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Calcium isotopes' place in the diagenetic toolbox

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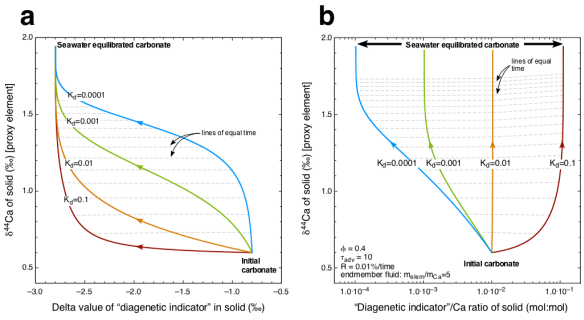
Diagenetic alteration of marine carbonate sediments complicates interpretation of geochemical proxy records, potentially skewing our understanding of Earth history. Accordingly, unraveling the diagenetic component in these records is paramount. There are a host of geochemical tools that can be used to fingerprint diagenesis, metal isotopes amongst them. However, the successful application of metals isotopes as diagenetic indicators depends on a clear understanding of the reactive length scales over which indicators are relevant in a given system. When the length scales between proxy and indicator are either mismatched or simply not considered, proper utilization of these tools is not possible.

In this talk, we set forth a practical framework for the application of metal isotopes, Ca isotopes in particular, as diagenetic indicators in carbonate sediments. The reactive length scales of several metals in carbonates (e.g., Ca, Mg, Sr), in addition to their significant oceanic residence times (>10^6 years), make them useful for evaluating diagenetic impacts on carbonate geochemistry. We illustrate several examples in which indicator-proxy pairs help demystify diagenetic systems, and we discuss where in the sedimentary column such tools are appropriate. For example, the terms 'sediment-buffered' and 'fluid-buffered' have historically been used to describe whether a reactive sedimentary system is open or closed to alteration. However, the reactive length scale over which each proxy element may be impacted by diagenesis is determined by mineral reactivity, pore fluid abundance, and mineral-fluid partitioning. Accordingly, the length scales of carbonate-hosted elements can vary by orders of magnitudes, such that a system described as closed with respect to Ca may be open with respect to Mg. Model simulations that pair Ca isotopes with proxies of interest demonstrate how diagenetic studies should approach the use of indicators to identify appropriate trends along diagenetic trajectories. Reactive length scales dictate the utility of metal isotopes as diagenetic indicators and their inclusion in geochemical studies with complementary proxies can elucidate the role of diagenesis in carbonate sediments, promoting more accurate proxy-based reconstructions of the past over geologic time.



Diagenetic trajectories in (a) isotope-isotope and (b) isotope-element space for an advection-dominated system (τ_{adv} = 10) in which the K_d of a generic diagenetic indicator varies from 0.0001 to 0.1. An initial carbonate composition is assumed, and the model is run until both the proxy and indicator elements equilibrate with the endmember model fluid (10.3 mM Ca^{2+}, 52 mM indicator, $\delta^{44}Ca$ = 1.9‰, $\Delta^{44}Ca_{s-f}$ = 0‰, $\delta_{indicator}$ = −0.8‰, $\delta_{indicator}$ = −2‰; all $\delta^{44}Ca$ values are reported on the SRM-915a scale). The dashed gray lines connect points of equal time on the various model trajectories.