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**Key Points:**
- The 6,710 measurements of $\delta^{34}S$ of sulfate in Phanerozoic sedimentary rocks were compiled and systematically updated to a consistent timescale
- Records derived from evaporites, barite, and carbonate-associated sulfate are similar and also contain dramatic short-term discrepancies
- Variation created by diagenetic and depositional processes increases with age in all records, obscuring temporal trends in marine sulfate

**Supporting Information:**
- Supporting Information S1
- Data Set S1

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# Variability in Sulfur Isotope Records of Phanerozoic Seawater Sulfate

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**Abstract** The $\delta^{34}S$ of seawater sulfate reflects processes operating at the nexus of sulfur, carbon, and oxygen cycles. However, knowledge of past seawater sulfate $\delta^{34}S$ values must be derived from proxy materials that are impacted differently by depositional and postdepositional processes. We produced new time series estimates for the $\delta^{34}S$ value of seawater sulfate by combining 6,710 published data from three sedimentary archives—marine barite, evaporites, and carbonate-associated sulfate—with updated age constraints on the deposits. Robust features in multiple records capture temporal trends in the $\delta^{34}S$ value of seawater and its interplay with other Phanerozoic geochemical and stratigraphic trends. However, high-frequency discordances indicate that each record is differentially prone to depositional biases and diagenetic overprints. The amount of noise, quantified from the variograms of each record, increases with age for all $\delta^{34}S$ proxies, indicating that postdepositional processes obscure detailed knowledge of seawater sulfate's $\delta^{34}S$ value deeper in time.

**Plain Language Summary** Sedimentary rocks deposited in ancient marine basins preserve a record of seawater composition. We compare the sulfur isotopic composition of three sedimentary materials that contain sulfate—a major ion in seawater important for carbon and oxygen cycling. Evaporite salts, the mineral barite, and trace sulfate in limestone each reveal the same first-order trends over the last $541 \times 10^6$ years and also display substantial shorter-order discrepancies that reflect how the materials capture and store paleooceanographic information. These discrepancies partially obscure understanding of the relationship between life, ocean chemistry, and climate.

## 1. Introduction

Seawater sulfate acts as a major oxidant of organic carbon, controlling the cadence of its burial in sediments and connecting the carbon, sulfur, and oxygen cycles (Bowles et al., 2014; Jørgensen, 1982). Microbial sulfate reduction (MSR), reoxidation of sulfide, and the burial and oxidation of pyrite govern sedimentary inorganic carbon and alkalinity fluxes (Ben-Yaakov, 1973; Froelich et al., 1979). Pyrite in sedimentary rocks may be exposed and oxidized during uplift, erosion, and weathering—impacting Earth's dioxygen and carbon dioxide budgets on tectonic timescales (Burke et al., 2018; Kump & Garrels, 1986; M. A. Torres et al., 2014). Over Phanerozoic time (the past 541 Myr), the burial of sulfide and disulfide minerals must have balanced the acid produced and dioxygen consumed during terrestrial pyrite weathering. Therefore, tracking ancient sulfate fluxes related to these processes illuminates when, how, and where the Earth system achieves this balance, and what happens during intervals of unsteadiness.

Thode et al. (1953) first recognized that a record of ancient marine sulfur isotopic compositions ($\delta^{34}S$) could constrain changes to Earth's biogeochemical cycles, and Ault and Kulp (1959) applied mass balance assumptions in an early effort to quantify important sulfur fluxes. Isotope fractionations during MSR preferentially enrich the residual sulfate in $^{34}S$ by several percent (Bradley et al., 2016; Harrison & Thode, 1958; Sim et al., 2011). When more sulfate is reduced and fixed into pyrite, removing more light sulfur isotopes from the oceans, the remaining sulfate in seawater becomes enriched in the heavy, rare isotopes. Holland (1973) first attempted to calculate changes in dioxygen fluxes from $\delta^{34}S$ data. Holser (1977) further recognized that rapid changes in the $\delta^{34}S$ value of seawater coincide with intervals of biotic crises and dramatic reorganizations of Earth's climate and biosphere. The subsequent 40 years have seen many efforts to derive an accurate and precise record of how the $\delta^{34}S$ value of seawater sulfate has changed over Earth history.

Three sedimentary materials constitute proxy archives of Phanerozoic seawater sulfate $\delta^{34}S$ values: (1) marine evaporites, which include sulfate salts precipitated from evaporated seawater in marginal marine basins;

(2) marine barite, which forms from a suite of biogeochemical processes associated with sinking particles in pelagic waters; and (3) carbonate-associated sulfate (CAS), which is minor sulfate incorporated into the crystal lattice of biogenic and abiogenic calcite, aragonite, and dolomite phases that accumulate in sedimentary rocks.

