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Shi, W., Mills, B.J.W., Algeo, T.J. et al. (8 more authors) (2023) Heterogeneous sulfide reoxidation buffered oxygen release in the Ediacaran Shuram ocean. Geochimica et Cosmochimica Acta, 356. pp. 149-164. ISSN 0016-7037

https://doi.org/10.1016/j.gca.2023.07.018

Heterogeneous sulfide reoxidation buffered oxygen release in the Ediacaran Shuram ocean

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Abstract

Ediacaran (~635-539 Ma) carbonate rocks record the largest negative carbonate-carbon isotope excursion in Earth history, termed the Shuram Excursion (SE). This event has been attributed to anaerobic oxidation of dissolved organic carbon as a result of enhanced weathering inputs of sulfate to the ocean during the amalgamation of Gondwana. However, the effect of carbon-sulfur cycle interplay on the net redox state of the ocean-atmosphere system remains unclear, impeding our understanding of the co-evolution of life and the environment during the Ediacaran. Here, we generate high-resolution records of paired sulfate sulfur and oxygen isotopes, in addition to phosphorus concentrations, for the SE interval in South Australia (Parachilna Gorge) and South China (Jiulongwan and Xiang'erwan sections, Three Gorges), and we evaluate these data in the context of COPSE biogeochemical model simulations to assess net long-term redox changes. Our results support widespread H_2S reoxidation in shelf areas during the SE, which would have buffered the net release of oxygen sourced from the burial of organic carbon and pyrite. Varying degrees of H_2S reoxidation on different cratons likely contributed significantly to high spatial heterogeneity in both local oceanic redox state and nutrient availability, which characterized local oxygen-deficient conditions in an overall oxygenated SE shelf ocean, and likely affected the distribution of the Ediacaran Biota. Our study highlights the important role of H_2S reoxidation in the coevolution of marine redox conditions and complex life during the critical Ediacaran period.

Keywords: Shuram Excursion; C-S cycles; sulfate oxygen isotopes; H_2S reoxidation; COPSE model; Neoproterozoic

1. INTRODUCTION

The middle-late Ediacaran Period was marked by the early diversification and radiation of metazoans, as represented by the Ediacaran Biota (Xiao and Laflamme, 2009). This bioevent coincided with major changes in the biogeochemical cycles of carbon and sulfur, including the largest negative carbonate-carbon isotope ($\delta^{13}C_{carb}$) excursion in Earth history, termed the Shuram Excursion (SE) (Fike et al., 2006; Le Guerroué et al., 2006). The SE event is also known as the 'DOUNCE' (DOUshantuo Negative Carbon isotope Excursion) (Lu et al., 2013; Zhu et al., 2013) or 'EN3' (McFadden et al., 2008) in South China platform facies, and as the 'Shuram-Wonoka Excursion' in South Australia platform facies (e.g., Husson et al., 2015a). During this event, oceanic $\delta^{13}C_{carb}$ records from Oman, South Australia, South China, northwestern Canada, southwestern USA and Siberia show a decline from >+3 ‰ to <–10 ‰ (Busch et al., 2022; Macdonald et al., 2013; Lu et al., 2013) (Fig. 1), starting roughly at ~575 Ma and terminating at ~565 Ma (Rooney et al., 2020; Yang et al., 2021). These records likely reflect secular variation in seawater dissolved inorganic carbon (DIC) composition, with the minimum values being significantly below that of mantle inputs (~–6 ‰). These extreme $\delta^{13}C_{carb}$ anomalies are difficult to interpret in the context of a conventional steady-state carbon cycle, as they imply negative rates of organic carbon burial (i.e., net oxidation of organic carbon over ~10 Myr). In other words, the negative $\delta^{13}C_{carb}$ excursion generated by organic oxidation may have been quantitatively sufficient to overwhelm the isotopic buffering effect of concurrent organic carbon burial during the SE. As a result, it has been suggested that this $\delta^{13}C_{carb}$ excursion was the result of secondary alteration of marine carbonates by meteoric or hydrothermal fluids (Derry, 2010; Knauth and Kennedy, 2009) or by formation of authigenic carbonates (Cui et al., 2017). However, recent in-situ petrographic and chemical analyses emphasize the primary origin of the global SE signal with little or no overprinting by meteoric fluids or late burial diagenesis (Busch et al., 2022; Cui et al., 2021; Husson et al., 2020).

A mechanistic hypothesis that accounts for the extreme negative $\delta^{13}C_{carb}$ values of the SE in the context of primary depositional processes invokes anaerobic oxidation of a dissolved organic carbon (DOC) (Rothman et al., 2003) [or other types of marine organic carbon, e.g., continental weathered fossil organic matter (Kaufman et al., 2007) or petroleum seeps hydrocarbons (Lee et al., 2015)] reservoir. This oxidation event was enabled by increased weathering inputs of sulfate driven by tectonic uplift related to the amalgamation of Gondwana (Fike et al., 2006; McFadden et al., 2008; Li et al., 2017), as supported by a coeval increase in seawater $^{87}Sr/^{86}Sr$ from <0.708 to >0.709 (e.g., Sawaki et al., 2010). However, simple numerical treatments of carbon mass balance have questioned whether the oxidant content of the Ediacaran Earth system [below 1 PAL (present atmosphere level) of pO_2 (Lyons et al., 2014) and 5 mM of $[SO_4^{2-}]_{sw}$ (Algeo et al., 2015)] could have sustained the oxidation of an DOC reservoir for ~10 Myr, even with inclusion of the oxygen supply from background organic carbon burial (Bristow and Kennedy, 2008) (termed the 'Shuram oxidant paradox' in this study), especially when considering $[SO_4^{2-}]_{sw}$ estimates of < 2 mM before the Ediacaran SE event (Loyd et al., 2012; Osburn et al., 2015). To address this quandary, two hypotheses have been proposed: (1) spatially heterogeneous oxidation of DOC with oxidant demand limited mainly to shelf areas (Li et al., 2017, Shi et al., 2017), and (2) a balanced oxidant budget despite net oxidation of organic carbon (Shields et al., 2019) through a large pulse of sulfate to the ocean derived from tectonic inversion and weathering of basin-scale evaporite deposits of Tonian age (hereafter called 'S_{pulse}'), as supported by palaeomagnetic (Evans, 2006) and S-isotopic evidence (Prince et al., 2019). These models can potentially resolve the 'Shuram oxidant paradox', yet the details of carbon-sulfur cycle interaction during the SE event remain uncertain.

Studies continue to question the 'oxidation' mechanisms for the SE, noting that the original 'decoupled' organic and carbonate isotope ratios noted by Rothman et al. (2003) are not seen in all sections (Johnson et al., 2012), and that a DOC reservoir might be difficult to sustain at high concentrations due to biological utilization (Arrieta et al., 2015; Fakhraee et al., 2021). Furthermore, recent lithologic and geochemical observations suggest that the SE may also reflect global changes in the locus and intensity of primary productivity and/or evaporation in shallow-water environments (Busch et al., 2022). None of these studies necessarily falsifies the 'oxidation' hypothesis. The above stated limits for DOC oxidation appear to ignore environmental context (Jiao et al., 2014; 2015), and current models for DOC accumulation do not consider changes in oxygen levels (Fakhraee et al., 2021). Furthermore, alternative mechanisms based on sea level changes are not able to easily explain the Shuram carbonate-associated sulfate (CAS) sulfur isotopic ($\delta^{34}S_{CAS}$) shift or other coexisting isotopic perturbations (e.g., $\delta^{238}U$).

A pronounced shift toward more negative marine $\delta^{34}S_{CAS}$ values coincided with the SE in globally correlated sections in Oman (Miqrat-1; Fike et al., 2006; Fig. 1B), the USA (Death Valley; Kaufman et al., 2007; Fig. 1C), South China (Jiulongwan, Three Gorges; Shi et al., 2018; Fig. 1D), and northwestern Mexico (Sonora; Loyd et al., 2013), reflecting systematic coupling between the sulfur and carbon cycles over a timescale of millions of years. However, if the Shuram negative $\delta^{13}C_{carb}$ excursion relied on elevated sulfate inputs and removal of ^{34}S-depleted sulfur due to microbial sulfate reduction (MSR; $SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$) and thus pyrite burial, this would have acted to increase the $\delta^{34}S$ value of the parent sulfate reservoir, which is not consistent with a large negative excursion in $\delta^{34}S_{CAS}$ records. Moreover, despite a similar nadir in $\delta^{13}C_{carb}$ (ca. –10 ‰) during the SE in each of the three sections discussed above, their $\delta^{34}S_{CAS}$ records show significant differences (Fig. 1B-D). The $\delta^{34}S_{CAS}$ profile for Miqrat-1 (the Shuram Formation, Oman) exhibits a shift of –7 ‰, from ~+30 ‰ to ~+23±1 ‰ (Fig. 1B; Fike et al., 2006), that for Death Valley (the Rainstorm Member, Johnnie Formation) shows a shift of –11 ‰, from ~+27 ‰ to ~+16±1 ‰ (Fig. 1C; Kaufman et al., 2007), that for Jiulongwan (Members III-IV, Doushantuo Formation) shows a shift of –18 ‰, from ~+32±2 ‰ to ~+14±2 ‰ (Fig. 1D; Shi et al., 2018), and that for Sonora, Mexico (the Clemente Formation) shows a shift of –7.5 ‰, from >+27.5 ‰ to ~+20±2 ‰ (Loyd et al., 2013). In theory, the fixed stoichiometry between DOC and sulfate during MSR (i.e., $[CH_2O]:[SO_4^{2-}] = 2:1$) should yield a systematic relationship between shifts in $\delta^{13}C_{carb}$ and $\delta^{34}S_{CAS}$ linked to anaerobic oxidation of DOC, so a similar nadir in $\delta^{13}C_{carb}$ among multiple regions should represent a similar rate of MSR and H_2S production, and thus similar variability in $\delta^{34}S_{CAS}$. Yet the existence of variability in $\delta^{34}S_{CAS}$ excursions among sections associated with a similar rate of DOC oxidation indicates a possible spatial heterogeneity in the sulfur sub-cycle. However, the mechanisms behind the $\delta^{34}S_{CAS}$ shift and spatial heterogeneity during the SE remain unclear.

