$\delta^{11}B$ and B/Ca systematics in scleractinian corals show strong seasonal controls on calcifying fluid pH and DIC: implications for the $\delta^{11}B$ seawater pH proxy

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The $\delta^{11}B$ record preserved within the skeletons of biogenic carbonates provides an important tool to determine the pH of past oceans. However its utility depends upon knowledge of the relationship between the pH of the calcifying fluid (pH_{cf}) and that of ambient seawater (pH_{sw}). Recent studies [1,2] have shown that aragonitic corals have the ability to up-regulate pH_{cf}, with the relationship between pH_{cf} and pH_{sw} being mainly derived from corals grown in aquaria under constant temperature and pH_{sw} regimes. These studies [1,2] found that the coral pH_{cf} reflected only ~1/3 to 1/2 of the changes in ambient seawater pH_{sw}.

We now report the results of a high-resolution (monthly) study of $\delta^{11}B$ and B/Ca ratios in *Porites* coral from the central Great Barrier Reef (Davies Reef) subject to natural seasonal cycles in reef-water temperature and pH for the period 2008-2013. We find systematic, seasonally driven changes in pH_{cf} with lower values in summer (~8.32) compared to winter (~8.48), but with an annual amplitude ~x2 larger than the ambient reef-water (pH_{sw} ~8.02 to 8.08), in marked contrast to previous findings. Similar seasonal changes are found in coral B/Ca ratios from which we infer antipathetic increases in summer DIC_{cf}. We surmise that summer enhancement of zooxanthellate photosynthetic processes act to increase the supply of DIC to the coral host. Thus counter-intuitively, during the summer months *Porites* from Davies Reef act to moderate their rate of calcification by reducing their pH_{cf}. Regardless, this implies strong seasonal and likely temperature controls on pH_{cf} that are significantly larger (~x4 to x5) than those expected from changes in ambient reef-water pH_{sw} alone. Our findings while confirming the importance of pH_{cf} and DIC_{cf} up-regulation in symbiont-bearing corals, show that seasonal controls (e.g. temperature) are the dominant driver of $\delta^{11}B$ rather than seawater pH_{sw}.

[1] Trotter et al., Earth Plan.Sci. Lett. 393, 163-173, 2011 [2] McCulloch et al., Nat. Climate Change v2, 623-627, 2012