Important reviews (Bottrell & Newton, 2006; Claypool et al., 1980; Holser et al., 1989; Strauss, 1997; Veizer et al., 1980) on the evolution of the Phanerozoic sulfur cycle have assumed that these proxies accurately preserve the isotopic composition of ancient seawater sulfate. This assumption is reasonable because Phanerozoic seawater likely contained abundant sulfate as a conservative, well-mixed anion. Modern seawater has 28 mmol/kg sulfate, which has an approximate residence time of more than 10 Myr—much longer than the mixing time of the oceans (Bottrell & Newton, 2006; Walker, 1986). Supergiant gypsum and anhydrite deposits in the sedimentary record indicate that sulfate was a major constituent in ancient seawater, as well. These deposits, which represent long-lived intervals of basin recharge and evaporation of seawater (Warren, 2010), formed episodically from Mesoproterozoic through Phanerozoic time (Grotzinger & Kasting, 1993; Pope & Grotzinger, 2003). The composition of fluid inclusions in halite from evaporite deposits further suggested that sulfate maintained at least millimolar concentrations throughout Phanerozoic time (Lowenstein et al., 2003).

Important features in the $\delta^{34}$S age curves were observed in multiple data sets on both long and short timescales. All archives exhibited high $\delta^{34}$S values (>30‰) in early Paleozoic time, fell to minima (~10‰) in the late Paleozoic, and increased to modern values (~21‰) over Mesozoic and Cenozoic time. This pattern was originally noted in the evaporite record by Ault and Kulp (1959) and reaffirmed by more extensive evaporite compilations (Claypool et al., 1980; Holser et al., 1989; Holser & Kaplan, 1966; Strauss, 1997). Burdett et al. (1989) produced the first continuous biogenic CAS data set for the Neogene Period and demonstrated that it agreed with the evaporite $\delta^{34}$S record. Kampschulte et al. (2001) and Kampschulte and Strauss (2004) then demonstrated that biogenic CAS captured the first-order features of the Phanerozoic evaporite record and could be correlated with higher resolution and confidence than evaporites to the carbonate carbon isotope record. The $\delta^{34}$S pattern covaries with many other geochemical records of changing seawater composition (Hannisdal & Peters, 2011; Prokoph et al., 2008) and so has been interpreted to reflect long-term changes related to the assembly and breakup of Pangea (Turchyn & DePaolo, 2019).

In addition to long-term trends, Holser (1977) identified shorter fluctuations (5–50 Myr) in the Upper Devonian and lower Triassic evaporite record; these excursions are recorded by CAS as well (Kampschulte & Strauss, 2004). Increased temporal resolution from barite and CAS found additional rapid excursions, notably associated with Jurassic and Cretaceous intervals of widespread organic-rich shale deposition (Gill, Lyons, & Jenkyns, 2011; Paytan et al., 2004) and Paleogene carbon cycle perturbation (Paytan et al., 1998; Rennie et al., 2018). In addition, some $\delta^{34}$S records with high temporal resolution, especially derived from CAS, have rapid variability (Kah et al., 2016; Kampschulte et al., 2001), and data from multiple locations containing similar-age strata have $\delta^{34}$S heterogeneity (Gill, Lyons, Young, et al., 2011; Present et al., 2015).

Although seawater sulfate was likely well-mixed for much of Phanerozoic time, these rapidly varying data sets indicate that short periods of sulfate drawdown may have been expressed as high spatial and temporal $\delta^{34}$S gradients (Holser, 1977; Kah et al., 2004, 2016). If these gradients represent globally relevant budgets of carbon, nutrients, and oxidizing capacity, then the residence time of sulfate in ancient oceans must have been much shorter than today. An analogy to the carbon cycle is illustrative. Isotopic fractionations between oxidized and reduced species are comparable for carbon and sulfur. The biological pump—remineralization of sinking organic matter that is fractionated by tens of permille from dissolved inorganic carbon—is only capable of creating inorganic carbon isotopic gradients of less than 3‰ given Pliocene-age to present nutrient inventories and ~2 mmol/kg bicarbonate (Toggweiler & Sarmiento, 1985). Therefore, even small gradients in the $\delta^{34}$S of marine sulfate, of similar magnitude to carbon isotope gradients driven by the biological pump, would have required both a higher proportion of anaerobic organic carbon remineralization and more than an order of magnitude smaller sulfate inventory.

However, the implicit assumption that proxies for seawater $\delta^{34}$S values are suitably accurate and precise to demonstrate rapid changes in seawater's composition has not been tested. The processes by which the proxy materials form and incorporate sulfate from seawater may affect their $\delta^{34}$S value, complicating the