In this study we hypothesize that, while organic remineralization proceeded dominantly through MSR, the spatial heterogeneity in $\delta^{34}S_{CAS}$ was linked to a local sub-cycle of the marine C-S cycle, in which H_2S reoxidation altered $\delta^{34}S_{CAS}$ while exerting little to no influence on $\delta^{13}C_{carb}$ signals. In order to test this hypothesis, we generate a new high-resolution dataset of $\delta^{13}C_{carb}$, $\delta^{34}S_{CAS}$, CAS-oxygen isotopes

($\delta^{18}O_{CAS}$) and major elements (including P/(Ca+Mg), a proxy for aqueous phosphorus concentrations; Ingalls et al., 2020) from well-preserved carbonate rocks through the SE interval of three sections (one in South Australia and two in South China) (Fig. 2). Measuring $\delta^{34}S_{CAS}$ and $\delta^{18}O_{CAS}$ in marine sediments can provide important information about biologically induced fluxes of sulfur among various reservoirs (e.g., sulfide reoxidation and pyrite burial can leave a distinct imprint on the isotopic composition of the marine sulfate pool; Goldberg et al., 2005; Gomes and Johnston, 2017; Newton et al., 2004). The study sections accumulated in mid-depth carbonate platform settings that do not record any stratigraphic break caused by sudden sea-level changes and exposure, and their $\delta^{13}C_{carb}$ profiles preserve complete records of the SE. We then utilized the COPSE (Carbon-Oxygen-Phosphorus-Sulfur-Evolution) global biogeochemical model to evaluate each of these distinct isotopic trends by setting up forcing parameters in line with the DOC oxidation hypothesis. Modelling the combined stratigraphic patterns in these CAS sulfur and oxygen isotope records provides new insight into carbon-sulfur-oxygen cycling during the SE event, thus enabling the assessment of its potential impact on marine redox as well as the distribution and radiation of the Ediacara Biota.

2. GEOLOGICAL SETTING

2.1 Paleogeography

Ediacaran strata, dating to ca. 635 to 539 Ma, overlie end-Cryogenian 'Marinoan' glacial deposits at a global scale, with age equivalence demonstrated using a variety of techniques, including chemostratigraphy, paleobiology and geochronology (see review by Yang et al., 2021). The South China Craton and the South Australia Craton were microcontinents located at low Northern Hemisphere paleolatitudes in the middle of the Ediacaran (Fig. 1A; Merdith et al., 2017). In South China, paleogeographic reconstructions for the Doushantuo Formation, spanning most of the Ediacaran Period, envisage shallow platform, slope and basin environments along a northwest-to-southeast transect, based on lateral variations in lithofacies and stratal thicknesses (Jiang et al., 2011; Zhu et al., 2013). The Doushantuo Formation in the Yangtze Gorges area consists of four members: Member I is a 3- to 7-m-thick cap carbonate dated to 635.2 ± 0.6 Ma (Condon et al., 2005), Member II consists of organic-rich black shale with carbonate interbeds, Member III is dominated by carbonate with subordinate shale, and Member IV is composed of 10- to 20-m-thick black shale (Zhu et al., 2007, 2013). Members I and IV are marker strata that are widely traceable across South China, whereas Members II and III exhibit considerable variations in lithology and thickness between sections, and the position of their contact remains uncertain in many sections in South China. In South Australia, Ediacaran strata deposited in the Flinders Ranges were exposed during the Delamerian Orogeny of the Early Paleozoic (Preiss, 2000). The Wonoka Formation belongs to the Ediacaran Wilpena Group, and the base of the Nuccleena Formation and the cap dolostone overlie the glacial Elatina Formation of the underlying Umberatana Group. The Wonoka Formation begins as a deep-shelf sequence of red siltstones interbedded with thin-bedded, often fluted turbidite carbonate beds with abundant climbing-ripples. Carbonate beds become thicker and coarser upward, culminating with the first unequivocally shallow-water carbonates ~600 m above the base of the Wonoka Formation (Husson et al., 2015a and b).

2.2 Study sections

Since there is uncertainty in extrapolating geochemical signatures from a single basin to the global ocean, we sampled two contemporaneous basins located on the South China and South Australia cratons to test our hypothesis. Fresh rock samples were collected from the Doushantuo Formation Member III in the Jiulongwan (30°47′51″N, 110°59′32″E) and Xiang'erwan (31º13'6.2"N, 110º57'26.8"E) sections of the Three Gorges region (South China) (Fig. 2A-B), and the Wonoka Formation in the Parachilna Gorge section (31º9'51.6"S, 138º31'43.2"E) of the Flinders Ranges (South Australia) (Fig. 2C-D). The study sections were deposited on the marine shelves of two different passive continental margins (Jiang et al., 2011; Husson et al., 2015a and b) (Fig. 1A). The Jiulongwan and Xiang'erwan sections are outcrop sections near Yichang City, Hubei Province, representing inner-shelf settings and providing representative loci for marine primary productivity and pyrite burial on the Yangtze Platform (An et al., 2015; Zhu et al., 2013) (Fig. 2B). The two sections are located 43 km apart and show similar lithostratigraphy and carbon isotope stratigraphy. They can be correlated on the basis of two facies changes, comprising a shift from medium-thick bedded dolostone to shaly dolostone in the middle of Doushantuo Member III, followed by a shift to calcareous shale between Members III and IV (An et al., 2015). The SE was recorded in the Ediacaran Doushantuo Members III and IV of the Jiulongwan and Xiang'erwan sections, with very similar $\delta^{13}C_{carb}$ features between the two sections (An et al., 2015). The negative $\delta^{13}C_{carb}$ signals in both sections start from the thick dolostone of lower Member III, decline towards a nadir of –10 ‰ accompanied by a lithological change from dolostone to limestone in the middle of Member III, and then shift back towards positive values at the contact between Members III and IV. Member IV consists of ~10 m of black, organic-rich shale that is widespread across the Three

Gorges area and marks the lithologic contact between Member IV and the overlying Dengying Formation. Carbonate strata in the two study sections contain the full SE, and the detailed stratigraphic framework provided by facies changes (An et al., 2015) allows accurate correlations of their $\delta^{13}C_{carb}$, $\delta^{34}S_{CAS}$ and $\delta^{18}O_{CAS}$ records, on the basis of which temporal and spatial variation in C-S cycling on the Yangtze Platform as well as possible relationships to atmospheric oxygen and marine redox conditions can be investigated.

We used the correlation method proposed by Verdel et al. (2011) to compare and combine $\delta^{13}C$ profiles from the Jiulongwan and Xiang'erwan sections (Fig. 3A). This method plots stratigraphic positions of samples normalized to a range of 0 to 1, making use of age-equivalent lower and upper tie-points. The lower tie-point of 0 was defined at $\delta^{13}C_{carb}$ equal to +5 ‰, just prior to a decrease in $\delta^{13}C_{carb}$ (i.e., about 20 m and 18 m above the Doushantuo Member II/III contact at Jiulongwan and Xiang'erwan, respectively), and the upper tie-point of 1 was defined at the contact between the Doushantuo Formation and the overlying Dengying Formation in both sections. The normalized $\delta^{13}C_{carb}$ and related $\delta^{34}S_{CAS}$, $\delta^{18}O_{CAS}$, P/(Ca+Mg) and $\delta^{238}U_{carb}$ data, shown in Figure 3A and Table S1, agree with the results of prior studies (An et al., 2015).

