



pH and pCO₂ at the site of calcification in Scleractinian corals: evidence from boron-based proxies

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Anthropogenic CO₂ uptake by the oceans has potentially serious consequences for calcifying organisms such as those that are the basis of coral reef ecosystems. Determining the impact of future seawater pH and carbonate chemistry changes on coral reef ecosystems requires a detailed understanding of the process of biomineralization in scleractinian coral. One gap in our knowledge is the extent to which coral physiology modifies and controls pH at the site of calcification.

In our study, two ecologically important reef-building coral species, massive *Porites sp.* and *Stylophora pistillata*, were cultured for up to 14 months under controlled pCO₂ experimental conditions corresponding to seawater pH values of 8.2, 7.6, and 7.3, respectively. The response of both species to the three different seawater pH conditions was monitored using skeletal $\delta^{11}\text{B}$ and B/Ca, in addition to a suite of other skeletal tracers and physiological measures. It is well established that the relative concentration of the two main boron species in the ocean, boric acid [B(OH)₃] and the borate ion [B(OH)₄⁻], is pH dependent and that a 27‰ difference in $\delta^{11}\text{B}$ occurs between these two chemical species. This study applies the recent innovations in $\delta^{11}\text{B}$ analysis of carbonates by multi-collector inductively coupled mass spectrometry (MC-ICPMS) that have revolutionised the measurement of this palaeo-pH proxy in other biogenic carbonates [3].

It is evident from this study that both *S. pistillata* and massive *Porites sp.* significantly modify the pH at site of calcification relative to the external seawater. All the coral fragments in our long-term culturing experiment survived and added new skeleton, even under conditions where the ambient seawater was undersaturated with respect to aragonite. The skeletal $\delta^{11}\text{B}$ values plot above seawater $\delta^{11}\text{B}$ -pH borate fractionation curves calculated using either the theoretically derived α_B value of 0.981 [1] or the empirical α_B value of 0.974 [2]. This offset can be reconciled with the ambient experimental seawater pH values by invoking a shift in pH at the site of calcification towards more alkaline conditions. The magnitude of this pH shift increases significantly in coral grown under higher pCO₂. The $\delta^{11}\text{B}$ -pH estimates, and the magnitude of the internal pH modification within the coral's tissue, are within the range predicted from physiological processes occurring within symbiont-bearing coral and measured in microsensors studies. A shift in the ratio of skeletal material laid down during dark and light calcification and/or greater manipulation of internal pH by the coral polyp via ion-transport enzymes can explain the increased pH shift at higher pCO₂. Between coral species it is apparent that fast calcifying, branched species typically have lower $\delta^{11}\text{B}$ for a given external pH than slower calcifying, massive forms.

Massive *Porites sp.* are important palaeoclimate archives. Although bulk coral $\delta^{11}\text{B}$ is recording pH at the site of calcification rather than ambient seawater pH, the internal coral $\delta^{11}\text{B}$ -pH response to the external seawater pH can be established. As a result, the skeletal $\delta^{11}\text{B}$ values of massive *Porites sp.* may be used to reconstruct paleo-pH using an effective fractionation value, β_B , of 0.8915 in place of α_B .

[1] Kakhana *et al.*, 1977. *Bull. Chem. Soc. Japan* **50**, 158-163. [2] Klochko *et al.*, 2006. *Earth Planet. Sci. Lett.* **248**, 261-270. [3] Foster *et al.*, 2008. *Earth Planet. Sci. Lett.* **271**, 254-266.