Do Boron isotopes in shallow marine carbonate record marine pH?

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The boron isotope-pH proxy has been widely used to reconstruct the past ocean pH values. In both foraminifera and corals, species-specific calibration is required in order to reconstruct absolute values of pH, due to the existence of so-called vital effects: interferences on environmental signals that derive from the physiology of the calcifying organisms.

Shallow marine abiotic carbonate (e.g. ooids and cements) could potentially avoid any such calibration requirement and so could be a potentially useful archive for reconstruction in deep time. However, despite recent applications of the boron isotope proxy to ooids and cements, there has been limited work to test the validity of the proxy in modern settings. In this study, we present boron isotope measurements (using MC-ICP-MS) from shallow modern marine carbonate, specifically ooids and hardground from the Bahamas Band and reef cements from Belize, and compare them with measurements of in situ seawater pH values. Our B based pH estimates (7.98–8.47, 2σ = 0.23), with limited exception, do not match modern seawater (mean = 8.04). Also, most (81%) of our pH estimates fall out of the range of in situ pre-industrial seawater pH values (8.12–8.20). In short sediment cores from the Bahamas there we did not observed a correlation between in situ pH values of the pore water and the sediment pH estimates, suggesting B isotope variability was depositional rather than early diagenesis. The large variance of the pH estimates throughout the whole sample sequence argues against the application of the δ^{11}B-pH proxy to such shallow marine carbonates. The pH variance may arise either from the heterogeneous sedimentation through space and time or the microbial-mediated pH change in the microenvironment of abiogenic carbonates during their growth.