Significant Fluctuation in the Global Sulfate Reservoir and Oceanic Redox State During the Late Devonian Mass Extinction

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Abstract

Sulfate plays an important role in the biosphere, hydrosphere, atmosphere, and lithosphere, and its concentration might have fluctuated greatly throughout the Earth's history, in response to perturbations in the ocean-atmosphere system. Coupling high-resolution experimental results with an inverse modeling approach, we, here, show an unprecedented dynamic in the global sulfate reservoir during the Frasnian-Famennian (F-F) mass extinction, as one of the "Big five" Phanerozoic biotic crises. Notably, our results indicate that, in a relatively short time scale (~ 200 thousand years), seawater sulfate concentration would have dropped from several mM before the Upper Kellwasser Horizon (UKH) to a few hundreds of μM or perhaps lower at the dawn and during the UKH (more than 100 times lower than the modern level), and returned to around mM range after the event. The extremely low oceanic sulfate concentrations during the UKH would have enhanced the biological production of methane, leading to an increase in the methane efflux from the ocean and a warmer climate. Taken together, our findings indicate that the instability in the global sulfate reservoir may have played a major role in driving the Phanerozoic biological crises.

Introduction

Sulfate (SO_4^{2-}) as the second-most abundant anion after chloride in the modern ocean plays a crucial role in biogeochemical cycles of major elements (e.g., carbon, oxygen, phosphorous, and iron). Despite its overwhelmingly high modern concentration, oceanic sulfate level is widely viewed to have substantially varied throughout the Earth's history¹⁻², with sub mM range for most of the first 3.5 billion years and several to tens of mM for most of the Phanerozoic Eon (<0.5 billion years ago). Such change in seawater sulfate is conveniently linked to change in the redox state of the ocean-atmosphere system. Specifically, by promoting microbial sulfate reduction, predominantly anoxic iron-rich conditions throughout most of the Precambrian (>0.5 billion years ago) would have impeded the accumulation of seawater sulfate to high levels, whereas oxygenated Phanerozoic oceans would have allowed the first significant ingrowth in seawater sulfate pool¹. Notable exceptions for oxygenated oceans during the Phanerozoic, however, come during the oceanic anoxic events (OAEs), where pervasive anoxia in the oceans would have led to a rapid decrease in the biodiversity of Earth, broadly referred to as extinction events³⁻⁴. In concurrence with low oxygen availability, the concentration of seawater sulfate during the mass extinction events is considered to have been low as well³⁻⁴. The precise quantification of such dynamic in oceanic sulfate level remains, however, uncertain, resulting in an incomplete understanding of the link between large-scale perturbation in the Earth system and chemistry of the ocean during the mass extinction events.

The Late Devonian Frasnian–Famennian (F–F) biotic crisis – one of the "Big five" Phanerozoic mass extinction events, wiped out almost 80% of extant marine invertebrate species, especially low latitude shallow-water faunas, and metazoan reefs⁵, or 16 to 20% of genera⁶. The cause of the extinction is debated, but it has been attributed to changes in climatic dynamics⁷⁻⁹, oceanic anoxia^{4,10}, eutrophication, and/or volcanic/hydrothermal activity¹¹. While there is a relative consensus on the presence of ocean

anoxia during the event, the nature of anoxia is not well constrained, in part, due to the lack of high-resolution geochemical data. Generally, the anoxic condition can be categorized into ferruginous (iron-rich) or euxinic (sulfide-rich) condition, with important implications on nutrient cycling and global cycling of bio-essential elements. For instance, while euxinic conditions hamper the recycling of trace metal micronutrients, it promotes the recycling of phosphorus – as a major limiting factor on oceanic primary productivity. Oppositely, trace metal may not be as efficiently removed under ferruginous conditions, but recycling of phosphorus may be less efficient, owing to the strong association of P with Fe minerals¹². An accurate reconstruction of the redox state of oceans during the Frasnian–Famennian boundary (FFB) is thus a crucial step toward understanding the cause(s) of the F-F mass extinction.