The Parachilna Gorge section outcrops within the Adelaide Syncline in the Flinders Ranges of South Australia (Fig. 2C). In this section, the Wonoka Formation, overlying the Bunyeroo Formation, consists of ~700 m of mixed shelf limestones and siliciclastics that is subdivided into 11 units from bottom to top (Fig. 2D). Units 1 and 2 are dominated by thin dolomitic beds with intercalated shale and calcareous sandstone, respectively. Units 3 and 4 consist of thinly bedded micritic limestone with intercalated shale, and Units 5-7 of silty and micritic limestones with varying clastic content. Units 8 and 9 are composed of shaly limestone and peloidal limestone, respectively. Unit 10 is a calcareous sandstone, and Unit 11 consists of stromatolitic and oolitic limestones and microbialites. Geological observations (e.g., excellent preservation of sedimentary structures in Wonoka carbonates, absence of top-down alteration profiles associated with exposure surfaces) do not provide evidence of meteoric or authigenic carbonate precipitation (Husson et al., 2015a). We sampled a section that is roughly equivalent to (~100 m distant from) the No. 6 Wonoka section reported in Husson et al. (2015a), which captures all of the SE except for the initial decline in $\delta^{13}C_{carb}$, recording a $\delta^{13}C_{carb}$ excursion from 0 ‰ to –12 ‰ (Fig. 2D and 3B). Given the similar locations of these sections, we correlated our $\delta^{13}C_{carb}$, $\delta^{34}S_{CAS}$ and $\delta^{18}O_{CAS}$ profiles with the $\delta^{13}C_{carb}$ data from Husson et al. (2015a and b) and Gong et al. (2023) (Fig. 2C and 3B).

3. ANALYTICAL METHODS

3.1 Carbonate carbon-oxygen isotopes

Large fresh blocks of rock were collected from study outcrop sections for petrographic and geochemical analyses, and any weathered surfaces and diagenetic veins were removed. Each block was broken into small pieces (~1 cm^3), and only those pieces with no visible weathering or veins were selected and crushed to powder finer than 200 mesh. A total of 78 samples (30 from the Xiang'erwan section, and 48 samples from the Parachilna Gorge section) was analyzed for $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ (i.e., carbonate $\delta^{18}O$). About 60 to 300 μg of sample powder were dried at 70°C for 24 h in an argon atmosphere and then were loaded into a vial. The samples were then reacted with 100% phosphoric acid under a vacuum at 70°C for 220 s using a Kiel IV device. The resulting CO_2 was subsequently introduced into a MAT 253 isotope ratio mass spectrometer (IRMS) for isotopic measurements. Delta values were calibrated relative to international reference standard NBS-19 ($\delta^{13}C_{carb} = +1.95$ ‰; $\delta^{18}O_{carb} = -2.20$ ‰) and Chinese national standard GBW04416 ($\delta^{13}C_{carb} = +1.61 \pm 0.03$ ‰; $\delta^{18}O_{carb} = +1.59 \pm 0.11$ ‰). Carbon and oxygen isotope data for carbonates are reported relative to Vienna Pee Dee Belemnite (VPDB), with a precision of better than ±0.1 ‰ based on duplicate analyses of GBW04416 ($n = 5$) and selected study samples ($n = 10$).

3.2 Carbonate-associated sulfate (CAS) sulfur and oxygen isotopes

A total of 84 samples (35 samples from the Parachilna Gorge section, 24 samples from Jiulongwan section, and 25 samples from the Xiang'erwan section) were analyzed for the isotopic composition of CAS sulfur ($\delta^{34}S_{CAS}$) and oxygen ($\delta^{18}O_{CAS}$). CAS was extracted using the method of Luo et al. (2010) as modified by Shi et al. (2018). For each sample with total inorganic carbon (TIC) >3 %, ~30 g of powder were washed in a 10 % NaCl solution for 24 h with magnetic shaking in a custom-made threaded plastic vessel with a sealed cap. After centrifuging (1000 rev/min), the supernatant was aspirated and the residual powder rinsed with Ultrapure water. These steps were repeated more than 10 times until no barite precipitate formed when saturated $BaCl_2$ solution (~350 g/L) was added to the supernatant (i.e., all non-CAS sulfate was removed). The residual powder was then dissolved through slow addition of 4 M HCl and stirring until the reaction went to completion, during which the derived CO_2 maintained a positive pressure, thus preventing significant O_2 introduction into the system and, hence, direct pyrite oxidation via molecular oxygen. The contents of the sealed plastic vessel were immediately centrifuged (1000 rev/min) to segregate the residue and supernatant in order to avoid oxidation of pyrite, and the supernatant was collected after filtering. About 125 mL of a saturated $BaCl_2$ solution was then added in order to precipitate dissolved sulfate as barium sulfate ($BaSO_4$), which was dried for CAS sulfur isotopic analysis. The sulfur isotopic composition of dried $BaSO_4$ (representing recovered CAS, thus $\delta^{34}S_{CAS}$) was measured on a Thermo Fisher Scientific Delta V Plus IRMS coupled with a Flash elemental analyzer. Results are expressed in standard delta notation as per mille deviations relative to the international Vienna Cañon Diablo Troilite (VCDT) standard, where $\delta^{34}S = [(^{34}S/^{32}S)_{sample} / (^{34}S/^{32}S)_{standard} - 1] \times 1000$ ‰. Analytical reproducibility was generally better than ±0.2 ‰ (1σ) calculated from replicate analyses of IAEA standards [NBS-127 (+21.1 ‰), IAEA-SO-5 (+0.49 ‰), IAEA-SO-6 (–34.05 ‰)].

Residual dried $BaSO_4$ powders from $\delta^{34}S_{CAS}$ analysis were purified for $\delta^{18}O_{CAS}$ analysis using the DTPA dissolution and reprecipitation (DDARP) method of Bao (2006). For each sample, about 20 mg of $BaSO_4$ powder were washed in a 1-L DTPA solution (with 40 g NaOH and 20 g DTPA in 1-L Ultrapure water) for 48 h to achieve complete $BaSO_4$ dissolution, after which the supernatant was filtered and collected. These steps were designed to remove other species (e.g., $BaCO_3$) from $BaSO_4$. The supernatant was treated dropwise with 3.5 mL of concentrated (10-M) HCl to obtain a pH of ~3-4. Barite was quantitatively reprecipitated within 1 h, but in cases where the solution was very dilute in terms of $[SO_4^{2-}]$, addition of saturated $BaCl_2$ solution helped to promote $BaSO_4$ precipitation. After centrifugation and decantation, barite was rinsed with ultrapure water (18.2 MOhm/cm at 25°C) three times and then dried in an oven at ~105°C. The oxygen isotopic composition of purified $BaSO_4$ was measured on a Thermo Fisher Scientific Delta V Plus IRMS coupled with a Flash elemental analyzer. Results are expressed in standard delta notation as per mille deviations relative to the international Vienna Standard Mean Ocean Water (VSMOW) standard, where $\delta^{18}O = [(^{18}O/^{16}O)_{sample} / (^{18}O/^{16}O)_{standard} - 1] \times 1000$ ‰. Samples were analyzed in duplicate, and the total analytical error is estimated to be <0.5 ‰ based on repeated measurements of laboratory standards (USGS34 = –27.8‰; IAEA-NO3 = +25.6‰; USGS35 = +56.8‰).

3.3 Elemental concentrations

A total of 80 samples (49 samples from the Jiulongwan section and 31 samples from the Xiang'erwan section) were analyzed for elemental concentrations. Approximately 5 g of each sample were dissolved in 1-M hydrochloric acid (HCl) for 24 h in a 25°C bath with agitation at 60 rev/min. Digests were centrifuged, and the supernatant was separated. The concentrations of major and trace elements of the HCl supernatant (i.e., the dissolved carbonate) were measured on a Thermo iCAP™

quadrupole inductively coupled plasma mass spectrometer (Q-ICP-MS). The analytical error was better than 3 % and 5 % for major and trace elements, respectively, based on repeat analyses of in-run check standards (Dolomite Kuzuu, JDo-1).

3.4 Mineralogical analyses

Thin sections of 9 samples (4 samples from the Jiulongwan section, and 5 samples from the Xiang'erwan section) were analyzed for mineralogy and microfabrics using a Zeiss Axio Scope with 5× objectives in both the transmitted and reflected light modes. Polished sections (2 cm × 2 cm) of 4 samples from the Xiang'erwan section were made for *in situ* observation of pyrite framboids using a field emission scanning electron microscope (SEM) in the backscattered electron (BSE) mode. The mineralogical compositions of 6 carbonate samples from the Xiang'erwan section were determined by X-ray diffraction (XRD) using a Dandong TD-3500 advance diffractometer equipped with nickel-filtered CuKα radiation (35 kV, 25 mA). The dried powder-mount samples were scanned from 3° to 65° with a step size of 0.02°2θ and a scan speed of 0.25°/min.