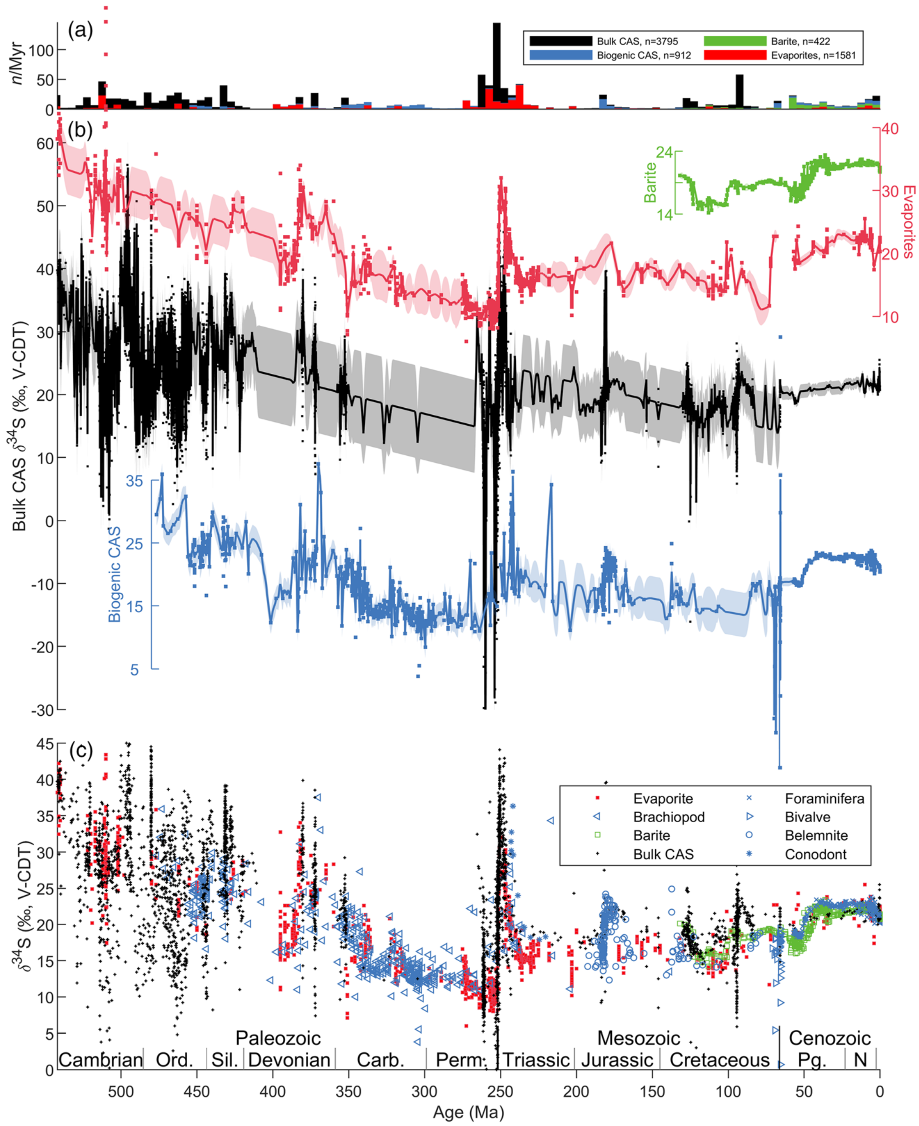


**Figure 1.** Records of Phanerozoic seawater sulfate $\delta^{34}$S generated from proxy materials. (a) The average number of $\delta^{34}$S analyses of each proxy per Myr, in 5 Myr bins, illustrates the temporal bias in the sampling of each material through Phanerozoic time. (b) Interpolated proxy records of the $\delta^{34}$S composition of sulfate over Phanerozoic time. Shading indicates the kriged 1$\sigma$ confidence intervals. (c) All compiled proxy data for the $\delta^{34}$S of Phanerozoic seawater.

reconstruction of Phanerozoic seawater's composition but providing nuance on biogeochemical sulfur cycling and its imprint on the rock record.

We produced a new time series to estimate the Phanerozoic history of the $\delta^{34}$S value of seawater sulfate by synthesizing published geochemical data with updated geochronology and stratigraphic correlations. We attribute some of the differences between archives to mechanics of how sulfate is incorporated into and preserved in sedimentary rocks. This approach tests the assumption that each archive samples the same history of seawater $\delta^{34}$S values, quantifies uncertainty in proxy archives, and reveals that some major sources of variance are themselves produced by biogeochemical processes that may have varied through Phanerozoic time.

## 2. Synthesis of Phanerozoic Seawater Sulfate $\delta^{34}$S Proxy Data

We compiled 6,710 measurements from 108 references that reported $\delta^{34}$S values in Phanerozoic marine evaporites, bulk rock CAS, biogenic CAS, or marine barite. Each $\delta^{34}$S value was assigned an age using the International Commission on Stratigraphy 2016/04 timescale (Cohen et al., 2013; updated) (Figure 1). The

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supporting information enumerates the $\delta^{34}S$ data, assigned age, data type, data source, and method and literature used for each age assignment.

Each proxy material has different, irregularly spaced temporal distributions (Figure 1a). To estimate Phanerozoic $\delta^{34}S$ trends, each proxy record was interpolated at 50 kyr resolution (Figure 1b). These interpolations estimate the $\delta^{34}S$ time series present in each archive and the resulting trends are not necessarily an estimate of seawater's true $\delta^{34}S$ value through time. Kriging—a geostatistical approach using autocorrelation to quantify stochastic components in spatiotemporal data—was used to weight data for interpolation and estimate confidence intervals (Gebbers, 2010). Because kriging uses the empirical autocorrelation structure of the data to produce weights, it is well suited for irregularly spaced data. Autocorrelation varies between two end-members of linearly detrended variance: The maximum scatter has no autocorrelation and the variance is that of all points in that geologic interval, and the minimum scatter is the unresolved chatter between data closely spaced in time that otherwise are part of a consistent trend. The kriged uncertainty on the interpolations reflects this increase in variance, such that interpolated values further from data have larger uncertainties up to the population variance according to the observed range of autocorrelation. Kriging was done on each geologic material, partitioned by era, by modeling variograms—functions describing how the variance per point (semivariance) of pairs of linearly detrended data varies with their average separation distance in time computed at integer factors of the mean minimum time between pairs of data (supporting information). Paleogeography was not considered, so spatial variability was collapsed into the temporally unresolved chatter within each era.