Herein, we couple high-resolution experimental data with an inverse modeling approach to offer a more detailed picture of the change in oceanic chemistry during the event, and use that knowledge to quantify the dynamic in seawater sulfate concentration during the Frasnian–Famennian (F–F) extinction event. We show an unprecedented fluctuation in the ocean chemistry as well as the global sulfate reservoir within several hundred thousand years with substantial impacts on global biogeochemical cycles of elements, marine biology as well as the climate.

To reconstruct the oceanic redox-state during the F-F mass extinction, we recruit a combined experimental and modeling approach. A well-exposed Xikuangshan section (Fig. S1) was chosen for this study and has been systematically studied for biostratigraphy, sedimentology, and chemostratigraphy^{13,14} with a positive excursion in $\delta^{13}\text{C}_{\text{org}}$ of $\sim 2\text{‰}$ across the FFB (Fig. 1). We first conducted a high-resolution analysis of iron speciation on a suite of sedimentary rocks, Hunan Province, South China wherein the ratios of different iron pools (e.g., pyrite, highly reactive, and total iron) were quantified in order to distinguish between anoxic iron-rich and anoxic sulfide-rich condition. We further performed sulfur speciation analysis to quantify each pool of sulfur with different oxidation states as well as measured the isotopic composition of each sulfur pool. The detail of the geological background along with the experimental methods is discussed in the supplement.

The experimental data were, then, used to quantify the seawater sulfate concentration during the Late Devonian mass extinction event. Taking an inverse modeling approach, our model is based on a well-established mass balance framework for sulfate isotope where the concentration of seawater sulfate through time is controlled by riverine flux of sulfate (J_{in}) and its composition value (δ_{in}), the flux of reduced sulfur as pyrite (J_{py}), the isotopic difference between seawater sulfate and pyrite (Δ), and flux of sulfate evaporites (J_{ev}) and its isotopic composition (δ):

$$\frac{d[\text{SO}_4]\delta}{dt} = J_{\text{in}}\delta_{\text{in}} - J_{\text{ev}}\delta - J_{\text{py}}(\delta - \Delta)$$

The flux of pyrite (J_{py}) was parameterized so that it varies with seawater sulfate concentration (Fig. S2). The values of $d\delta/dt$, δ , and Δ and in the model were taken from our measurements. We also used

measurements from other parts of the world to provide a more global-scale range for oceanic sulfate concentration (Table S3). Finally, to account for the uncertainty involved with choosing model parameters, we employed a stochastic approach, in which, instead of using fixed values, the modeling input parameters were randomly sampled within their most reasonable ranges, assuming a uniform distribution, and the most probable range of seawater sulfate concentration during the Upper Kellwasser Horizon (UKH) were obtained (Fig. S2).

Results

Almost all the samples in this study have total Fe (Fe_T) > 0.5 wt% (Table S1), thus iron speciation can be used to reflect ocean redox conditions in this carbonate-rich section by considering the fractional abundance of Fe in highly reactive Fe (Fe_{HR}) and pyrite Fe (Fe_{Py})¹⁵. In most modern and ancient sediments deposited beneath anoxic bottom waters, Fe_{HR}/Fe_T exceeds 0.38, but this threshold value can be reduced to 0.15 for thermally altered ancient sedimentary rocks¹⁶. For a euxinic water column, Fe_{Py}/Fe_{HR} in the underlying sediments usually exceeds 0.8. Fe_{HR}/Fe_T ratios are < 0.38 prior to the L6 deposition (Fig. 2A). They rise sharply from a minimum of 0.11 in L5 to a maximum of 0.88 in L6, followed by a decrease to 0.54 in L9a. This changing trend resembles that of Fe_{Py}/Fe_{HR} (Fig. 2B), which increases from 0.03 in L5 to 0.83 in L6, and then decreases to 0.11 in L9a. The Fe_{HR}/Fe_T ratios of L9b and the lower part of L10 are < 0.38 and are > 0.38 at the top of the section. Thus, based on the iron speciation, the sediments across the FFB are further divided into intervals (I, IIa, IIb and III, Fig. 2A & B). Interval I sediments have Fe_{HR}/Fe_T < 0.38 and low Fe_{Py}/Fe_{HR} , interval II has Fe_{HR}/Fe_T > 0.38 and can be further divided into interval IIa with Fe_{Py}/Fe_{HR} > 0.7 and interval IIb with Fe_{Py}/Fe_{HR} from 0.25 to 0.58, and interval III has Fe_{HR}/Fe_T < 0.38 and significantly lower Fe_{Py}/Fe_{HR} ratios from 0.07 to 0.22..

