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

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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 $\delta^{34}S$ 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, $\delta^{18}O$ values decrease across these same fronts by 0.85‰ on average. The $\delta^{13}C$ 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, $\delta^{34}S$ 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 $\delta^{34}S$ 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.