The impact of mineralogy and diagenesis on bulk carbonate δ¹¹B: a multi-proxy approach

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The isotopic composition of boron ($\delta^{11}B$) in marine calcifiers, such as foraminifera and deep-sea corals, has emerged as a potent tool for reconstructing past oceanic pH dynamics [1]. Given the abundance of shallow-marine carbonates preserved in the geological record, there has been considerable interest in utilizing bulk carbonates for analogous purposes, which could potentially yield paleo-pH records for older intervals of Earth history. Notably, δ^{11} B excursions in shallow-marine carbonates during the Neoproterozoic and Early Triassic have been interpreted as indicative of oceanic acidification events [2]. However, interpreting geochemical data from bulk carbonates is challenging due to the potential for alteration of their primary values through diagenetic processes. Few studies suggest $\delta^{11}B$ and B/Ca in platform carbonates decline due to meteoric and marine burial diagenesis [3, 4]. However, the influence of earlymarine diagenesis, including dolomitization, remains underexplored. In this study, we propose an analytical framework for identifying diagenetic alterations of boron in bulk carbonates. Our investigation focuses on Eocene-age shallowmarine carbonates from the Avon Park Formation in Florida (USA), which have undergone lithification and dolomitization. This site offers an exceptional opportunity for studying early, near-surface diagenetic processes, without complication from burial diagenesis. We combine $\delta^{11}B$ and B/Ca measurements with traditional (δ^{13} C, δ^{18} O, and δ^{34} S of carbonate-associated sulfate (CAS)) and non-traditional (δ^{44} Ca and δ^{26} Mg) isotopic analyses, alongside major-, minor-, and trace-element measurements (e.g., Mg, Sr, Mn, Li, Na). Our findings reveal significant variability in $\delta^{11}B$ (~10%) and B/Ca (~90%) throughout the core, comparable in magnitude to previous observations attributed to diagenetic processes such as meteoric [4] and marine burial influences [3]. Additionally, we observe correlations with Mg/Ca ratios and CAS abundance, suggesting potential mineralogical and crystallographic controls on boron incorporation. Our comprehensive multi-proxy approach allows us to discern the processes and diagenetic styles influencing boron variability, emphasizing the importance of carefully considering potential resetting of boron signatures in bulk carbonates.

[1] Foster (2008), Earth and Planetary Science Letters 271, 254–266.

[2] Kasemann et al. (2005), *Earth and Planetary Science Letters* 231, 73–86.

[3] Zhao et al. (2023), American Journal of Science 323.