Isotopic compositions of sulfur species show wide ranges from - 9.3‰ to + 15.4‰ for organic sulfur ($\delta^{34}S_{Kero}$), + 7.1‰ to + 26.2‰ for carbonate-associate sulfate ($\delta^{34}S_{CAS}$), and - 15.2‰ to + 22.0‰ for pyrite ($\delta^{34}S_{Py}$). Within the section, there are three dramatic transitions (A, B, and C) (Fig. 2C). Samples from L5 (interval I) show synchronous positive shifts in the $\delta^{34}S$ value of the three sulfur species and a gradual decrease in $\Delta^{34}S_{CAS-Py}$ value (Fig. 2D). Both $\delta^{34}S_{Kero}$ and $\delta^{34}S_{Py}$ show an abrupt decrease from 15.7‰ to -9.3‰ and from 2.3‰ to -11.4‰, respectively, at transition A across the L5-L6 boundary. Interestingly, $\Delta^{34}S_{Kero-Py}$ shows a correspondingly sharp fall from 13.3‰ to 2.0‰ (Fig. 2D). At transition B in the interval IIa, $\delta^{34}S_{Kero}$ and $\Delta^{34}S_{Kero-Py}$ show coupled positive shifts alongside a decrease in $\delta^{34}S_{Py}$. Further upwards within interval IIb, $\delta^{34}S_{Kero}$, $\delta^{34}S_{Py}$, and $\Delta^{34}S_{Kero-Py}$ show increasing trends, and $\delta^{34}S_{CAS}$ shows a decrease towards the FFB. Across the FFB, there is a dramatic positive excursion of $\delta^{34}S_{Py}$ with a magnitude of 32.3‰ in this study (Fig. 2C). Similar negative shifts in $\delta^{34}S_{CAS}$ and positive shifts in $\delta^{34}S_{Py}$ leading up to the FFB followed by dramatic positive shifts after the FFB occur at sections in the Poland¹⁷⁻¹⁸, Belgium¹⁹, and the Great basin, USA⁴ (Fig. S3), suggesting that this sulfur isotope trend is a global signal, although the magnitudes are different - partially due to the different sample

resolutions. Within interval III, which follows transition C at the FFB, $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{Py}}$ show fluctuations and a decoupled changing trend while $\delta^{34}\text{S}_{\text{Kero}}$ keeps relatively stable.