3.5 COPSE modeling

To explore how changes in sulfide reoxidation rate may have affected sulfate S-O isotopes during the SE, we used the COPSE global biogeochemical model, which was modified to include a dynamic deep-ocean DOC reservoir coupled to a pulsed sulfate weathering flux. COPSE is a forward model in which processes are driven by a set of evolving boundary conditions (geological forcings) and internal dynamics, including a nutrient-driven biosphere (Bergman et al., 2004; Lenton et al., 2018). Figure 4 shows the fluxes, reservoirs, and their relationships in the COPSE model. Oxygen is released via burial (B) of photosynthetically-derived carbon and pyrite sulfur, and is removed by weathering (W) or metamorphic degassing (D). The source-sink mass balance for O_2 is:

$$\frac{dO_2}{dt} = B_G - \mathrm{W}_G - \mathrm{D}_G + 2 \times (B_{PYR} - \mathrm{W}_{PYR} - \mathrm{D}_{PYR}) \qquad (1)$$

where the subscripts G and PYR represent the crustal organic carbon and pyrite reservoirs, respectively, and the coefficient (2) represents the 1:2 stoichiometric relationship between pyrite sulfur and organic carbon (and thus oxygen) during microbial sulfate reduction and photosynthesis. Burial, weathering and degassing of carbonate carbon and gypsum sulfur impact estimated O_2 concentrations indirectly, by affecting the size of the ocean-atmosphere inorganic carbon (A) and sulfate (S) reservoirs and the overall elemental cycling rate (Lenton et al., 2018). Here, we used the latest version of the COPSE model (Tostevin and Mills, 2020), which includes forcing information for the evaporite sulfate pulse and simplified DOC reservoir dynamics (Shields et al., 2019) (see Tables S3-S7 for full model description, and *https://bjwmills.com* for MATLAB code).

We first ran the COPSE model for 10 million years to an 'Ediacaran-like' steady state characterized by $p\mathrm{O_2}$ = 0.1 PAL, $p\mathrm{CO_2}$ = 6 PAL, and $[SO_4^{2-}]_{sw}$= 0.1 of present oceanic level (POL), which was achieved by adjusting the phosphorus weathering inputs and gypsum burial rates. Note that the initial steady state of $p\mathrm{O_2}$ = 0.1 PAL is regarded as the minimum for the appearance of red beds and early animals during the early Neoproterozoic (~700 Ma) (Sperling et al., 2015a), although a higher $p\mathrm{O_2}$ may have existed by the time of the SE event (Shi et al., 2022; Krause et al., 2022). Following Shields et al. (2019), we imposed a sulfate input event (S_{pulse}) coincident with the observed negative $\delta^{13}\mathrm{C_{carb}}$ excursion to examine atmospheric-oceanic dynamics during the SE:

$$S_{pulse} = interp1([-10\ 0\ 3\ 6\ 10\ 30],\ [0\ 0\ 7\ 7\ 0\ 0]) \quad (2)$$

Where *interp1* represents 1-dimensional interpolation, and the following vectors in brackets in equation (2) are the interpolation points for time (1) in million years relative to the start of the SE of ~575 Ma (see Section 1) and (2) an additional sulfate input relative to the background sulfate weathering flux. In our model simulations, steady-state weathering sulfate inputs include both the 'background' and additional 'pulsed' inputs of pyrite and gypsum:

$$W_{PYR} = W_{PYR\_bg} + S_{pulse} \cdot W_{PYR\_bg} \quad (3)$$

$$W_{GYP} = W_{GYP\_bg} + S_{pulse} \cdot W_{GYP\_bg} \quad (4)$$

where W_{PYR_bg} and W_{GYP_bg} are the background sulfate weathering fluxes of pyrite and gypsum. Although the evaporite sulfate weathering flux was set as the main source of oxidants to the Shuram ocean, pyrite weathering was also included to match natural conditions. In the poorly-oxygenated and redox stratified Neoproterozoic ocean, microbial decay of organic matter was largely coupled to sulfate reduction rather than aerobic pathways (Bristow and Kennedy, 2008). We modified the COPSE model to oxidize DOC directly via MSR (rather than by O_2), parameterizing the flux of H_2S produced as $H_2S_{MSR} = DOC_{ox}/2$ in moles, although oxidation by O_2 or other oxidants (e.g., NO_3^-, Mn^{4+}, Fe^{3+}) may have occurred. We modified the rate of DOC oxidation to respond to both the weathering sulfate pulse and relative concentrations of reactants (i.e., $[SO_4^{2-}]_{sw}$ and DOC; Fig. 4):

$$\frac{d\text{DOC}}{dt} = \begin{cases} 0, & DOC < 10^{12}\, mol \\ -2 \cdot S_{pulse} \cdot (W_{PYR\_bg} + W_{GYP\_bg}) \cdot \frac{S_t}{S_0} \cdot \frac{\text{DOC}_t}{\text{DOC}_0}, & DOC \geq 10^{12}\, mol \end{cases} \tag{5}$$

where S_t and S_0 are the masses of the marine sulfate reservoir at time ***t*** and at present (0), DOC_t and DOC_0 are the masses of the DOC reservoir at time ***t*** and 30 times the modern DOC reservoir (Shields et al., 2019), respectively. In nature, the remineralization of old DOC occurs dynamically with the production of new DOC. Here, we modeled only the net consumption of the DOC reservoir because new DOC production was counteracted by oxidation of an equal amount of old DOC. The weathering sulfate pulse was modeled as a trapezoidal function spanning ~10 million years, which is consistent with seawater $^{87}Sr/^{86}Sr$ records (Sawaki et al., 2010) as well as with Re-Os isotopic evidence for the duration of the Shuram Excursion (Rooney et al., 2020; Yang et al., 2021). DOC oxidation was terminated when DOC reservoir size was reduced to less than 10^{12} moles (equal to the annual flux, i.e., 10^{12} mol yr^{-1}) rather than zero, to prevent model instability (Shields et al., 2019). This is necessary because the COPSE model can become unstable when quantities become extremely low (e.g., when yearly fluxes become larger than the size of the model reservoir). Our COPSE model simulation assumes that net oxidation of the DOC reservoir was coupled with the weathering sulfate pulse, and that part of the MSR-derived H_2S was re-oxidized to sulfate. A partitioning constant f_{reox} was used to determine what fraction of MSR-derived H_2S was re-oxidized into sulfate:

$$Reox = H_2S_{MSR} \cdot f_{reox} \tag{6}$$

where $Reox$ is the flux of re-oxidized H_2S. The COPSE model treats the atmosphere, oceans and surface sediment as a single box, so MSR-produced sulfide that is not re-oxidized is assumed to be buried as pyrite (Fig. 4). Additional sulfate that is not buried as pyrite is assumed to be partly buried as gypsum, and the remainder was left as an aqueous phase in seawater, allowing an increase in $[SO_4^{2-}]_{sw}$. For the model run in this study, total burial fluxes of marine pyrite sulfur (B_{PYR_tot}) and gypsum sulfur (B_{GYP_tot}) were quantified as follows:

$$B_{PYR\_tot} = k_{mpsb} \cdot \left(\frac{S_t}{S_0}\right) \cdot \left(\frac{O_0}{O_t}\right) + H_2S_{MSR} \cdot (1 - f_{reox}) \tag{7}$$

$$B_{GYP\_tot} = ((W_{PYR\_bg} + W_{GYP\_bg}) \cdot S_{pulse} - H_2S_{MSR} + k_{mgsb}) \cdot \left(\frac{S_t}{S_0}\right) \tag{8}$$

where subscripts 'tot' and 'bg' denote total and background, respectively. k_{mpsb} and k_{mgsb} are today's burial rates of pyrite and gypsum, respectively, and O_t and O_0 are the masses of the atmosphere-ocean oxygen reservoir at time ***t*** and at present, respectively. To model the effect of H_2S reoxidation on marine sulfate S-O isotopes, we denoted f_{reox} as the ratio of H_2S oxidized to H_2S produced (i.e., H_2S_{MSR}), which can range from 0 to 1, with the non-oxidized H_2S fraction being buried as pyrite. We set the isotopic compositions of the sulfate weathering pulse as $\delta^{34}S_{GYP\_pulse}$ = +15 ‰, $\delta^{18}O_{GYP\_pulse}$ = +14 ‰ (VSMOW) and $\delta^{34}S_{PYR\_pulse}$ = 0 ‰ to match the average values of Tonian gypsum deposits (Crockford et al., 2019; Fike et al., 2015) as mentioned above. In order to explore how H_2S reoxidation affects the $\delta^{34}S$ and $\delta^{18}O$ values of marine sulfate, which is relevant to our dataset, we integrated the following equations of Turchyn and Schrag (2006) for marine sulfate S isotopes into the COPSE model:

$$\frac{\mathrm{d}\delta^{34}S_{SO4}}{\mathrm{dt}} \cdot \mathrm{S} = (W_{GYP\_bg} + D_{GYP}) \cdot \delta^{34}S_{GYP\_bg} + \left(W_{PYR\_bg} + D_{PYR}\right) \cdot \delta^{34}S_{PYR\_bg} + W_{GYP_{pulse}} \cdot \delta^{34}S_{GYP\_pulse} + W_{PYR\_pulse} \cdot \delta^{34}S_{PYR\_pulse} - B_{\mathrm{PYR\_tot}} \cdot (\delta^{34}S_{SO4} - \Delta^{34}S_{MSR}) - B_{GYP\_tot} \cdot \delta^{34}S_{SO4} \tag{9}$$

and for marine sulfate O isotopes:

