

## Quantifying Controls on Coral Calcifying Fluid pH: Implications for Paleo-pH Reconstruction

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Boron isotope composition of coral skeleton, which tracks the pH of its calcifying fluid, holds great promise as an proxy for past seawater pH. Many studies have shown significant correlations between the pH derived from boron isotope measurements and the pH of the seawater in which coral grew. However, quantitative reconstruction of seawater pH based on this proxy remains challenging, because the observed correlations vary within and among different coral species. Such variations reflect the regulation of the calcifying fluid pH by corals, and highlight the need to better understand the fundamental calcification processes involved.

Here I present a numerical model that simulates pH regulation by corals based on physicochemical principles, and determine the physicochemical and biological factors that control it. I show that coral calcifying fluid pH depends not only on seawater pH ( $pH_{sw}$ ), but also on other seawater physicochemical parameters. Specifically, my model shows that  $pH_{sw}$  exerts the strongest control on the pH elevation in coral calcifying fluid ( $\Delta pH$ , i.e. the pH offset between the calcifying fluid and external seawater), yielding apparent  $\Delta pH \sim pH_{sw}$  slopes of about  $-0.7 \sim -0.8$  over the  $pH_{sw}$  range of 7.5–8.2 for different species. Note, however, the model predicted  $\Delta pH \sim pH_{sw}$  correlations are not linear over large  $pH_{sw}$  ranges and are best fitted with polynomial functions. Besides  $pH_{sw}$ , seawater temperature and DIC concentration also affect  $\Delta pH$ , yielding sensitivities of  $-0.017 \sim -0.031/^{\circ}C$  and  $-0.018 \sim -0.026/(100 \mu mol \cdot kg^{-1})$  respectively for different species. In contrast, changes in salinity have much smaller effects on  $\Delta pH$ , with sensitivities of  $-0.005 \sim -0.007$ . Furthermore, my model suggests enzymatic alkalinity pumping and the exchange between the calcifying fluid and external seawater also influence  $\Delta pH$ .

The fact that coral calcifying fluid pH depends not only on seawater pH but also on other physicochemical and biological factors complicates the interpretation of pH records in coral skeleton. An inverse method for reconstructing paleo-pH that takes into account these effects will also be discussed at the meeting.