Behavior of Carbonate-Associated Sulfate during Meteoric Diagenesis and Implications for the Sulfur Isotope Paleoproxy

Benjamin C. Gill¹, Timothy W. Lyons¹, Tracy D. Frank²

[']University of California-Riverside ²University of Nebraska-Lincoln

Abstract

Although carbonate-associated sulfate (CAS) is used widely as a proxy for the sulfur isotope composition of ancient seawater, little is known about the effects of diagenesis on retention of primary δ^{34} S signals. Our case study of the Key Largo Limestone, Pleistocene, Florida, is the first systematic assessment of the impact of meteoric diagenesis on CAS properties. Geochemical and petrographic data show that meteoric diagenesis has affected the exposed coralline facies to varying degrees, yielding differences now expressed as sharp reaction fronts between primary and secondary carbonate minerals within individual coral heads. Specifically, analyses across high resolution transects in the Key Largo Limestone show that concentrations of strontium and sodium decrease across the recrystallization front from original aragonite to meteoric low-magnesium calcite by factors of roughly 5 and 10, respectively. Predictably, δ^{18} O values decrease across these same fronts by 0.85‰ on average. The δ^{13} C relationships are more complex, with the most depleted values observed in the latest-formed calcite. Such trends likely reflect carbon isotope buffering capacity that decreased as reaction progressed, as well as protracted development of soil profiles and the associated terrestrial biomass, and thus depleted $\delta^{13}C$ during sea-level lowstand. Conversely, δ^{34} S values of CAS vary within a narrow 'buffered' range from 20.6 to 22.6‰ (compared to 21.8-22.0‰ of coeval Pleistocene seawater) across the same mineralogical transition, despite sulfate concentrations that dropped in the diagenetic calcite by an average factor of 12. Collectively, these data point to robust preservation of primary δ^{34} S for carbonates that have experienced intense meteoric diagenesis, which is encouraging news for those using the isotopic composition of CAS as a paleoceanographic proxy. At the same time, the vulnerability of CAS concentrations to diagenetic resetting is clear.



XRD and Petrographic Data

Photograph of KL1 sample transect from the Key largo Limestone. XRD traces are included to illustrate the change in mineralogy between the light core (aragonite) and dark alteration rim calcite



Elemental Data





Cabonate Associated Sulfate Data and Alteration Model

Model for the alteration of CAS in the Key Largo Limestone

Meteoric Alteration reduces the concentration of CAS by ~10 fold in the meteoric calcite as compared to the aragonite.

Sulfate Reduction results in the ³⁴S enrichment of the sulfate incorported into the meteoric calcite.

 δ Oxidation of ³²S enriched sulfide may account for the low δ ³⁴S_{CAS} values seen in some of our samples.

The Key Largo Limestone shows classic meteoric diagenetic behavior within its elemental and stable isotope systems.



The meteoric calcite of the Key Largo shows depleted Sr, Na, and SO₄ (CAS) concentrations and depleted δ^{13} C and δ^{18} O values as compared to the primary aragonite.



Spatial δ^{13} C data reveals a temporal trend in the meteoric calcite that reflects decreasing buffering capacity of the Key Largo as the water:rock ratios increased during alteration.





CAS concentration and sulfur stable isotope data from all transects plotted as distance from reaction front, defined as the boundary between the aragonite and meteoric calcite.

Light gray band represents the range of published range Pleistocene seawater (21-22‰).





CONCLUSIONS



reflects changes in the diagenetic environment (i.e. vadose vs. phreatic alteration).

Despite pervasive meteoric alteration of the Key Largo Limestone the original $\delta^{34}S_{CAS}$ is preserved.

 δ^{18} O of the meteoric calcite is highly variable, which likely

CAS concentrations are severely compromised and decrease by an order of magnitude. Caution should be used in interpreting ancient CAS concentrations.