

MASTS Marine Biogeochemistry Forum Small Grant

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The impact of ocean acidification and rising seawater temperatures on the DIC chemistry of coral calcification fluids

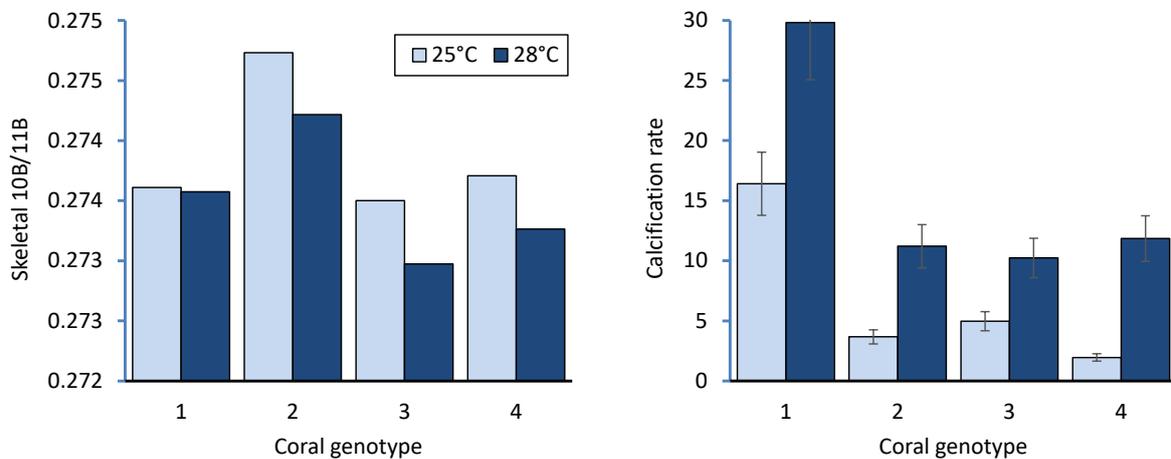
Coral reefs are among the world's most biologically diverse ecosystems and are of substantial economic importance in terms of fisheries, tourism and coastal protection. Rising atmospheric CO₂ is causing ocean warming and has fundamentally affected seawater carbonate chemistry, lowering seawater pH. Understanding the impact of these changes on the accretion of coral aragonite is essential for predicting the future of reef ecosystems. However, attempts to assess increasing pCO₂ and temperature effects, either separately or in combination, have generated contradictory reports¹. Most laboratory and field studies indicate that coral calcification is reduced at lower seawater pH but there is considerable disagreement on the magnitude of this effect both within and between coral species. Seawater temperature increases of 2-3°C may increase or decrease calcification rate² and increasing both seawater pCO₂ and temperature in combination may increase, decrease or have no significant effect on calcification rate². Unravelling the source of the discrepancies between studies is key to accurately predicting the effects of increasing seawater pCO₂ and temperature in different coral species and reef environments. Understanding how coral calcification fluid DIC responds to changes in seawater pCO₂ and temperature is key to predicting the impact of future seawater temperature increases and ocean acidification on reef development.

The boron geochemistry of coral skeletons offers a potential method to reconstruct the dissolved inorganic carbon (DIC) chemistry of the coral calcification fluid³. Dissolved boron in seawater occurs primarily as boric acid, B(OH)₃, and borate, B(OH)₄⁻, and speciation is controlled by ambient pH. Most reports suggest that B(OH)₄⁻ is selectively incorporated into aragonite substituting for CO₃²⁻ in the lattice and is depleted in ¹¹B compared to B(OH)₃. Hence aragonite δ¹¹B reflects the pH of the fluid from which it precipitates while [B] (usually measured as B/Ca) reflects both fluid pH and the concentration of the DIC species competing with B(OH)₄⁻ for inclusion in the carbonate³.

I analysed the skeletal boron chemistry of a suite of massive *Porites* spp. corals cultured over both increased seawater temperatures (25 and 28°C) and seawater pCO₂ (400 and 750 μatm) to determine how calcification fluid DIC chemistry responds to these environmental changes. *Porites* are major components of coral reefs in the Indo-Pacific. Skeletal ¹⁰B/¹¹B, was lower at 28°C than at 25°C in 3 of the four massive *Porites* spp. coral genotypes cultured at 750 μatm (Figure 1) indicating that calcification fluid pH was lower at 28°C.

Project Outcomes – These data show that coral calcification fluid pH is typically lower at 28°C than at 25°C in massive *Porites* spp. corals. This is unexpected. Increasing seawater temperature enhanced calcification in all the corals studied (Figure 1, after Cole et al, 2018⁴) and I anticipated that the coral calcification fluid pH would be higher at 28°C than at 25°C potentially reflecting an increase in the activity of the enzyme Ca-ATPase which pumps H⁺ out of the calcification site. Coral aragonite precipitates from an extracellular calcifying fluid enclosed in a semi-isolated space between the coral tissue and underlying skeleton (see ³ for a review of this). The calcification fluid is derived from seawater but corals actively increase its pH above that of seawater altering the fluid dissolved inorganic carbon (DIC) chemistry. Increasing calcification fluid pH shifts the fluid DIC equilibrium in favour of carbonate (CO₃²⁻) at the expense of CO₂ and bicarbonate (HCO₃⁻) and creates a concentration gradient

Figure 1. Left: Skeletal $^{10}\text{B}/^{11}\text{B}$ in 4 massive *Porites* spp. genotypes cultured at 750 μatm pCO_2 . Right: Calcification rates ($\mu\text{mol CaCO}_3 \text{ cm}^{-2} \text{ d}^{-1}$) for each coral genotype at 25°C and 28°C. Bars represent means of 3-4 incubations over a 5 week period. The error indicates the typical standard deviation of these multiple incubations.



facilitating the diffusion of CO_2 from the overlying coral tissue into the fluid³. This CO_2 can react to form more HCO_3^- and CO_3^{2-} , thereby increasing calcification fluid DIC. Low calcification fluid pH corals typically have low fluid $[\text{CO}_3^{2-}]$ and $[\text{HCO}_3^- + \text{CO}_3^{2-}]$, the DIC species implicated in precipitation, and low calcification rates.

This unexpected result demonstrates that coral calcification rate is not simply controlled by the pH (and saturation state) of the coral calcification fluid but is also dependent on other, as yet unknown, factors. Increases in seawater temperature, below the thermal stress threshold, may mitigate against reductions in calcification caused by ocean acidification in this coral genus but this moderation is not mediated by an increase in calcification site pH.

References

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