Single-brachiopod $\delta^{34}S_{CAS}$ indicates a dynamic, climatically-influenced Permo-Carboniferous S cycle

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Early isotopic studies of sulfate present as a minor constituent of carbonates – i.e., carbonate-associated sulfate (CAS) – inspired optimism that carbonates could provide a reliable, well-dated archive of S cycle variability to integrate with exisitng knowledge of C and O cycle variations from high-resolution C and O isotopic records. However, subsequent research has shown that diagenetic alteration can impose highly heterogenous CAS S isotopic compositions among different carbonate phases within sediments, necessitating targeted sampling of well-preserved, primary carbonate phases in generating robust records. Here, we present a new record of Carboniferous and Early Permian seawater $\delta^{34}S$ generated from S isotopic measurements of CAS from 151 individual, well-preseved brachiopods from the United States and Russia. Our record indicates a ~7‰ drop in $\delta^{34}S$ over the first ~20 Myr of the Carboniferous, with an abrupt increase in $\delta^{34}S$ associated with major glaciation at the Mississippian-Pennsylvanian boundary. A subsequent Early Pennsylvanian decrease in $\delta^{34}S$ occurs with little to no change in contemporaneous $\delta^{13}C$, suggesting a decoupling of the C and S cycles during this time. Latest Pennsylvanian and Early Permian $\delta^{34}S$ values remain stable at ~+12‰.

Our single brachiopod approach also enables what is to our knowledge the first attempt to examine $\delta^{34}S_{CAS}$ within and among coeval brachiopod specimens and evaluate the potential for taxon-associated variability in $\delta^{34}S_{CAS}$. Results from synchotron XRF mapping and $\delta^{34}S_{CAS}$ measurements indicate [CAS] heterogeneity within specimens and very little variability in $\delta^{34}S_{CAS}$. However, we find a $\delta^{34}S$ range among codepositional taxa that in some cases exceeds 2‰, with *Composita subtilita* commonly displaying an enrichment in ^{34}S. Our results suggest that the timing and magnitude of changes in seawater $\delta^{34}S$ may be constrained more precisely with the careful, taxon-specific sampling enabled by our method.