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merged continental area) yield results that are consistent both internally and with existing observations of seawater sulfate concentration and $\delta^{34}\text{S}$. Large and stable pyrite weathering and burial fluxes highlight the importance of oxidation-reduction feedbacks between carbon, iron, and sulfur (24) and imply a greater role for the sulfur cycle in regulating Phanerozoic atmospheric oxygen.

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Supplementary Materials

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Rapid Variability of Seawater Chemistry over the Past 130 Million Years

Ulrich G. Wortmann^{1*} and Adina Paytan^{2*}

Fluid inclusion data suggest that the composition of major elements in seawater changes slowly over geological time scales. This view contrasts with high-resolution isotope data that imply more rapid fluctuations of seawater chemistry. We used a non-steady-state box model of the global sulfur cycle to show that the global $\delta^{34}\text{S}$ record can be explained by variable marine sulfate concentrations triggered by basin-scale evaporite precipitation and dissolution. The record is characterized by long phases of stasis, punctuated by short intervals of rapid change. Sulfate concentrations affect several important biological processes, including carbonate mineralogy, microbially mediated organic matter remineralization, sedimentary phosphorous regeneration, nitrogen fixation, and sulfate aerosol formation. These changes are likely to affect ocean productivity, the global carbon cycle, and climate.

The chemical composition and mineralogy of skeletal limestones and biogenic carbonates vary systematically through time, indicating that the Mg/Ca ratio as well as other constituents of seawater have also changed (1). Fluid inclusion studies are also consistent with variable magnesium, calcium, sodium, and sulfate concentrations through time (2, 3). Several hypotheses have been proposed to explain these secular trends, including changes in global weathering patterns (4), sea-floor spreading rates (5), or burial rates of these elements (6).

Evaporites play an important role in the latter process because their precipitation/dissolution rates exceed those of other sediments by three orders of magnitude (7, 8). Halite is the dominant evaporite phase, but the effect of halite precipitation/dissolution on seawater chemistry is limited because the marine Na^+ and Cl^- reservoirs are large ($\approx 6.47 \times 10^{20}$ and 7.5×10^{20} mol respectively). Sulfur-bearing evaporites (such as CaSO_4) comprise on average 20% of an evaporite sequence (9) but have a 20 times smaller marine reservoir size than that of Cl^- .

The role of sulfur-bearing salts in controlling seawater chemistry is often overlooked. In the modern ocean, pyrite burial is not limited by sulfate availability (10), and the strong link between pyrite burial rates and sulfate concentration has just recently been recognized (11). Furthermore, basin-scale evaporites (BSEs) occur only

sporadically in the geologic record and are not always visible, and the chemical composition of seawater does not depend on the mass of existing evaporites (Fig. 1A) but on the amount of salts that have already been eroded (Fig. 1B) and/or were originally extracted (Fig. 1C). The past 130 million years saw only two BSE events (Fig. 1C): one caused by the desiccation of the Mediterranean during the Messinian (12), and the second related to the Early Cretaceous opening of the South Atlantic (11, 12).

Until recently, all available data supported the assumption of slow secular changes to major seawater constituents and their related biogeochemical fluxes. However, as the temporal resolution of proxy data increases, it becomes evident that the rate of change is often faster than expected from the residence time of major species.

High-resolution data sets of seawater $\delta^{34}\text{S}$ record two major events, at 130 to 120 million years ago (Ma) and 55 to 45 Ma, that require large changes to the S-fluxes and/or their isotopic composition. Previous interpretations of the $\delta^{34}\text{S}$ record called for changes in the planetary degassing flux and/or S burial rates (6). Clearly, volcanic activity and pyrite burial are major parameters, but we propose to broaden the discourse by including the effects of evaporite precipitation and dissolution. If these processes occur on a basin-wide scale, they will modify the flux and $\delta^{34}\text{S}$ of the sulfur input/output and change the marine sulfate concentration, which in turn affects pyrite burial in a nonlinear way (11), further affecting seawater isotopic composition. Under modern conditions, this effect is negligible. However, with decreasing sulfate concentrations, the importance of sulfate availability increases until it becomes the dominant parameter controlling pyrite burial (11).

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Here, we evaluate the effect of basin-scale precipitation/dissolution events, consider the evidence for such a scenario, and discuss alternative explanations for the existing data.