## 3. Discussion

### 3.1. Distribution of $\delta^{34}S$ in Proxies

During 70 years of effort to determine a history of Phanerozoic seawater sulfate $\delta^{34}S$ from different geologic materials, it has implicitly been assumed that each proxy samples the same primary population of seawater $\delta^{34}S$ compositions through space and time. However, comparison of all Phanerozoic $\delta^{34}S$ data for each proxy indicates that the four data sets do not come from the same distribution (supporting information, nonparametric Kruskal-Wallis one-way analysis of variance, $\chi^2[3,6709] = 684.54$, $p \ll 0.001$). Therefore, each proxy likely has different temporally or spatially variable sampling biases or reflects different biogeochemical processes that contribute to variance in the time series of ancient sulfate's $\delta^{34}S$ values.

Major $\delta^{34}S$ trends and excursions in Cenozoic, Mesozoic, and late Paleozoic records are exhibited in multiple archives, but significant discrepancies and gaps are apparent in records from Cambrian to Devonian time (Figure 1c). In early- to mid-Paleozoic strata, biogenic carbonates are sparse, marine barite is absent, and bulk CAS $\delta^{34}S$ values diverge from evaporites by greater than 10‰ (Figure 2a). Additionally, Paleozoic variance is highest for all records (Figure 2b).

The evaporite record, composed of massive amounts of sulfate but limited in spatial and temporal extent, likely captures long-term $\delta^{34}S$ trends. The bulk CAS, biogenic CAS, and barite records have higher temporal resolution than the evaporite record for much of the Phanerozoic, potentially capturing shorter $\delta^{34}S$ excursions.

### 3.2. Sources of $\delta^{34}S$ Variance

The $\delta^{34}S$ variability for each proxy is plotted in Figure 2b. The maxima in each era on each curve represents the standard deviation of detrended $\delta^{34}S$ data over each geologic era. For example, the standard deviation of linearly detrended Paleozoic bulk CAS data is 7.4‰ (excluding 1st and 99th percentile outliers), while that of all Cenozoic barite data is 1.3‰. These standard deviations can be interpreted as a naive description of expected variability where data is sparse and reflect the combination of local temporal trends in the proxy record plus an uncorrelated random component. The uncorrelated, random component is estimated by the semivariance of pairs of data that are closer together than the mean minimum time between all pairs of data (Gebbers, 2010). The uncorrelated variances for each proxy are plotted as the minima in each era on each curve in Figure 2b.

Uncorrelated variance is a metric that convolves multiple sources of uncertainty. Sources of variance of geologic interest include temporally unresolved variability in seawater $\delta^{34}S$ values and temporally incoherent

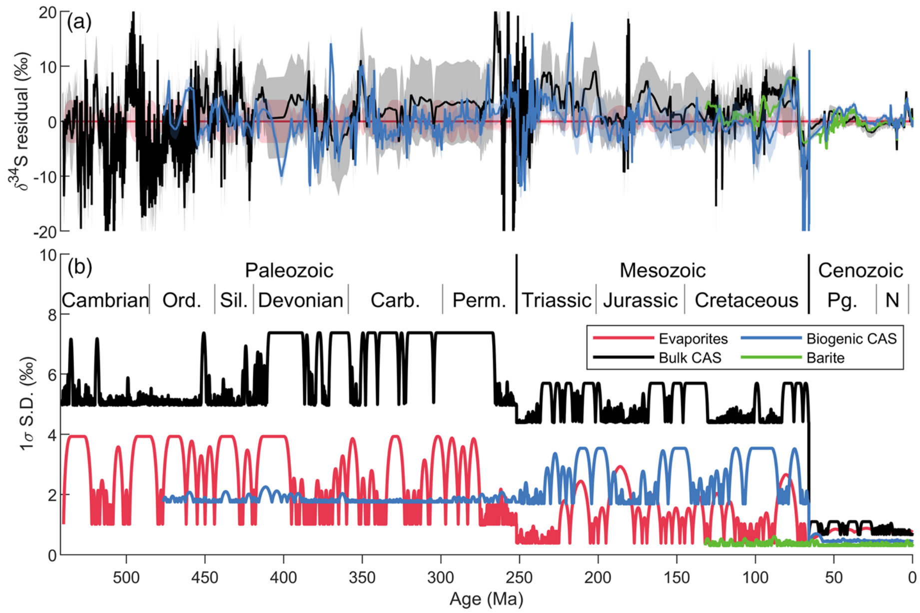


**Figure 2.** Comparison of $\delta^{34}S$ values and variance generated from proxy materials. (a) Residuals between the evaporite record and each other record shaded with kriged 1$\sigma$ confidence intervals. (b) Confidence intervals produced from kriging data from each proxy in each era. Where data is sparse, the confidence intervals approach the standard deviation of linearly detrended data in each geologic era, excluding 1st and 99th percentile outliers. Where there is data, the confidence interval is the uncorrelated chatter determined from the semivariance of data temporally closer than the mean minimum time between data pairs.

