for DSC skeletal-based proxy records of ocean circulation and ventilation (Adkins et al., 1998; Frank et al., 2004; Robinson et al., 2005; Sherwood et al., 2008; van de Flierdt et al., 2010; Burke and Robinson, 2012), biological productivity and nutrient concentrations (Sherwood et al., 2005, 2011; Montagna et al., 2006; LaVigne et al., 2011; Anagnostou et al., 2011), temperature (Smith et al., 2000; Thresher et al., 2004, 2010; Lutringer et al., 2005; Case et al., 2010; Hill et al., 2011; Kimball et al., 2014; Montagna et al., 2014), and isotopic and elemental properties of seawater (Rollion-Bard et al., 2009; Hill et al., 2012). However, reconstructions of deep-sea carbonate chemistry from boron proxies in DSC have proven challenging. Specifically, boron isotope studies in scleractinian DSC (subclass Hexacorallia) suggest physiological processes related to biomineralization overprint environmental information (Blamart et al., 2007; Anagnostou et al., 2012; McCulloch et al., 2012).

Deep-sea gorgonian corals (subclass Octocorallia) have recently generated interest as potential paleoceanographic archives. Gorgonian corals of the family Isididae are long lived (up to several centuries, Roark et al., 2005; Thresher, 2009) and globally distributed in intermediate to deep waters (Watling et al., 2011), making them attractive targets for proxy calibration and paleoceanographic reconstructions (Thresher et al., 2004; Sherwood et al., 2008; Hill et al., 2011, 2012; LaVigne et al., 2011). To date, however, there have been no studies on the feasibility of carbonate system reconstructions from boron proxies in deep-sea gorgonian corals. Here we present results from the first investigation of boron isotopes in deep-sea gorgonian corals (genus *Keratoisis*), and evaluate controls on their boron isotopic composition using coupled stable isotope ($\delta^{13}C$ and $\delta^{18}O$) measurements. We compare *Keratoisis* boron isotope ratios in a suite of modern specimens to hydrographic pH measurements, and test whether isotopic time-series derived from individual North Atlantic corals reflect projections of seawater-pH change due to C_{ant} addition.

2. MATERIALS AND METHODS

2.1. Bamboo coral morphology and biomineralization

Isidiid gorgonian corals, named "bamboo corals" for their visual resemblance to bamboo, grow a solid axial skeleton composed of non-scleritic calcareous material, surrounded by a relatively thin coenenchyme with rod-shaped sclerites longitudinally arranged on the polyps (Watling et al., 2011). Bamboo coral axial skeletons are characterized by alternating high-Mg calcitic internodes (7–10 mol% $MgCO_3$, Noé and Dullo, 2006) and organic nodes composed of gorgonin, a collagen-like protein (Fig. 1). Cross-sections through the internodes reveal visual light–dark banding attributed to the orientation and relative organic content of Mg-calcitic crystal bundles (fascicles) (Noé and Dullo, 2006), with the strength and symmetry of banding varying within and between specimens (Fig. 1b–d). The interior of the internode is occupied by a central axis that varies from an open, cylindrical channel (Fig. 1c) to a darkly colored, calcified or organic-filled region (Fig. 1b). At the microstructural scale, bamboo coral internodes do not exhibit centers of calcification or density banding (as evidenced from X-radiographs, Noé and Dullo, 2006), both fundamental structural features of scleractinian corals (Ogilvie, 1896; see also Cohen and McConnaughey, 2003).

Distinct differences in both skeletal microstructures and composition between calcitic bamboo corals and aragonitic scleractinian corals imply divergence in calcification mechanisms, which therefore distinguish the sampling strategy for each coral type. Gorgonian coral biomineralization is poorly understood, particularly in comparison to the wealth of geochemical approaches used to infer biomineralization mechanisms in scleractinian corals (which are nonetheless debated, e.g., McConnaughey, 1989; Adkins et al., 2003; Cohen and McConnaughey, 2003; Rollion-Bard et al., 2003a,b; Sinclair, 2005; Blamart et al., 2007). Noé and Dullo (2006) proposed a biomineralization mechanism for bamboo corals whereby gorgonin serves as a structural framework for a Ca^{2+}-binding soluble glycoprotein monolayer that facilitates crystal nucleation. Although this mechanism is broadly similar to organic matrix-mediated calcification mechanisms proposed for scleractinian corals (e.g., Cohen and McConnaughey, 2003; Allemand et al., 2011), the geochemical effects of such a mechanism, and more broadly, the geochemical consequences of dissimilarities between scleractinian and gorgonian calcification, are largely unknown (e.g., Kimball et al., 2014). Consequently, our sampling strategy follows simple visual structural features, as described below.