We used a non-steady-state box model of the global S-cycle to investigate how precipitation/dissolution events affect the weathering fluxes of ^{32}S , ^{34}S , and the sulfate concentration of the ocean, which in turn controls the burial fluxes of ^{32}S and ^{34}S (13). Our model demonstrates that we can match the first-order shape of the marine $\delta^{34}\text{S}$ record (Fig. 2) with two events: the deposition of a BSE between 122 and 120 Ma and the dissolution of a BSE between 51 and 47 Ma (1.02×10^{19} mol and 1.97×10^{19} mol CaSO_4 , respectively) (fig. S2), which are well within existing estimates of known BSE deposits (Fig. 1).

The timing and magnitude of the evaporite sequences in the South Atlantic are well documented (14, 15), and the decrease in seawater sulfate concentration is supported by geochemical data that suggest decoupling between iron and sulfur burial during the Early Aptian (11). BSEs affecting seawater $\delta^{34}\text{S}$ at this time is consistent with multiple lines of evidence, although increased volcanic activity also may have contributed to the trend (16, 17).

For an Eocene dissolution event, much of the direct evidence has been literally dissolved; however, large swaths of the Paleotethys margins are lined with massive evaporite deposits of latest Neoproterozoic to Early Cambrian (LNPEC) age, likely formed during the breakup of Rodinia and/or Pannotia. The known outcrops stretch

from Oman to Iran, to Afghanistan, to Pakistan, and into western India (9). This area is the most extensive evaporite belt on Earth and contains large amounts of sulfate (9), the erosion of which could explain the Eocene event.

However, evaporite erosion is usually treated as a continuous process—an assumption that is problematic because the long-term preservation of salt requires burial below the regolith-forming zone, and reactivation does not occur before renewed exhumation. More specifically, studies on modern dissolution processes suggest that the highest dissolution rates are achieved if evaporites act as aquifer with an active flow regime (18). Accordingly, the reactivation of old evaporites requires gentle tilting, sufficient precipitation, and efficient drainage. It is unlikely that such conditions persist over geological time scales in convergent margin settings. Therefore, the BSE deposits presently found along the Paleotethys margin probably experienced a window of drastically increased weathering rates during the initial phases of the India Eurasia collision, which occurred between 53.7 to 50.6 Ma (19, 20). These ages are in agreement with the age range predicted by our model for evaporite dissolution and input into the ocean (51 to 47 Ma). If we accept the idea of BSE dissolution/precipitation events, this implies that marine sulfate concentrations changed considerably during the Early Cretaceous and the Early Eocene. The predicted sulfate concentrations are within the range of values derived from fluid inclusion studies (Fig. 2). Furthermore, the increased number of Eocene formations

that contain gas-hydrate-related seep carbonates can be explained by the sudden availability of sulfate—a prerequisite for anaerobic methane oxidation and the subsequent precipitation of seep carbonates.

A prior model to explain the rapid Eocene 5 per mil (‰) raise in seawater $\delta^{34}\text{S}$ proposed that global pyrite burial rates increased four-fold as a result of euxinic conditions in the wake of the Eocene sea-level rise (6). The sedimentary evidence for increased pyrite burial is, however, controversial (21).

If the formation and dissolution of large-scale evaporite deposits is episodic as we suggest, this has several important consequences. Specifically, the salinity estimates (12) for much of the Phanerozoic have to be revised because large amounts of the LNPEC evaporites remained stored until the Eocene collision of India and Eurasia, and we need to recognize that the major ion composition of seawater varies considerably faster than previously thought. In addition, the dissolution and precipitation of large evaporite sequences affects the distribution of coprecipitating elements (such as strontium) and exerts a major control on the skeletal chemistry of calcifying organisms, possibly controlling the transition from calcite to aragonite seas (22). Furthermore, low sulfate concentrations imply reduced rates of organic matter remineralization, which affects the bioavailability of phosphorus, whereas sulfate concentrations above 8 mM may inhibit nitrogen fixation (23). Accordingly, variable sulfate concentrations are likely to modulate