variability in how the sedimentary archives were formed or altered. These sources of variance may be temporally unresolved due either to spatial variability at a given time, or to temporal variability more rapid than the resolution of the record. In addition, the uncorrelated variance captures analytical uncertainty related to making $\delta^{34}S$ measurements in each archive, and nonsystematic error in age assignments of proxy materials. Variability in both the $\delta^{34}S$ and age dimensions of the data are empirically described by semivariance, and thus captured by the uncorrelated variance. While the relative contributions of each of these sources of uncertainty may differ between proxies or with age, the uncorrelated variance metric—like the population variance—describes the data's structure and how predictive a given $\delta^{34}S$ measurement is of other nearby values. Further, the kriging interpolation produced using empirical descriptions of the structure of the data—namely, the uncorrelated variance, detrended population variance, and temporal range of autocorrelation—is itself an empirical description of the time series of each $\delta^{34}S$ archive.

This analysis produced two key results: The uncorrelated variance is different for each archive, and for all archives it increases with age. Cenozoic and Mesozoic CAS data have uncorrelated variance larger than that of evaporites and barite. Uncorrelated Paleozoic bulk rock CAS data have a standard deviation more than twice that of biogenic CAS and evaporites. These variography results, which empirically describe the time series structure of the $\delta^{34}S$ data, augment statistical descriptions of temporally binned data. For example, the interquartile range of $\delta^{34}S$ values of all archives from each geologic period increases with age, and the interquartile range of CAS data is greater than that of other archives in each period (supporting information). Differences between multiple proxies of the same age indicate that the uncorrelated variance is likely caused, in part, by variability inherent to how $\delta^{34}S$ is preserved, rather than just inadequate sampling of primary spatial and temporal variability of seawater sulfate.

The remaining analysis considers the sources of variance in each archive that may have contributed to the uncorrelated variance. Importantly, trends statistically distinguishable from the uncorrelated variance need not represent true trends in the $\delta^{34}S$ of Phanerozoic seawater. The same sources of variance controlling the uncorrelated data may themselves have spatial or temporal components that lead to biased estimates of Phanerozoic seawater's composition in the proxy records. A component of the uncorrelated variance quantifies the disagreement between contemporaneous records from different localities. Trends in the data smaller than the uncorrelated variance are indistinguishable from random noise. This is true even for individual records from stratigraphic successions with coherent $\delta^{34}S$ trends: A given stratigraphic succession may clearly resolve a trend in the $\delta^{34}S$ of the proxy but fail to statistically resolve a global trend in the $\delta^{34}S$ values of seawater sulfate.

#### 3.2.1. Evaporites

Deposits of carbonate, sulfate, and halide salts form as seawater evaporates in restricted basins. Throughout Phanerozoic time, bedded marine evaporites formed subaqueously, in salinas (hypersaline lagoons) and salt pans, and subaerially, in supratidal sabkha environments. Extremely thick (greater than hundreds of meters) evaporite deposits have also formed in deeper-water environments. Deposition and preservation of evaporites require favorable climatic and tectonic conditions where restricted basins experience net evaporation (Warren, 2010). Therefore, the evaporite record has limited spatial and temporal continuity (Claypool et al., 1980; Strauss, 1997).

Because evaporites are massive products of seawater sulfate, they are largely expected to provide an accurate proxy for the $\delta^{34}S$ of ancient seawater sulfate. However, because they form in marginal marine environments often with biologically adverse salinities, it can be difficult to constrain their geologic age with biostratigraphy. In many deposits, it is also challenging to discern depositional environment or deconvolve marine and nonmarine geochemical signatures (Hardie, 1984; Kendall & Harwood, 1989; Lu & Meyers, 2003). The restricted, marginal marine settings in which many evaporites form are prone to changes in fluid source or depositional environment with minor base-level changes (Playà et al., 2007). Basins rich in evaporites also often form diapirs that drive salt tectonics, which complicates a deposit's internal stratigraphy (Nielsen, 1989).

Evaporites can have a $\delta^{34}S$ range of 1‰ to 6‰ within a formation (Thode & Monster, 1965). This variability cannot be attributed to fractionation during gypsum precipitation, which produces sulfate salt prior to halite saturation that has a $\delta^{34}S$ composition 1‰ to 2‰ higher than the unevaporated seawater (Raab & Spiro, 1991). Salinity stratification in evaporating basins can promote water column anoxia and allows MSR to distill sulfate to higher $\delta^{34}S$ compositions than the original seawater; in some cases, evaporite $\delta^{34}S$ compositions are higher than other proxies from the same depositional basin (Fike & Grotzinger, 2010). Consequently, early workers hypothesized that the isotopic composition of ancient seawater was best reflected by the lowest $\delta^{34}S$ value in an evaporite succession (Ault & Kulp, 1959; Davies & Krouse, 1975; Thode & Monster, 1965). However, evaporite basins in marginal marine environments are recharged by, in addition to unadulterated seawater, groundwater and runoff with $\delta^{34}S$ compositions biased either higher or lower than seawater from remobilized older evaporite deposits or weathered sedimentary pyrite and organic sulfur (Nielsen & Ricke, 1964; Utrilla et al., 1992). Finally, high organic carbon concentrations in many evaporite deposits can promote isotope fractionation by thermochemical sulfate reduction during burial diagenesis (Vinogradov, 2007).

