Isotopic constraints on the calcifying fluid pH of corals grown under elevated Ca^{2+} concentrations

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Coral calcification is widely accepted to be related to the saturation state of seawater, controlled by the ion activity product of Ca^{2+} and CO_3^{2-}. While considerable attention has been paid to CO_3^{2-} and its relationship to pCO_2 and pH, there has been less work regarding the role of Ca^{2+}, which also oscillates in concentration, in consort with pCO_2 . In order to remedy this, we grew corals (*Pocillopora damicornis*) in seawater with Ca^{2+} concentrations characteristic of ancient greenhouse climates. Our experiments indicate that there are no significant differences in calcification rates with increasing Ca^{2+}, suggesting that elevated Ca^{2+} concentrations reduce the need for corals to pump H^+ ions from the site of calcification (i.e. lower pH in calcifying fluid). To investigate this, we measured the $\delta^{13}C$ and $\delta^{11}B$ values of the new growth. While $\delta^{13}C$ and $\delta^{11}B$ values should decrease as the pH of the calcifying fluid decreases, the change in $\delta^{13}C$ value relative to $\delta^{11}B$ value will differ depending on the initial pH of the calcifying fluid. For example, a high initial pH will favour a greater change in the $\delta^{13}C$ value relative to $\delta^{11}B$. As demonstrated here, when corals are grown in seawater elevated in Ca^{2+} by 7 mM, $\delta^{13}C$ values decrease by ~0.4‰ relative to the control, while there is no significant decrease in $\delta^{11}B$ values. Such data suggest that the pH values at the site of calcification must be higher than previously suggested (pH > 9.5). This work has significant implications for using carbonate minerals to understand major fluctuations in seawater chemistry throughout time.

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