Discussion

A substantial variation in the oceanic redox state

Our experimental results point toward a substantial variation in the oceanic chemistry in the Late Devonian mass extinction, UKH. More precisely, the results from iron speciation indicate a switch from a pervasively oxic condition with $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ of < 0.38 before the event to extensive anoxia during the event ($\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} > 0.38$) (Fig. 2A). While pervasive anoxia during the event has been reported by previous studies^{17–21}, our analysis shows a substantial change in the nature of anoxia. Explicitly, the beginning of the events is marked with a widespread sulfide-rich condition, as indicated by $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ value of 0.88 and a FePy/FeHR ratio of 0.83 in L6 in interval IIa (Fig. 2A & B), consistent with the biological crisis at this time^{8,22}. The euxinic condition at the beginning of the UKH is in line with the results from the isotope composition of sulfur species as well. Generally, the isotopic difference between organic sulfur (kerogen) and pyrite ($\Delta^{34}\text{S}_{\text{kero-Py}} = \delta^{34}\text{S}_{\text{Kero}} - \delta^{34}\text{S}_{\text{Py}}$) can be used to assess the availability of sulfide pool, with smaller difference associated with the sulfidic condition, owing to the concurrent formation of pyrite and organic sulfur under sulfide-rich condition²³. Comparably, larger values mirror a decrease in sulfide availability and formation of pyrite and organic sulfur at different depths²³. In line with the iron speciation results, the near-zero value of $\Delta^{34}\text{S}_{\text{kero-Py}}$ at the beginning of the UKH provides further support for the pervasive sulfidic condition in the ocean at this time. Such euxinic conditions were, however, ephemeral and replaced by large-scale ferruginous conditions, as shown by $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ratios between 0.38 and 0.7 in interval IIb (Fig. 2A). This is consistent with the high values of $\Delta^{34}\text{S}_{\text{kero-Py}}$ during this interval which indicates that pyrite and organic sulfur formed under sulfide-limited conditions. This anoxic ferruginous bottom water at the end of L9a was changed to the oxic as indicated by the decrease in $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ratio from 0.52 to 0.23, signaling an enhancement in the oceanic oxygen availability, and thus paving the road for the biological recovery in the aftermath of the event. As suggested by the results from iron speciation on the top of the section, this oxygenated condition was again replaced by anoxic ferruginous condition, indicating a highly variable oceanic redox state during and after the UKH.

Large dynamic in the seawater sulfate level

Our results from isotope-driven modeling reveal a great fluctuation in the global sulfur reservoir during the UKH. Notably, our modeling results that are informed by our measurements presented herein, indicate a significant contraction and expansion in the global sulfate reservoir (Fig. 3). More precisely, based on our results, the concentration of seawater sulfate would have fallen from several mM before the event to several hundred μM at the beginning and during the event (about two orders of magnitude decrease) and returned to mM range after the event in a relatively short geological timescale (~ 200 thousand years; Fig. 3). The transition from high sulfate to extremely low sulfate condition at the beginning of the event

would have considerably elevated the sulfide concentration in the ocean, leading to the biological wipeout, which is also consistent with our Fe speciation results. While the modeled seawater sulfate concentration before the UKH is in line with the suggested range of seawater sulfate (~ 11 mM) in the Late Devonian from fluid inclusion data^{24–25}, our results indicate a much lower sulfate concentration caused by anoxia during the event.

The modeling results are intimately tied with the change in the measured isotopic composition of pyrite ($\delta^{34}\text{S}_{\text{Py}}$) and isotopic difference between pyrite and water column sulfate ($\Delta^{34}\text{S}_{\text{CAS-Py}} = \delta^{34}\text{S}_{\text{CAS}} - \delta^{34}\text{S}_{\text{Py}}$). Mechanistically, due to the Rayleigh distillation effect, limited supply of sulfate from overlying water (low-sulfate condition) leads to an isotopically semi-closed system wherein isotopic composition of precipitant pyrite become more positive (enriched in ^{34}S) and approaches to the isotopic composition of source sulfate, resulting in a small isotopic difference between pyrite and water column sulfate ($\Delta^{34}\text{S}_{\text{CAS-Py}} = \delta^{34}\text{S}_{\text{CAS}} - \delta^{34}\text{S}_{\text{Py}}$)^{26,27,2}. Building upon this framework, the decrease in the measured $\Delta^{34}\text{S}_{\text{CAS-Py}}$ values at the dawn and the terminal of the event are then suggestive of a contraction in the seawater sulfate pool. The decreasing trend in the measured $\Delta^{34}\text{S}_{\text{CAS-Py}}$ at the Frasnian–Famennian boundary has also been reported from other sections worldwide (e.g., the Great Basin, USA, and Kowala Poalnd)^{20,4,18}, implying a global dynamic in the global sulfate reservoir during this time (Fig. S3).