$$\frac{\mathrm{d}\delta^{18}O_{SO4}}{\mathrm{dt}} \cdot \mathrm{S} = (W_{GYP\_bg} + D_{GYP}) \cdot \delta^{18}O_{GYP_{bg}} + \left(W_{PYR_{bg}} + D_{PYR}\right) \cdot \delta^{18}O_{H2O} + W_{GYP_{pulse}} \cdot \delta^{18}\mathrm{O}_{GYP_{pulse}} + W_{PYR_{pulse}} \cdot \delta^{18}O_{H2O} - B_{GYP_{tot}} \cdot \delta^{18}\mathrm{O}_{SO4} - \left(B_{\mathrm{PYR_{bg}}} + H_2S_{MSR}\right) \cdot (\delta^{18}O_{SO4} - \Delta^{18}O_{MSR}) + Reox \cdot [(1 - \lambda) \cdot (\Delta^{18}O_{Reox} + \delta^{18}O_{H2O} - \delta^{18}O_{SO4}) + \lambda \cdot (\Delta^{18}O_{Reox} + \delta^{18}O_{O2} - \delta^{18}O_{SO4})] \tag{10}$$

where the $\Delta^{34}S_{MSR}$ is the sulfur isotope fractionation associated with MSR, $\delta^{18}O_{H2O}$ is the oxygen isotope composition of seawater (i.e., 0 ‰ VSMOW) and $\Delta^{18}O_{MSR}$ and $\Delta^{18}O_{Reox}$ represent oxygen isotope fractionations associated with MSR and sulfide reoxidation, respectively. Considering that O_2 may also have acted as an oxidant, we denoted a constant parameter of λ as the fraction of H_2S oxidized directly by O_2 (1/4), with the remaining H_2S (3/4) oxidized by Fe^{3+}. Note that the version of COPSE utilized in this study is different from that of a recent publication, i.e., Dodd et al. (2023), in which a dependency between Fe^{2+} and P burial was integrated to evaluate decoupling of the P and O_2 cycles in Ediacaran oceans.

4. RESULTS

Geochemical data through the SE interval of the Parachilna Gorge, Jiulongwan and Xiang'erwan sections are summarized in Supplemental Table S1-2. Chemostratigraphic profiles for our new C-S-O-P dataset are shown in Figure 3 (green symbols). The new isotope records from the Xiang'erwan section exhibit a negative $\delta^{13}C_{carb}$ shift from +5 ‰ to a nadir of –10 ‰ and then back to –5 ‰ at the end of the SE, as well as a monotonic $\delta^{34}S_{CAS}$ decrease from +31 ‰ to a nadir of +13 ‰ (Fig. 3A). These profiles are consistent with previous $\delta^{13}C_{carb}$ and $\delta^{34}S_{CAS}$ records from the Jiulongwan section (McFadden et al., 2008; Li et al., 2017). The $\delta^{18}O_{CAS}$ profiles for the Jiulongwan and Xiang'erwan sections exhibit a decrease from >+20 ‰ before the onset of the SE, to <+10 ‰ (i.e., the $\delta^{18}O_{sulfate}$ value of the modern oceanic sulfate reservoir) close to the nadir in $\delta^{13}C_{carb}$, parallel with the falling $\delta^{34}S_{CAS}$ trend, and remain nearly uniform thereafter (Fig. 3A). P/(Ca+Mg) in the Jiulongwan section shows a sharp increase from <5.5 to >12.2 during the initial decline in $\delta^{13}C_{carb}$ and $\delta^{34}S_{CAS}$, then a sharp decrease towards values of <5.6 as $\delta^{13}C_{carb}$ values reach their nadir, followed by an increase to >11.7 in the upper part of the section (Fig. 3A; note cited P/(Ca+Mg) ratios are median values). The new C-S-O isotope data for the Parachilna Gorge section show significant negative shifts during the Shuram-Wonoka Excursion, including decreases in $\delta^{13}C_{carb}$ from ~–2 ‰ to ~–10 ‰ and then back to ~–5 ‰, in $\delta^{34}S_{CAS}$ from ~+31 ‰ to ~+18 ‰, and in $\delta^{18}O_{CAS}$ from ~+20 ‰ to ~+13 ‰ (Fig. 3B).

5. DISCUSSION

5.1 Evaluation of diagenetic influences

Diagenetic influences on the primary marine carbonate signal in the SE units at Jiulongwan and Parachilna Gorge sections were carefully evaluated in Li et al. (2017), Shi et al. (2018), Husson et al.

(2015b, 2020) and Gong et al. (2023) using petrographic, mineralogical and geochemical data, yielding little to no evidence of burial diagenetic effects in either section. In the present study, an evaluation of the carbon, sulfur and oxygen isotope records of Xiang'erwan based on geochemical crossplots, as well as petrographic and mineralogical observations, suggests that this section archives primary marine geochemical signals (Figs. 5-6). Post-depositional alteration of marine carbonate rocks commonly produces a decrease in both $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values, and extremely low $\delta^{18}O_{carb}$ (e.g., $< -10‰$) and positive covariation between $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ have been cited as evidence for a diagenetic origin of negative C-isotope excursions (Knauth and Kennedy, 2009), including the Shuram Excursion (Derry, 2010; Grotzinger et al., 2011). Diagenetic alteration ultimately leads to geochemical and even mineralogical changes in carbonate mineral phases, and so systematic correlation of isotopic compositions with petrographic evidence for recrystallization and/or dolomitization, as well as trace element proxies such as Mn/Sr and Mg/Ca, may be used to test for post-depositional isotopic exchange (Brand and Veizer, 1981; Jacobsen and Kaufman, 1999).

The Xiang'erwan section was divided into two intervals for the purpose of evaluating diagenetic effects: the Pre-Shuram Excursion interval is from 0 to 25 m (green squares in Fig. 5A-B), and the Shuram Excursion interval is from 30 to 72 m (brown squares in Fig. 5A-B). $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values show negative covariation for Pre-Shuram Excursion samples ($R^2 = 0.73$, $n = 13$) but positive covariation for Shuram Excursion samples ($R^2 = 0.48$, $n = 17$) (Fig. 5B), suggesting that ^{12}C and ^{16}O may have been sourced by the same geological process but with little possibility of post-depositional alteration due to $\delta^{18}O_{carb}$ being mostly $> -10‰$. Three samples with $\delta^{18}O_{carb} < -10$ ‰ are randomly distributed in the Xiang'erwan section (e.g., at 48.4 m, 57.6 m and 66.4 m; Fig. 5A; Table S6) and uncorrelated with $\delta^{34}S_{CAS}$ ($R^2 = 0.02$, $n = 10$ for the Pre-Shuram Excursion interval; $R^2 = 0.43$, $n = 14$ for the Shuram Excursion interval) or $\delta^{18}O_{CAS}$ ($R^2 = 0.11$, $n = 8$ for the Pre-Shuram Excursion interval) (Fig. 5B). Mn/Sr and Mg/Ca are uncorrelated within both the Pre-Shuram Excursion interval ($R^2 = 0.30$, $n = 13$) and the Shuram Excursion interval ($R^2 = 0.11$, $n = 18$). Mn/Sr is not significantly correlated with $\delta^{34}S_{CAS}$ ($R^2 = 0.02$, $n = 10$ for the Pre-Shuram Excursion interval; $R^2 = 0.13$, $n = 15$ for the Shuram Excursion interval) or $\delta^{18}O_{CAS}$ ($R^2 = 0.34$, $n = 8$ for the Shuram Excursion interval) (Fig. 5B), indicating that these proxies are unlikely to have been measurably altered by diagenetic or exogenous (e.g., meteoric or groundwater) fluids (Kaufman and Knoll, 1995). P/(Ca+Mg) is not significantly correlated with Mg/Ca ($R^2 = 0.06$, $n = 31$) or Mn/Sr ($R^2 = 0.12$, $n = 31$), suggesting that P/(Ca+Mg) ratios were not related to lithology or diagenetic alteration (Fig. 5C).

Microphotographs of 9 randomly chosen samples from Jiulongwan and Xiang'erwan show uniform microcrystalline textures with more-or-less uniform recrystallization (Fig. 6). The BSE images of pyrite show a mixture of small amounts of authigenic pyrite (formed via in situ microbial sulfate reduction) with a generally larger quantity of framboids precipitated within the water column or pore water. In the SE interval, most framboids are small (<10 μm), randomly distributed, have clearly defined subgrains, and lack visible aggregation or overgrowths (Fig. S3). The XRD analyses of carbonate samples from the Xiang'erwan section indicate that the bulk samples are composed mostly of calcite and dolomite with small quantities of quartz, smectite and illite (Fig. S4; Table S8), with calcite/dolomite ratios being consistent with measured Ca/Mg values (Fig. S4). Collectively, these relationships indicate that the Xiang'erwan section is likely to have retained its primary marine sulfate $\delta^{34}S_{CAS}$ and $\delta^{18}O_{CAS}$ signals throughout the SE/EN3/DOUNCE carbonate unit subject to only limited late-stage diagenetic alteration.

