Variance in Phanerozoic marine sulfate $\delta^{34}S$ proxies

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The Phanerozoic history of the sulfur isotopic composition ($\delta^{34}S$) of marine sulfate informs changes in carbon, oxygen, and weathering fluxes. We compiled over 4,000 measurements from three proxy archives for ancient seawater $\delta^{34}S$ and present them on a consistent geologic time scale. One of these proxies, bulk-rock carbonate-associated sulfate (CAS), provides the most temporally- and spatially-complete coverage, but exhibits much more variability over the Phanerozoic (standard deviation = 9.5‰) than data from marine evaporites (6.7‰), biogenic carbonate CAS (4.9‰), and marine barite (2.3‰). The variance of all records, especially that of bulk-rock CAS, decreases from the early Paleozoic to the recent. To unpack sources of variance in bulk-rock CAS and guide sampling of Precambrian strata for which the other proxies are unavailable, we undertook a systematic study of the depositional and diagenetic controls on the $\delta^{34}S$ of CAS.

In late Paleozoic-age (Guadalupian) strata from the Capitan Reef in west Texas, we demonstrate facies-dependent heterogeneity in the $\delta^{34}S$ of CAS, which is influenced by diagenetic pore fluid processes. These processes variously modify the $\delta^{34}S$ of incorporated sulfate from syndepositional seawater in shelf crest, outer shelf, shelf margin, and slope depositional settings. Peritidal facies in the Yates and Tansill formations preserve the $\delta^{34}S$ of Guadalupian seawater sulfate despite alteration of the carbon and oxygen isotopic compositions by meteoric and dolomitizing diagenetic processes. However, limestones deposited in reef and slope facies in the Capitan and Bell Canyon Formations largely incorporate sulfate from anoxic marine-phreatic pore fluids whose $\delta^{34}S$ is modified from seawater by microbial sulfate reduction. Both early and late meteoric calcite cements have CAS with $\delta^{34}S$ distinct from that of Permian seawater. Carbonates that diagenetically stabilize in high-energy environments without pore fluid sulfate gradients provide a robust archive of ancient seawater's $\delta^{34}S$.

We show how rock texture accounts for some of the variance in the $\delta^{34}S$ of Phanerozoic bulk-rock CAS, which will allow for improved reconstructions of ancient seawater $\delta^{34}S$ and diagenetic conditions in ancient carbonate platforms.