Our results do not confirm the causal link between the fluctuation in the eustatic sea-level and the pervasive anoxic low-sulfate condition during the UKH. One of the main environmental features in the Late Devonian is the evidence of a large fluctuation in the sea level, with a substantial fall and rise at the Frasnian–Famennian boundary^{22,20}. By influencing the sedimentation rate and the input flux of nutrient into the ocean, change in sea-level is believed to have modulated the extent of anoxia in the ocean, whereby changing the seawater sulfate level^{28,29}. For instance, an increase in the sea-level is considered to elevate the nutrient input into the continental shelves, resulting in higher oxygen consumptions and more anoxia. This, in turn, could lead to an enhancement in the rate of sulfate drawdown through organoclastic sulfate reduction, resulting in an overall lower seawater sulfate level²⁹. However, our results for an increase in the isotopic composition of pyrite ($\delta^{34}\text{S}_{\text{Py}}$) and decrease in the $\Delta^{34}\text{S}_{\text{CAS-Py}}$ during the UKH that temporally co-occurs with the low sea-level condition is not consistent with this paradigm, suggesting a minor, if any, role for the sea-level fluctuation on oceanic sulfur cycle. The observed trend in the measured isotopic composition may have, instead, been the result of low-sulfate condition and or re-oxidation of sulfide^{20,30}. Specifically, in the low-sulfate seawaters, the sulfate produced by abiotic oxidation of parent H_2S is depleted in ^{34}S by 4 – 5‰, which leads to the ^{34}S enrichment in sulfide compare to sulfate, owing to Rayleigh distillation effect^{20,30}. However, the fraction of H_2S re-oxidized in reduced environments is considered to be low (0.11–0.42)³¹, implying an unlikely role of the re-oxidation of sulfide in driving the observed isotopic trend during the UKH. Thus, the low sulfate concentrations during the UKH is the most likely explanation for the decreasing trend in $\Delta^{34}\text{S}_{\text{CAS-Py}}$.

Link of change in seawater sulfate to P contents and biotic crisis

The great variation in the seawater sulfate level provides insight into the nutrient cycling, and oceanic productivity during the UKH. Specifically, given the fact that the rate of sulfate drawdown is a function of both organic matter and sulfate availability and rate of sulfate reduction at mM range is mainly controlled by organic matter³², the falling of the seawater sulfate concentration from mM range to less than 500 μM is then indicative of an enhancement in the rate of microbial sulfate reduction, caused by an elevation in the availability of organic matter. This implies a highly productive ocean with ample macronutrients, most notably, phosphorous. Such conclusion is, indeed, consistent with the measured P data of sediments that show a rise in the P content from 299 to 470 ppm at the beginning of the event (Fig. 2E, Table S2; Fig. S4). The oceanic P concentrations are related to sediment P contents and sedimentation rates, and high P sediments with high sedimentation rates must have deposited from the elevated seawater P values. Coarser sediments prior to the UKH than the UKH sediments suggest, in general, more rapid sedimentation. It can be estimated that UKH sediments were deposited at a sedimentation rate of about 1/4 of sediments before and after the UKH. The higher P sediments show higher sedimentation rates prior to and after the UKH in the FF sections, suggesting that sediment P contents can well be used to reflect relative changing trends of seawater P concentrations with the highest value at the beginning of the event and the lowest during the UKH (Fig. 2E, Table S2). The rise in P contents at this time is recorded in other sections worldwide such as the Appalachian basin (USA)³³ and Steinruch Schmidt (Germany)³⁴, making a case for increased P availability at this time (Fig. S3). Increased P availability can be a result of enhanced volcanic activity before the event that would have enhanced the delivery of the nutrient to the ocean¹². A pervasive iron-rich condition during the event, as indicated by Fe speciation results, along with low seawater sulfate concentration point toward a famine ocean with respect to P which is consistent with low P content at this time (Fig. 4). While such low P and iron-rich conditions may have not been common during the Phanerozoic, it is widely invoked to have prevailed in the Precambrian ocean, where the strong association of P with Fe minerals¹² would have led to a P crisis, resulting in suppressed oceanic productivity and smaller biosphere³⁵. This environmental condition is suggested to have delayed the emergence of animals as well³⁶. Taken together as a whole, while the catastrophically chemical transition to sulfidic condition at the beginning of the UKH might have been the trigger for the widespread biological wipeout by blood anoxia and olfactory nerve paralysis, the nutrient-poor oceans during the UKH would have likely hampered any biological recovery.