5.2 H_2S reoxidation within the SE carbon-sulfur cycle

Paired $\delta^{34}S_{CAS}$ and $\delta^{18}O_{CAS}$ records can be used to evaluate the relative fluxes of sulfate reduction versus sulfide reoxidation in modern and ancient settings, as they vary in response to changes in the biogeochemical S cycle: inputs from weathering and volcanism and outputs via pyrite burial and evaporite deposition (e.g., Paytan et al., 2004; Turchyn and Schrag, 2006; Gomes and Johnston, 2017). The $\delta^{18}O_{CAS}$ profiles of the Three Gorges and Parachilna Gorge study sections show significant negative shifts of differing magnitude during the falling limb of $\delta^{13}C_{carb}$ and $\delta^{34}S_{CAS}$ excursions (Fig. 3), which implies widespread reoxidation of H_2S in shelf areas during the SE but with varying intensity between basins. In nature, there exist fewer biogeochemical mechanisms to concurrently lower marine $\delta^{34}S_{CAS}$ and $\delta^{18}O_{CAS}$ values than to raise them (Turchyn and Schrag, 2006). One mechanism for lowering both proxies is to increase rates of re-oxidation of MSR-generated free sulfide (i.e., H_2S + HS^-) at the oxic/anoxic interface (Turchyn and Schrag, 2006). This process transfers ^{34}S-depleted sulfate derived from oxidized H_2S back into the residual oceanic sulfate reservoir and decreases the pyrite burial flux, while the decrease in $\delta^{18}O_{CAS}$ is due to transfer of oxygen from potential oxidants to regenerated SO_4^{2-} (Goldberg et al., 2005; Fike et al., 2015) (Fig. 7A). Usually Fe^{3+}, not O_2, is utilized during H_2S oxidation around the oxic/anoxic interface because O_2 cannot form as strong a σ bond to the sulfide surface as Fe^{3+} in a redox transition state (Luther, 1987), and this competitive advantage may have been more significant in the chemocline of stratified anoxic Precambrian oceans, in which deep waters were widely ferruginous (e.g., Canfield et al., 2008; Li et al., 2010) and chemoclinal Fe^{3+} potentially reached a dynamic balance between surface dissolved O_2 and deep Fe^{2+}. The H_2S-reoxidation process produces sulfate that has oxygen isotopic compositions close to that of seawater (via iron oxide) (e.g., Van Stempvoort and Krouse, 1994) (Fig. 7B), unless deep-water H_2S concentrations increase beyond a critical threshold (e.g., 1 mmol kg^{-1}), triggering release of H_2S from the ocean surface to the atmosphere (Kump et al., 2005). Incorporation of any water oxygen into the final sulfate molecule should make it isotopically lighter, because the $\delta^{18}O$ of water is below ~0 ‰ VSMOW (e.g., Van Stempvoort and Krouse, 1994; Turchyn and Schrag, 2006).

Paired low $\delta^{34}S_{CAS}$-$\delta^{18}O_{CAS}$ compositions are rare in Ediacaran and lower Cambrian carbonate units (~635-521 Ma) because seawater sulfate was generally nearly completely utilized by sulfate-reducing microbes owing to the sulfate-poor condition of contemporaneous oceans, especially during the Pre-Shuram interval, resulting in extremely high $\delta^{34}S_{CAS}$ (up to ~+30 ‰) and $\delta^{18}O_{CAS}$ (up to ~+20 ‰) (green symbols in Fig. 7B). Increased MSR rates may have removed isotopically lighter SO_4^{2-} from the marine sulfate reservoir, leaving residual SO_4^{2-} isotopically heavy. However, the relatively low $\delta^{34}S_{CAS}$ and $\delta^{18}O_{CAS}$ values of this study (brown symbols in Fig. 7B) demonstrate that not all MSR-derived H_2S reacted with Fe^{2+} to form pyrite during the SE interval. Rather, a part of the H_2S was re-oxidized, generating ^{34}S- and ^{18}O-depleted sulfate that partially buffered the effects of pyrite burial on seawater $\delta^{34}S$ and $\delta^{18}O$, and forcing seawater sulfate toward the isotopic composition of the weathering sulfate pulse at that time [based on average values of $\delta^{34}S_{sulfate}$ = +15 ‰ and $\delta^{18}O_{sulfate}$ = +14 ‰ for Tonian (~1000-720 Ma) gypsum deposits; Crockford et al., 2019]. During the SE interval, H_2S that escaped reoxidation reacted with iron to form pyrite, whose burial sequestered the reduced products of microbial activity and, when that microbial activity included oxygenic photosynthesis, represented a net addition of oxygen to the ocean-atmosphere system. Rising oxygen availability, in turn, limited the pyrite burial rate via enhanced sulfide reoxidation rates, which created a self-limiting negative feedback on net oxygen production.

Concurrent negative excursions in $\delta^{13}C_{carb}$, $\delta^{34}S_{CAS}$ and $\delta^{18}O_{CAS}$ during the SE period support coupling of the C-S-O cycles as a feedback process driven by the anaerobic oxidation of a large DOC reservoir linked to a weathering sulfate pulse, causing a substantial release of H_2S and atmospheric CO_2, and hence subsequent H_2S reoxidation and additional climate feedbacks. To provide a context for interpreting the biogeochemical feedbacks between the C-S-O cycles and marine ecosystems during the

SE, we evaluated the P/(Ca+Mg) proxy as an indicator of nutrient phosphorus levels in the oceans (Ingalls et al., 2020). Figure 3A exhibits a significant peak in P/(Ca+Mg) (>20) at the onset of the SE, followed by a minimum with values below the initial levels (<5), showing a similar trend to $\delta^{138}Ba_{carb}$ (Wei et al., 2021) and CAP (Dodd et al., 2023) records. We infer that this P peak records both an initial release of organic P during DOC oxidation as well as a substantial rise in atmospheric CO_2 concentrations and, hence, increased continental silicate weathering rates caused by warmer temperatures. These changes led to sustained enhanced delivery of weathered phosphorus to the oceans, which fueled a long-term increase in P-limited productivity. The subsequent minimum in oceanic phosphorus resulted from increased P burial linked to a negative feedback involving marine oxygenation and P uptake by Fe^{3+}-oxyhydroxides (cf. Ingall et al., 1993; Algeo and Ingall, 2007). Eventually, increasing atmospheric pO_2 led to P-limited productivity and reduced pyrite burial, which is consistent with significant oxygenation during the mid-SE, as suggested by a large positive shift in $\delta^{238}U_{carb}$ (Zhang et al., 2019) (Fig. 3A). Therefore, concurrent variation in our $\delta^{34}S_{CAS}$, $\delta^{18}O_{CAS}$ and P/(Ca+Mg) records is well explained by subsequent H_2S reoxidation after the sulfate-driven oxidation of an organic matter reservoir.

If considering only its buffering effect on the marine sulfate reservoir, increased continental pyrite weathering might have lowered both $\delta^{34}S_{CAS}$ and $\delta^{18}O_{CAS}$ (Turchyn and Schrag, 2006). However, this explanation is not relevant to the Shuram Event because sustained low $\delta^{13}C_{carb}$ implies net oxygen consumption by the carbon cycle, implying that the main O_2 source was linked to pyrite burial, which is the only other major net source of oxygen to the Earth-surface system (Shields et al., 2019). Therefore, during the SE, oxygen production by pyrite burial must have exceeded oxygen consumption by pyrite weathering at a global scale. Our steady-state mass balance calculations for carbon-sulfur cycling show that oxygen consumption by pyrite weathering cannot have been balanced by oxygen production via pyrite burial if the weathering sulfate pulse came mostly from pyrite weathering (Figs. S1-S2) (more details are given in the Supplementary Material). Thus, to avoid falling into the ‘Shuram oxidant paradox’ (Bristow and Kennedy, 2008), it is necessary for the bulk of the weathering sulfate pulse to have come from evaporite dissolution rather than pyrite weathering.