Some of the uncorrelated variance in evaporite isotope ratio data also results from poor stratigraphic control (supporting information). Here we used updated stratigraphic information to better constrain the age of evaporite data, but the record can further benefit from higher-resolution sample collection with improved stratigraphic control during intervals where $\delta^{34}S$ changes appear in other records. Modern stratigraphic models permit correlation of evaporitic strata to better constrained carbonate and clastic strata. Bernasconi et al. (2017) recently produced a high-resolution evaporite record that resolved the major early Triassic $\delta^{34}S$ excursions seen in earlier data sets; thus, careful correlation and assignment of geologic ages permits tracking changes in the Phanerozoic sulfur cycle with evaporites. Indeed, the stratigraphic control for Mesozoic evaporites provided by Bernasconi et al. (2017) controls the low standard deviation of uncorrelated Mesozoic evaporite data (0.4‰), which is comparable to that of the marine barite record (0.3‰).

#### 3.2.2. Barite

Barite precipitates from hydrothermal fluids, sediment pore fluids, and particles within the marine water column (Paytan et al., 1993, 2002). Barite is undersaturated in most of the oceans (Chow & Goldberg, 1960; Church & Wolgemuth, 1972). However, barite has been observed in sediment traps in the upper 200 m in the water column, especially in high-productivity regions, and is associated with sulfate enrichment from decaying organic matter (Bishop, 1988). While barite supersaturation is achieved predominately by the addition of sulfate from oxidizing organic sulfur (Horner et al., 2017; Jacquet et al., 2007), marine barite apparently precipitates with $\delta^{34}S$ values within 0.4‰ of modern seawater (Paytan et al., 1998, 2002). Barite is subsequently transported to sediments by fecal pellets and marine snow (Bishop, 1988), and is preserved in oxic marine sediments in high-productivity regions where enough barite is delivered to saturate pore fluids (Church & Wolgemuth, 1972). Sulfate reduction in anoxic sediments can cause dissolution of barite, which reprecipitates at the base of the sulfate reduction zone with extremely high $\delta^{34}S$ compositions (M. E. Torres et al., 1996).

Marine barite is considered an accurate proxy for ancient seawater $\delta^{34}S$ because it precipitates in the open-ocean water column and is texturally distinguishable from diagenetic barite that forms in anoxic sediments at redox fronts (Paytan et al., 1993). However, the marine barite record is limited by the availability of open-marine sediments that deposited in high-productivity regions where both authigenic enrichment of barite occurs and pore fluid sulfate is not completely consumed (Paytan et al., 1993). Consequently, the barite $\delta^{34}S$ record is unlikely to be extended much further than the current data set spanning the last 130 Myr. Bedded barite deposits are associated with economically important disulfide mineral deposits (C. A. Johnson et al., 2009) but contain large $\delta^{34}S$ variability (>10‰) and do not resolve the ancient seawater record any better than other proxy materials. Additionally, with few exceptions (e.g., Yao et al., 2018), the temporal resolution of the marine barite $\delta^{34}S$ record is unlikely to dramatically improve, especially during biogeochemical events characterized by low marine productivity (such as the Cretaceous-Paleogene boundary) or bottom-water anoxia (such as ocean anoxic events) that would have limited authigenic barite enrichment or preservation.

#### 3.2.3. CAS

Limestones and dolomites deposited continuously throughout Phanerozoic time, accumulating in marginal marine and open-ocean environments. A minor amount of sulfate is incorporated into biogenic and abiogenic carbonate phases. Biogenic carbonates often contain part-per-thousand sulfate by mass, while inorganic cements typically contain hundreds of parts-per-million (Barkan et al., 2020; Busenberg & Plummer, 1985; Giri & Swart, 2019; Paris, Fehrenbacher, et al., 2014; Staudt & Schoonen, 1995). Recent sediments from various peritidal carbonate platform environments include CAS with $\delta^{34}S$ values similar to modern seawater, which suggests that marine carbonate rocks may preserve sulfate and its $\delta^{34}S$ from ancient seawater (Lyons et al., 2004). CAS, therefore, complements and exceeds the temporal resolution and completeness of the evaporite and barite records (Strauss, 1997).

Diagenetic processes may exchange sulfate with the primary carbonate and alter its isotopic composition (Fichtner et al., 2017; Murray et al., 2020; Present et al., 2015, 2019). Kampschulte and Strauss (2004) suggested that the variability of multiple $\delta^{34}S$ analyses from contemporaneous stratigraphic successions could be used to quantify the effect of diagenesis on the CAS record. However, rapidly changing and disparate CAS $\delta^{34}S$ compositions have since been generated and interpreted—especially in Paleozoic studies—as intervals of heterogeneous seawater sulfate $\delta^{34}S$ reflecting periods of low sulfate concentrations and low marine sulfate residence times (e.g., Gill, Lyons, Young, et al., 2011; Kah et al., 2004). Much of this variability may reflect postdepositional effects, rather than primary heterogeneity in seawater sulfate $\delta^{34}S$ values (Present et al., 2015).

