Influence of pH on boron and carbon isotopes in coral skeletons

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The boron isotopic composition of coral skeleton ($\delta^{11}B$) is a common proxy for reconstructing past seawater pH. However, because corals increase the pH of their calcifying fluid relative to seawater to aid calcification, $\delta^{11}B$-based pH estimates must be corrected for this pH difference. Unfortunately, instrumental records of seawater pH to empirically calibrate the $\delta^{11}B$ proxy are currently scarce. We show that there is a relationship between the boron ($\delta^{11}B$) and carbon ($\delta^{13}C$) isotopic composition in the skeletons of both deep-sea and tropical shallow-water corals. We further show that skeletal $\delta^{13}C$ is related to the pH difference between the calcifying fluid and seawater. This relationship can be explained by the effect that pH differences have on the rate of CO_2 diffusion from seawater to the calcifying fluid, because greater incorporation of isotopically-light carbon from CO_2 into the coral skeleton reduces skeletal $\delta^{13}C$. We used a numerical model to explore how physiological manipulation of the calcifying fluid by corals (through ion pumps and exchange with seawater) can give rise to the trends we observed in $\delta^{11}B$, $\delta^{13}C$, and the pH difference between seawater and the calcifying fluid. Although $\delta^{13}C$ in coral skeletons is undoubtedly also influenced by factors besides pH, our data indicate that $\delta^{13}C$ might potentially be a useful proxy measure to correct $\delta^{11}B$ data for the pH difference between calcifying fluid and seawater.