5.3 Modeling H_2S reoxidation using the COPSE model

Our modified COPSE model for the SE provides support for the H_2S reoxidation hypothesis. It can account for the observed negative excursions in the $\delta^{34}S_{CAS}$ and $\delta^{18}O_{CAS}$ compositions of SE carbonates, as well as associated changes in $\delta^{13}C$ and $\delta^{238}U$ (Figs. 3 and 8). We tested values of f_{reox} ranging from

0 (no H_2S reoxidation, full conversion to pyrite) to 1 (complete H_2S reoxidation, where pyrite formation was maintained by the background pyrite burial flux in this case) to match the spatial heterogeneity of S-isotopes on different Ediacaran cratons globally (Fig. 3). Figure 8A shows the model results for oxidation of the DOC reservoir (with $\delta^{13}C$ of –30 ‰) via MSR, using sulfate from weathering of sulfate evaporites to sustain a negative $\delta^{13}C_{carb}$ excursion down to ca. –10 ‰. Figure 8B shows that the $\delta^{13}C$ of the DIC reservoir is little affected in response to varying f_{reox}. The duration of the carbon isotope excursion depends on the timespan of the weathering sulfate pulse, which was assumed to be ~10 million years based on the latest radiometric age constraints for the SE (Rooney et al., 2020; Yang et al., 2021). Figure 8C-D shows the modeled changes in oceanic sulfate S-O isotopes as a function of f_{reox}. Values of f_{reox}= 0 (upper limit) result in decreases in $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ to ~+25 ‰ and ~+17 ‰, f_{reox}= 0.5 (mid-range) in decreases to ~+18 ‰ and ~+14 ‰, and f_{reox}= 1 (lower limit) in decreases to ~+16 ‰ and ~+12 ‰, respectively. The modeled $\delta^{13}C_{carb}$ and $\delta^{34}S_{SO4}$ relationships replicate trends in $\delta^{13}C_{carb}$ and $\delta^{34}S_{CAS}$ in global SE sections (Figs. 1 and 3), while the relative magnitude of the modeled $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ excursions are dependent on the fraction of re-oxidized H_2S. Comparing model results with measured data for $\delta^{34}S$ and $\delta^{18}O$ of the oceanic sulfate reservoir, we infer that the small $\delta^{34}S_{CAS}$ excursion in the Miqrat-1 section reflects limited local H_2S reoxidation with near-zero f_{reox}, which is consistent with the higher F_{pysb} calculated from S_{py} data in the Miqrat-1 section (see Section 5.4). By contrast, the large $\delta^{34}S_{CAS}$ excursions in the Jiulongwan section reflect f_{reox} values close to 1, suggesting that nearly all MSR-derived H_2S was re-oxidized, which is consistent with the lower F_{pysb} calculated from S_{py} data in the Jiulongwan section (see Section 5.4).

Increased H_2S reoxidation means a decreased pyrite burial rate (when rate of MSR stays constant), which was common in the Phanerozoic [e.g., during the Permian-Triassic transition (Schobben et al., 2015) and in the Oligocene (Paytan et al., 1998)], with the relative rates of H_2S re-oxidation and pyrite burial controlling local oxygen production rates. Our model results show that forced oxidation of a DOC reservoir via a weathering sulfate pulse releases organic phosphorus (with a C:P ratio of 250:1; Lenton et al., 2018), which leads to increased P-limited productivity and formation of particulate organic carbon (POC). This process operates rapidly to increase organic burial, triggering a rise in atmospheric pO_2 from 0.1 PAL to an average of about 0.6 PAL with a confidence range from ~0.25 PAL to ~0.95 PAL (Fig. 8E), in agreement with other recent estimates (Krause et al., 2022; Shi et al., 2022). This finding is also consistent with a significant oceanic P peak followed by a decline to levels below the initial steady-state value (Fig. 8F), demonstrating the complexity of biogeochemical feedbacks during such events. The balance between atmosphere-ocean O_2 availability and marine phosphorus concentrations determines oxygen supply to the ocean from the atmosphere and oxygen consumption during remineralization in the water column and, thus, the degree of marine anoxia (Canfield, 1998; Lenton et al., 2014; Dodd et al., 2023), as given by the parameter '*anox'* in the COPSE model (Lenton et al., 2018). Figure 8G shows '*anox'* marginally increasing at the onset of the SE due to P release, followed by a large decrease as a result of the co-evolution of pO_2 and oceanic P concentrations, indicating a significant increase in marine oxygenation. Increased organic carbon and pyrite burial, thus, net oxygen production, increases H_2S reoxidation, yet greater fractional reoxidation of H_2S, in turn, decrease the net oxygen production. Only when the rate of pyrite burial exceeded that of the sum of pyrite weathering, degassing and H_2S reoxidation was surplus oxygen generated to drive the ocean-atmosphere system toward more oxidizing conditions—otherwise, the redox deficit of the sulfur cycle is balanced by the redox surplus of the carbon cycle, as has generally happened throughout the Phanerozoic.

The current iteration of the COPSE model does not include the uranium cycle and cannot accurately predict its biochemical transformation because it has no explicit treatment of marine versus atmospheric oxygenation. However, marine anoxia would affect uranium isotopic fractionation, whereby more widespread ocean anoxia helps reduce dissolved U^{6+} to U^{4+}, facilitating U removal to the sediment (e.g., Weyer et al., 2008). Here, we follow the approach of Clarkson et al. (2018), who developed a simple uranium mass balance model giving consideration to the possible forcings related to uranium isotopic compositions (e.g., riverine input, hydrothermal and anoxic sinks) and incorporate this geochemical sub-cycle into COPSE via linking the riverine U input and anoxic U sink with silicate weathering rate and '*anox*', respectively. The modeled decrease in '*anox'* leads to a large positive shift in $\delta^{238}U$ from <-0.9 ‰ to -0.3 ‰ (assumed riverine value) (Fig. 8H), which is in accordance with previously published $\delta^{238}U_{carb}$ data for the SE (Zhang et al., 2019; Gong et al., 2023) (Figs. 1 and 3). Significantly, the modeled atmospheric pO_2 is still far below 1 PAL in the mid-SE, when f_{reox} is 0.5 (Fig. 8E), while $\delta^{238}U$ is very close to -0.3 ‰ (Fig. 8H). This indicates that changes in $\delta^{238}U$ may have occurred more rapidly than changes to the overall surface O_2 reservoir (Chen et al., 2022), probably due to oxygen-nutrient feedbacks and changes in oxic seafloor area (e.g., Alcott et al., 2019), although the assumption that the Precambrian marine uranium isotopic cycle operated in a manner similar to the modern one has been questioned (Chen et al., 2021).

Our model shows an overall strong level of qualitative and quantitative agreement for five independent geochemical proxies (carbon, sulfate-sulfur, sulfate-oxygen and uranium isotopes, and P/(Ca+Mg) ratios) and the calculated F_{pysb}. We therefore conclude that the oxidative sulfur sub-cycle, which is linked to anaerobic oxidation of DOC via H_2S production, buffered the effects of MSR, leading to negative excursions in both $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$. Thus, the relative rates of H_2S re-oxidation and pyrite burial would have controlled site-specific variations in $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$.

5.4 Implications for spatial heterogeneity of Ediacaran oceanic redox conditions

Compilations of oceanic redox proxies (e.g., redox-sensitive elements and iron speciation) document a degree of oxygenation of deeper watermasses during the SE, but this oxygenation event was not universal, and anoxic (i.e., both ferruginous and sulfidic) conditions persisted in some areas, reflecting variations in the interplay of the O-S-Fe cycles between depositional basins (e.g., Canfield et al., 2007, 2008; Johnston et al., 2013; Li et al., 2010; Sahoo et al., 2016; Zhang et al., 2023). After the first-order control of pO_2, the quantitative relationship between the fluxes of Fe^{2+} and H_2S to the seafloor was an important secondary factor controlling local redox conditions in Ediacaran shelf oceans (e.g., Li et al., 2010, 2020). The local persistence of ferruginous conditions, as in the Wernecke Mountains section at Goz Greek, northwestern Canada (Johnston et al., 2013), requires the molar flux of dissolved Fe^{2+} to the ocean to have been greater than half the flux of H_2S, the ratio needed to yield excess Fe^{2+} after formation of pyrite (Canfield et al., 2008). Where the flux of dissolved Fe^{2+} was less than half that of H_2S, residual H_2S after pyrite formation would have created an oxygen demand in the subsurface layer. In this case, either this oxygen demand would have been satisfied by oxygen liberated via oxygenic photosynthesis, leading to oxic conditions, or oxygen depletion would have led to the development of sulfidic conditions (e.g., Canfield et al., 2008; Li et al., 2020), as in the Wuhe section of South China (Sahoo et al., 2016). Although there are recent investigations that call into question the relevance of the Fe-speciation proxy as an indicator of ocean redox conditions in ancient rocks, when used in isolation (Hutchings and Turchyn, 2021; Pasquier et al., 2022), cerium anomaly (Ce/Ce*, a well-established paleo-redox proxy) values from the Jiulongwan (South China; Cheng et al., 2022) and Bunyeroo Gorge (South Australia; Gong et al., 2023) sections show a transient decrease to <0.8 at the onset of the SE followed by a rebound to 0.8-to-1.1 for most of the SE, suggesting a short-term oxygenation event that was dissipated by the extensive deoxygenation of the SE ocean, which is consistent with our arguments.

Changes in local environmental conditions (e.g., oxidant availability, iron supply, carbon substrate and temperature) can strongly influence the sulfur sub-cycle involving H_2S reoxidation, but the relative importance of these factors in the natural environment remains elusive. Modern observations from coastal ponds in the northeastern USA show that sulfide oxidation does not follow a consistent pathway because of local variations in oxidant availability and physical transport, which are likely influenced by atmospheric oxygen levels, local iron supply, upwelling and rates of H_2S diffusion (Gomes and Johnston, 2017). At a cellular level, the overall rate of MSR serves as a first-order control on H_2S reoxidation rates by regulating the exposure duration of free sulfide (Antler et al., 2013). In environments where sulfate reduction is slow, as in the deep-sea, sulfide reoxidation can be near-quantitative, with as much as 99 % of sulfide being re-oxidized. By contrast, in environments where sulfate reduction is fast, as in estuarine and marginal-marine settings, sulfide reoxidation is minimal, with most sulfate being reduced to H_2S and thus ultimately buried as pyrite (Antler et al., 2013).