Low seawater sulfate and high atmospheric methane

Extremely low sulfate concentrations coupled with TOC up to 0.9% in IIa during the earliest UKH are favorable for methanogenesis to release greenhouse methane to the atmosphere with implications on climate warming during the event. Mechanistically, methane production by methanogenesis enhances as sulfate reduction, the more energetically favorable metabolism, becomes progressively less competitive

at lower seawater sulfate concentrations. Thus, the several hundreds of μM of sulfate suggested by our model would not only encourage the substantial biological production of methane but would impede its efficient removal through sulfate-driven anaerobic oxidation of methane (AOM), leading to a large flux of methane from the oceans. Placed in a quantitative framework, based on the results from previous Earth system modeling³⁷, seawater sulfate concentration of hundreds of μM – similar to that suggested by our model – would lead to more than 10 Tmol/year flux of methane from the ocean, which would translate into tens of ppmv atmospheric methane, an order of magnitude higher than the modern level. The enhanced methane flux during this time is consistent with the evidence of sea-level fall at the beginning of the UKH, and relatively high average seawater temperature during this time^{8,38}.

Conclusions

The catastrophic biological crisis in the Late Devonian would thus indicate a significant and yet unrecognized dynamic in the global biogeochemical cycles of elements. Notably, within several hundred thousand years, the oceanic seawater sulfate concentration would have undergone a large fluctuation with significant fallings at the beginning of the UKH as a result of oceanic anoxia caused by enhanced oceanic productivity and phosphorous concentration and returning to mM levels at the end of the event. Such dynamic would have extended to nutrient cycling, oceanic productivity, and atmospheric methane level, implying a turbulent condition in the ocean-atmosphere system. A similar dynamic in the redox-state and elemental biogeochemical cycles would have likely occurred during the other Phanerozoic anoxic events, and it suggests that instability in Earth's surface redox budget may have played a major role in driving the biological crisis.

Declarations

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Figures

Figure 1

Diagrams showing, A) depositional cyclicity and relative sea-level changes (3rd-order) and sea-level fluctuations, modified from Ma and Bai (2002)13 and Zong et al. (2016) 14; B) organic matter $\delta^{13}\text{C}_{\text{org}}$ variation.

Figure 2

Xikuangshan (South China) F–F boundary section with stratigraphic column and sample number showing, A) FeHR/FeT; B) FePy/FeHR; C) Variations in $\delta^{34}\text{S}_{\text{Kero}}$, $\delta^{34}\text{S}_{\text{SCAS}}$, and $\delta^{34}\text{S}_{\text{Py}}$; D) Variations in $\Delta^{34}\text{SCAS-Py}$ and $\Delta^{34}\text{SKero-Py}$, and E) P contents in this study.

Figure 3

Non-steady sulfate concentration in the Late Devonian mass extinction event. The histograms are the modeled range of sulfate concentrations for periods of a) before, b) during, and c) after the UKH. The histograms resulted from the stochastic analysis in which input modeling parameters were randomly sampled within a reasonable range and the most probable range of seawater sulfate concentration was

obtained. The radical change in the seawater sulfate concentration during UKH signals a turbulent condition in the ocean-atmosphere system.

Satge 1: before and after UKH

Figure 4

Evolution of seawater sulfate concentrations, redox conditions, and the occurrence of phosphorus and trace elements in the euphotic zone and sediments during the Late Devonian mass extinction event, UKH.

Supplementary Files

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