Limestones and dolomites are comprised of mud or grains that precipitated both biologically and abiotically from seawater, with cements binding them together. Each of these components may recrystallize in pore fluids whose chemical composition reflects marine, meteoric, and burial diagenetic processes. A combustion CAS analysis typically requires 10 g to 100 g of carbonate (Wotte et al., 2012), and this mass requirement dictates that samples mix components that may have precipitated and/or recrystallized at different times. Further, CAS analyses may be contaminated by sulfur from co-occurring phases, including sulfide and disulfide minerals, sulfur-bearing organic material, and sulfate salts (Edwards et al., 2019; Marenco, Corsetti, Hammond, et al., 2008; Present et al., 2015; Theiling & Coleman, 2015; Wotte et al., 2012). Recent application of plasma-source mass spectrometry for sulfur isotope analysis has permitted $\delta^{34}S$ analyses on less than one thousandth as much sulfate, corresponding to 5 to 50 mg of carbonate (Paris, Adkins, et al., 2014; Paris et al., 2013; Present et al., 2015, 2019; Rennie et al., 2018). Well-preserved biogenic grains, recrystallized grains, matrix, and cements contain CAS with $\delta^{34}S$ compositions varying by as much as 25‰, spanning most of the range of CAS analyses from the entire Phanerozoic (Present et al., 2015, 2019). Therefore, much of the variability of CAS $\delta^{34}S$ data may not reflect the $\delta^{34}S$ composition of ancient seawater sulfate. Identifying components that retain the $\delta^{34}S$ of sulfate incorporated from syndepositional seawater is critical to exploit the CAS $\delta^{34}S$ archive precisely and accurately.

CAS can reflect the $\delta^{34}S$ value of syndepositional seawater sulfate if the carbonate component did not recrystallize after precipitation, if recrystallization and cementation occurred in contact with a low-sulfate fluid, or if the $\delta^{34}S$ value of pore fluid sulfate was not fractionated from seawater (Gill et al., 2008; Lyons et al., 2004; Rennie & Turchyn, 2014). Alteration occurs if the sediments recrystallize above the depth at which sulfate is completely consumed by MSR but deep enough that some distillation of sulfur isotopes within sediment pore fluid has occurred (Edwards et al., 2019; Fike et al., 2015; Present et al., 2019; Rennie & Turchyn, 2014; Witts et al., 2018). Additionally, some ancient carbonates contain CAS with anomalously low $\delta^{34}S$ values interpreted to result from the incorporation of sulfate from sulfide that was reoxidized during diagenesis or weathering (Baldermann et al., 2015; Edwards et al., 2019; Fichtner et al., 2017; Fike et al., 2015; Marenco, Corsetti, Kaufman, et al., 2008; Present et al., 2015, 2019; Rennie & Turchyn, 2014; Riccardi et al., 2006; Yan et al., 2013). Carbonates recrystallizing during burial may also be prone to diagenetic modification of the $\delta^{34}S$ value of CAS if the burial fluids were sulfate rich (Fichtner et al., 2017, 2018; Present et al., 2015). Burial fluids may have highly variable $\delta^{34}S$ values and include sulfate from hydrocarbon or organic matter degradation, dissolved evaporites, groundwater modified by MSR, or sulfate released by dissolution of CAS (Dogramaci et al., 2001; Fichtner et al., 2018; Murray et al., 2020; Present et al., 2019; Thode & Monster, 1965, 1970).

These diagenetic controls on the $\delta^{34}S$ values of CAS decrease the precision and accuracy of the proxy. This is quantified by its uncorrelated variance, which is much higher than that observed in other seawater sulfate $\delta^{34}S$ proxies. Uncorrelated Paleozoic CAS data has a standard deviation of 5.0‰, and that of Mesozoic CAS is 4.4‰, which is 5 to 10 times larger than that of Paleozoic and Mesozoic evaporites (1.0‰ and 0.4‰, respectively). Further, diagenesis may have impacted accuracy by systematically biasing the $\delta^{34}S$ values of CAS with respect to the primary composition of seawater sulfate. For example, base level often controls the stratigraphic arrangement of facies in carbonates successions, which can impart biases as large as 10‰ on the $\delta^{34}S$ of CAS (Present et al., 2019; J. A. Richardson, Keating, et al., 2019). Both the random and systematic variability is on the order of well-resolved rapid changes of 3‰ to 6‰ in the $\delta^{34}S$ values of marine barite and biogenic CAS.

#### 3.2.4. Biogenic CAS

Biogenic CAS may offer a more robust $\delta^{34}S$ record than bulk CAS because biogenic carbonate can often be readily separated from other limestone components, preservation quality can be assessed, and vital effects appear to be small in most taxa (Kampschulte et al., 2001; Paris, Fehrenbacher, et al., 2014; Present et al., 2015). In modern and cultured biogenic carbonates, the incorporated sulfate has an isotopic composition within 2‰ of the seawater from which it precipitated (Burdett et al., 1989; Kampschulte et al., 2001; Kaplan et al., 1963; Mekhtiyeva, 1974; Paris et al., 2013; Paris, Fehrenbacher, et al., 2014; Present et al., 2015). Recently, Rennie et al. (2018) produced a taxon-specific foraminiferal CAS record with variance and secular trends comparable to the marine barite record.