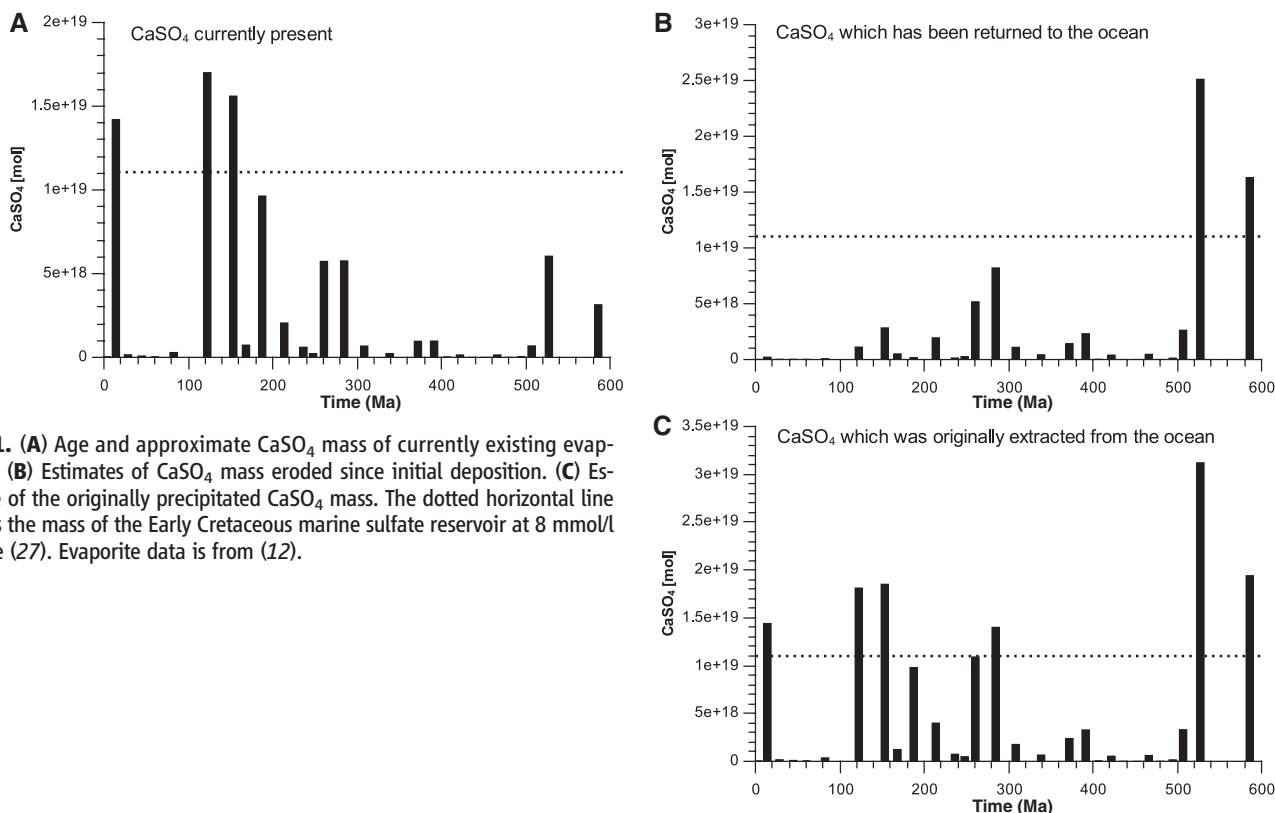


Fig. 1. (A) Age and approximate CaSO_4 mass of currently existing evaporites. (B) Estimates of CaSO_4 mass eroded since initial deposition. (C) Estimate of the originally precipitated CaSO_4 mass. The dotted horizontal line equals the mass of the Early Cretaceous marine sulfate reservoir at 8 mmol/l sulfate (27). Evaporite data is from (12).

