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Calcium isotopes in pore fluids to trace carbonate mineral precipitation, dissolution, and sedimentary alkalinity flux at the Iberian Margin

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Continental margin sediments play one of the most active roles in Earth's carbon cycle, accounting for the majority of organic carbon and carbonate minerals buried in marine sediments. Sedimentary carbonate minerals are predominantly biogenic, produced in the surface ocean and subsequently deposited on the seafloor, but they may also form authigenically through precipitation within sediments under changing geochemical conditions. While most research has focused on biogenic carbonate delivery and burial, less attention has been given to the interaction between biogenic carbonate dissolution and authigenic carbonate precipitation, and their combined role in sedimentary alkalinity flux. As a result, the fundamental controls on sedimentary alkalinity flux across contrasting depositional environments on the ocean floor remain poorly constrained.

We investigated authigenic carbonate precipitation and alkalinity generation at the Iberian Margin by combining calcium ($\delta^{44}Ca$) and carbon ($\delta^{13}C$) isotope compositions of pore fluids recovered during International Ocean Discovery Program (IODP) Expedition 397 with reactive-transport modeling. Four sites spanning water depths of ~1400–4500 m were examined, encompassing large variations in organic matter composition and sedimentation rates. This spatial variability provides a natural framework for assessing how depositional environment influences benthic alkalinity flux. At each site, pore fluids from the sediment–water interface to 100 m below the seafloor were analyzed to trace coupled microbial and mineral reactions.

The $\delta^{44}Ca$ records, interpreted alongside modeling results, demonstrate that anaerobic organic matter remineralization drives both carbonate precipitation and dissolution. The depth distribution and magnitude of authigenic carbonate formation are strongly influenced by sedimentation rate and organic matter reactivity. Moreover, the calcium isotope data indicate that carbonate recrystallization may occur at higher rates than previously recognized, with important implications for the integrity of calcium-carbonate-based palaeoceanographic proxies. Combined, these findings refine the application of $\delta^{44}Ca$ as a tracer of benthic biogeochemical processes and provide new constraints on sedimentary controls of alkalinity flux relevant to ocean pH.