Low-magnesium calcite, precipitated by many brachiopods, belemnites, and planktonic foraminifera, is stable at Earth's surface and shallow burial conditions. The low-magnesium calcite biogenic CAS $\delta^{34}S$ record has significantly improved the resolution of the Phanerozoic $\delta^{34}S$ record during two key periods. First, during the Toarcian (Jurassic) Ocean Anoxic Event, belemnite CAS displays a large (6‰) $\delta^{34}S$ excursion that is not well resolved in the evaporite record (Gill, Lyons, & Jenkyns, 2011; Newton et al., 2011). Second, during Carboniferous time, brachiopods record a prolonged recovery from a $\delta^{34}S$ maximum in middle Devonian time (D. L. Johnson et al., 2020; Kampschulte et al., 2001; N. Wu et al., 2014). However, aragonite and high-magnesium calcite, precipitated by many bivalves, gastropods, corals, trilobites, echinoderms, bryozoans, and marine algae, dissolves and/or recrystallizes much more readily than low-magnesium calcite (Brand & Veizer, 1980). Few studies have investigated CAS $\delta^{34}S$ values of formerly aragonitic fossils (Mekhtiyeva, 1974; Present et al., 2015; Witts et al., 2018).

Unfortunately, well-preserved biogenic carbonate is rare in the rock record, especially during intervals of climatic or biologic crisis (e.g., mass extinction events). Even apparently well-preserved biogenic carbonate can still be susceptible to diagenetic alteration (Fichtner et al., 2018; Witts et al., 2018). Like the marine barite record, a significant expansion of the biogenic CAS $\delta^{34}S$ proxy record is limited by the availability of suitable sample material.

### 3.3. Discrepant Early Phanerozoic Proxy Records

While all archives imperfectly estimate ancient seawater's composition, they provide generally indistinguishable estimates considering the sources of uncertainty discussed (Figure 2a). Paleozoic bulk rock CAS data, as a notable exception, commonly exhibit rapid $\delta^{34}S$ variability (Figure 1b), but other archives with less uncorrelated variance are absent or lack temporal resolution (Figure 1a). Throughout Phanerozoic strata, CAS data consistently display more uncorrelated variance than other archives, yet they record the same long-term trends (Figure 2), suggesting that some $\delta^{34}S$ excursions recorded by CAS may not represent changes in the composition of the ocean. The high uncorrelated variance in early Paleozoic bulk CAS may mask $\delta^{34}S$ excursions on the order of those well-resolved in younger strata by all archives. Variability in early Paleozoic CAS data may represent short residence times of sulfate in sulfidic oceans (e.g., Gill, Lyons, Young, et al., 2011; Kah et al., 2016), local diagenetic effects on the $\delta^{34}S$ of carbonate rocks (Present et al., 2015, 2019; J. A. Richardson, Keating, et al., 2019; J. A. Richardson, Newville, et al., 2019), or both (Edwards et al., 2019; Rose et al., 2019).

CAS $\delta^{34}S$ excursions often correlate with global perturbations evidenced by carbon isotope excursions and trace metal, pyrite sulfur isotope, and bioturbation intensity records (Canfield & Farquhar, 2009; Fike et al., 2015; Gill et al., 2007; Jones & Fike, 2013; Kah et al., 2016; Saltzman et al., 2015). Perhaps some CAS $\delta^{34}S$ excursions reflect widespread biogeochemical changes at the interface between pore fluid sulfur cycling and carbonate sediment diagenesis, including sulfate, dioxygen, and nutrient availability, organic productivity, or metabolic or oceanographic changes in carbonate mineral saturation (Rennie & Turchyn, 2014). Because part of the $\delta^{34}S$ variance in all archives derives from early diagenetic processes—such as MSR, pyrite formation, and sulfide reoxidation—consideration of these processes may reveal important temporal changes in carbon cycling in marine pore fluids (Present et al., 2019; J. A. Richardson, Keating, et al., 2019; N. Wu et al., 2010).

## 4. Conclusions

Phanerozoic $\delta^{34}S$ data were compiled from evaporites, barite, biogenic CAS, and bulk rock CAS and updated to a consistent timescale. The subset of seawater sulfate's $\delta^{34}S$ history possibly sampled by each proxy varied in space and time, and different suites of depositional and postdepositional processes added variance to each archive. The variance in each record increases with age, but the changing contribution of primary and secondary sources of variability over Phanerozoic time remains unclear.

Bulk CAS contains a statistically significant different distribution of $\delta^{34}S$ compositions than the biogenic CAS, evaporite, or barite records. Early diagenetic overprinting of CAS occurs in depositional environments where carbonate recrystallization and cementation coincides with sulfate-rich pore fluids with modified $\delta^{34}S$ values. Despite these complications, bulk CAS can be widely applied in ancient sedimentary basins and is the only archive readily able to resolve sulfur cycle changes during rapid biogeochemical events. Extending the breadth and resolution of the $\delta^{34}S$ record requires developing mechanistic understanding of how biogeochemical perturbations affect the marine diagenesis of carbonate rocks.

## Data Availability Statement

No new data were collected for this study. Data sets compiled for this research are tabulated in the supporting information and referenced below, and the compiled data are deposited in a freely accessible Open Science Framework repository available in Present et al. (2020).

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