

Platform carbonates fail to capture mid-Eocene isotopic shift in ocean sulfate

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The sulfur isotopic composition ($\delta^{34}\text{S}$) of carbonate-associated sulfate (CAS) has long been thought of as a proxy for the sulfur isotopic composition of ocean sulfate. Thus, variations in CAS- $\delta^{34}\text{S}$ throughout the sedimentary record have been used to infer temporal changes in the global sulfur cycle. Platform carbonates are common in the sedimentary record and yet the reliability of the CAS- $\delta^{34}\text{S}$ proxy has been insufficiently tested in this archive. To rectify this, we tested whether platform carbonates in Florida (Daytona Beach) and the Bahamas (Andros Island) capture a mid-Eocene shift in the sulfur isotopic composition of ocean sulfate that has been constrained from contemporaneous barites and foraminifera. These materials have complex diagenetic histories, including episodes of dolomitization, but have not experienced burial temperatures $>50^\circ\text{C}$. We did not find the expected ~ 3 per mil mid-Eocene increase in the $\delta^{34}\text{S}$ value of ocean sulfate in Florida or the Bahamas. Broadly, CAS- $\delta^{34}\text{S}$ values are either higher or lower than expected for most samples. Using a suite of other geochemical indices (e.g., Mg/Ca, $\delta^{44/40}\text{Ca}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Sr/Ca), we identified at least 4 possible mechanisms for the discrepancies between observed and expected CAS- $\delta^{34}\text{S}$ values: 1) meteoric diagenesis, which lowers CAS- $\delta^{34}\text{S}$ values by 1-5 per mil; 2) early marine diagenesis, which raises CAS- $\delta^{34}\text{S}$ values by up to 6 per mil; 3) late stage dolomitization, which resets CAS- $\delta^{34}\text{S}$ values to that of younger seawater, and 4) mineralogical effects on the $\delta^{34}\text{S}$ fractionation between ocean sulfate and CAS, with calcite preserving larger offsets from seawater than primary aragonite. The array of diagenetic processes operating in carbonate platforms can overprint CAS- $\delta^{34}\text{S}$ in ways that are difficult to unravel. This complexity has implications for the use of the CAS- $\delta^{34}\text{S}$ proxy in the deeper geologic record, with ~ 3 per mil excursions in the $\delta^{34}\text{S}$ value of ocean sulfate over a few million years likely to be unresolvable.