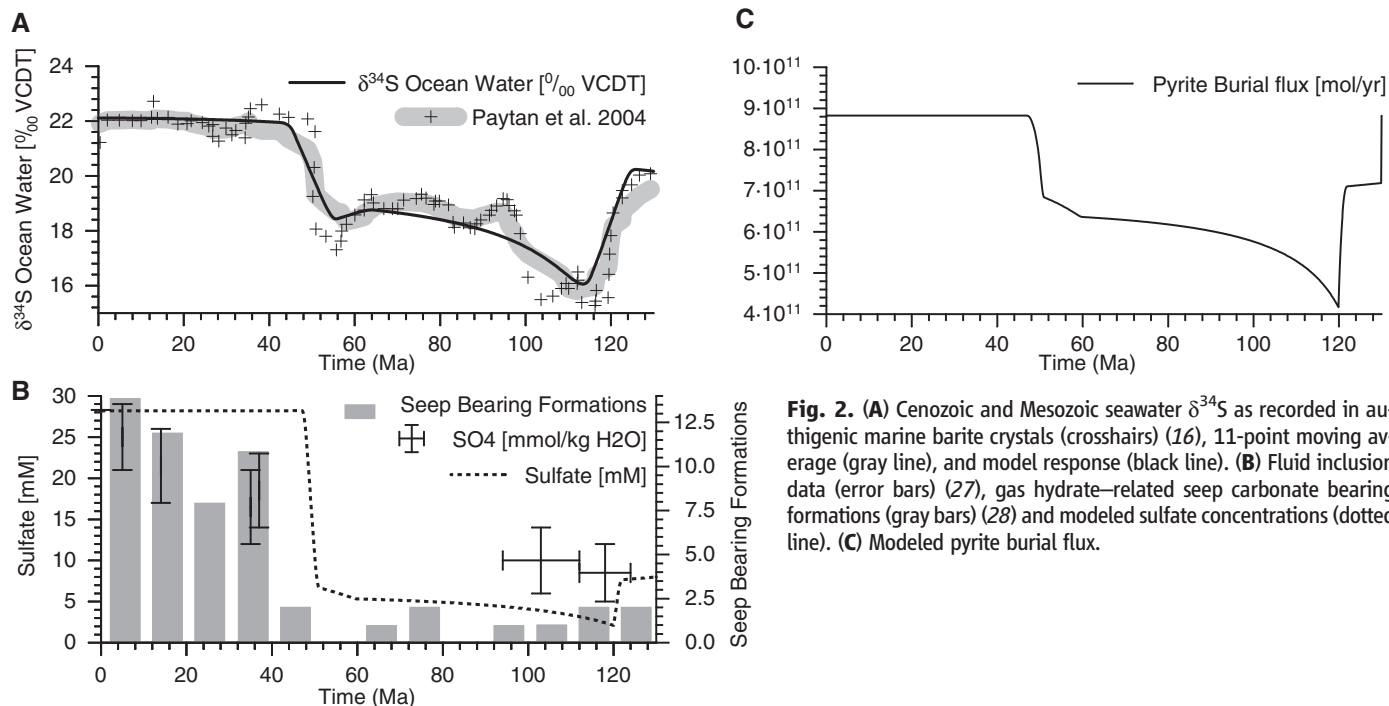


Fig. 2. (A) Cenozoic and Mesozoic seawater $\delta^{34}\text{S}$ as recorded in authigenic marine barite crystals (crosshairs) (16), 11-point moving average (gray line), and model response (black line). (B) Fluid inclusion data (error bars) (27), gas hydrate-related seep carbonate bearing formations (gray bars) (28) and modeled sulfate concentrations (dotted line). (C) Modeled pyrite burial flux.

long-term trends in marine ecology and ocean fertility (24). Indeed, the low sulfate concentration throughout the Mesozoic (11) may have been the very condition that enabled widespread episodes of black-shale formation (25) and probably resulted in higher methane fluxes across the benthic boundary layer (11). Moreover, because the ocean is a major source for sulfate aerosols, lower marine sulfate concentrations could have affected atmospheric aerosol chemistry, as well (26). Thus, times of high sulfate concentrations correlate with an increased aerosol load and global cooling, whereas times of low marine sulfate concentrations correspond with greenhouse periods. Specifically, the rapid rise of the marine sulfate concentrations during the Early Eocene probably increased the aerosol load in the atmosphere, which may have contributed to the demise of the Eocene Climatic Optimum and the onset of the long-term Cenozoic cooling trend.

Much remains to be learned about the contribution of BSEs to the evolution of ocean chemistry. It is evident, however, that the sheer size of these deposits as well as their dissolution/precipitation kinetics must have affected marine sulfate concentrations and thus the biogeochemical cycling of carbon, oxygen, and phosphorus. Most importantly, the assumption of slow secular seawater chemistry changes is neither necessary nor likely. Rather, sulfate concentrations remained stable over long periods of time but changed rapidly when continental breakup or collision events resulted in the creation or destruction of BSE deposits. This provides an explanation of the existing seawater S-isotope data, as well as exciting linkages between sulfur

and other biogeochemical cycles, long-term trends in evolution, ocean fertility, and climate. Although this study focuses on the past 130 million years, similar interactions have likely occurred throughout the Phanerozoic.

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