To test these influences in Ediacaran Shuram oceans, we compared the rate of the negative $\delta^{13}C_{carb}$ shift and the bulk accumulation flux of pyrite sulfur (F_{pysb}) between the Miqrat-1 drillcore (Oman) and Jiulongwan section (South China) (Fig. 9; Table S2). F_{pysb} was calculated for a time-stratigraphic unit of interest based on its thickness at the study site, and its estimated duration based on the radiometric ages, multiplied by the bulk density and percent abundance of sediment pyrite sulfur (S_{py}) (cf. Algeo and Twitchett, 2010). Here, we view the rate of the negative $\delta^{13}C_{carb}$ shift as a positive correlation with the overall sulfate reduction rate (SRR), while F_{pysb} has an inverse correlation with H_2S reoxidation rate when the SRR is unchanged, because only the H_2S escaping from reoxidation can be buried as pyrite (see detailed calculations in the Supplementary Material). Figure 9 shows that, compared to Jiulongwan, Miqrat-1 exhibits both a more rapid $\delta^{13}C_{carb}$ shift (–9.3 ‰/Myr) and a higher F_{pysb} (mean ~0.042 g m^{-2} Myr^{-1}) (Fig. 9A-B), indicating a faster SRR and minimal reoxidation of H_2S, which is supported by the relatively smaller magnitude of the negative $\delta^{34}S_{CAS}$ shift (from ~+30 ‰ to ~+22 ‰) in Oman (Fig. 1B). By contrast, Jiulongwan exhibits a slower $\delta^{13}C_{carb}$ shift (–4 ‰/Myr) as well as a lower F_{pysb} (mean 0.002 g m^{-2} Myr^{-1}, or <5 % of the flux at Miqrat-1) (Fig. 9C-D), indicating a slower SRR and more extensive reoxidation of H_2S, which is supported by the relatively larger magnitude of the negative $\delta^{34}S_{CAS}$ shift (from ~+32 ‰ to ~+15 ‰) (Fig. 1D). The above comparison demonstrates an inverse relationship between SRR (as proxied by rate of $\delta^{13}C_{carb}$ change) and H_2S reoxidation rate (as proxied by F_{pysb}). Where MSR was the dominant process of organic remineralization, and the former parameter (i.e., SRR) was controlled by either sulfate or organic carbon availability.

Ferruginous conditions persisted beneath the mixed layer of the Ediacaran ocean before the SE (~635-580 Ma) (e.g., Canfield et al., 2008; Li et al., 2010; Johnston et al., 2013; Sahoo et al., 2016). These conditions, which were linked to low aqueous sulfate concentrations and facilitated by a high Fe:S ratio, likely helped to sustain the productivity export necessary to accumulate a large DOC reservoir before the SE (Jiang et al., 2010; Swanson-Hysell et al., 2010) through a lack of electron acceptors in the water column. However, possible elevated evaporite sulfate inputs, as suggested by rising $^{87}Sr/^{86}Sr$ (Sawaki et al., 2010) and falling εNd(t) (Wei et al., 2019), and enhanced erosion rates around the Shuram Excursion during Trans-Gondwanan orogenic uplift and tectonic inversion drove net oxidation of the DOC reservoir, likely producing a sufficient quantity of H_2S to overwhelm the Fe^{2+} supply in some basins (cf. Li et al., 2020). Where iron supply was lower than half the H_2S production (on a molar basis), euxinic conditions developed with a higher fraction of H_2S reoxidation. Conversely, where iron supply was higher than half the H_2S production, ferruginous conditions persisted with a lower fraction of H_2S reoxidation.

5.5 Implications for the Ediacaran Biota

Although it remains unclear whether the Ediacaran animal diversification and increased ecosystem complexity were driven extrinsically by the expansion of permissive oxic niches, or by genetic or developmental innovations that enabled animals to expand into the oxic realm (e.g., Wood et al., 2019; Evans et al., 2022), global compilations of the fossil record indicate that major diversification of the Ediacaran Biota, comprising the Avalon (~575-560 Ma), White Sea (~560-550 Ma) and Nama (~550-540 Ma) biotas, most likely originated under a heterogeneous marine redox state with a relatively low level of atmospheric oxygen (e.g., Shi et al., 2018; Wood et al., 2019). While uranium and selenium isotopes suggest that there was general progressive oxygenation through the Ediacaran SE interval (Pogge von Strandmann et al., 2015; Zhang et al., 2019; Gong et al., 2023), integrated paleoredox proxy data and biotic distributions show continued redox instability after the first fossil evidence for Ediacaran metazoans, which were usually restricted to local oxygenated habitats (e.g., Li et al., 2015; Wood et al., 2019). At the local scale, Ediacaran fossil biotas are temporally highly variable and can differ dramatically within contemporaneous marine-shelf sections, and such differences have been confirmed to be unrelated to lithofacies, taphonomy or sampling bias (McFadden et al., 2009; Evans et al., 2022). As with the spatial heterogeneity of Ediacaran-early Cambrian redox conditions, contemporaneous benthic biotas also exhibit a pronounced spatial patchwork (Li et al., 2015; Bowyer et al., 2017; Wood et al., 2019). In the Jiulongwan section (South China), the lower-to-middle SE interval, despite being age-equivalent to strata in eastern Newfoundland containing the Avalon Assemblage, contains no metazoan fossils (McFadden et al., 2009); and the upper SE interval, despite being correlative with the White Sea Assemblage in northern Europe and the nearby fossil-bearing Miaohe section (Li et al., 2015), contains no Miaohe Biota.

Ediacaran animals had already evolved higher surface-area respiratory structures and body plans to facilitate O_2 uptake to survival in hypoxic benthic environments (e.g., Jeffreys et al. 2012), and most Neoproterozoic oceans contained abundant Fe^{2+} that buffered water-column sulfide buildup (e.g., Canfield et al., 2008). However, the sudden H_2S pulse derived from DOC remineralization during the SE likely overwhelmed this Fe-redox buffering capacity, at least in some basins (such as the Three Gorges) and inevitably exposed benthic biota to greater risk of H_2S toxicity. Under these conditions, body structures with higher surface-to-volume ratios became lethal physiological defects as H_2S readily diffused across membranes and into tissues (Sperling et al., 2015b). Although most H_2S was oxidized, this process would have further reduced oxygen availability and the areal extent of oxic habitats in marine systems. Our study provides a plausible scenario for locally variable rates of H_2S reoxidation, as recorded by the spatial characteristics of $\delta^{34}S_{CAS}$ and $\delta^{18}O_{CAS}$ excursions (Fig. 3), which can account for differential local shallow-seawater dissolved oxygen and H_2S availability and, thus, the patchy distribution of the Ediacaran Biota.

6. CONCLUSIONS

In this study, we presented paired C-S-O-P data for the Ediacaran Shuram Excursion from the inner-shelf Jiulongwan and Xiang'erwan sections (South China), and the Parachilna Gorge section (Australia). These profiles exhibit behavior similar to previously published profiles and demonstrate that widespread reoxidation of H_2S occurred along oxic/anoxic interfaces in the Ediacaran ocean. Three study sections show very different extents of H_2S reoxidation, which may have been caused by different iron supply and correspondingly differential internal oceanic cycling of C, S, O and P. The variable fraction of H_2S oxidized further determined the variable marine sulfate sulfur-oxygen isotopic compositions, as well as the spatial heterogeneity of marine dissolved oxygen and H_2S availability (i.e., oceanic redox conditions), in the stratified and anoxia-dominated late Ediacaran Ocean. These findings are consistent with regional differences in the distribution and patchiness of the Ediacaran Biota, highlighting the important role of

H_2S reoxidation in the coevolution of marine redox condition and complex life during the critical Ediacaran Period.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ACKNOWLEDGMENTS

We thank Maoyan Zhu, Graham A. Shields, Ying Zhou, Hongfei Ling, Zhihua Tang, Zhihui An, Yijun Xiong, Hailin Yang, Meng Cheng, Xi Chen and Fuencisla Cañadas for field assistance and/or helpful discussions, and Jun Hu, Biao Chang, Huyue Song, Yong Du, Kaiqi Huang, Haiyang Zhang and Haodong Gu for laboratory assistance. We are also grateful to Erik Sperling and two anonymous reviewers for their helpful comments. This study was supported by the NSFC, the National Key Research and Development Program of China, the NSFC-RCUK_NERC program and the 111 Project of China (grants # 42130208, 2022YFF0800100, 41825019, 42102342, 42050104, 41888101, 41661134048, and BP0820004).

APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data and additional information regarding the timescale and rate of the Shuram Excursion, burial flux of pyrite sulfur, steady-state mass balance of C-S cycles and the sensitivity test for the necessity of an oceanic organic matter reservoir

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Figure captions

Fig. 1. Global paleogeography at ~560 Ma, with locations of studied or discussed sections in this study (red stars) (A) and integrated chemostratigraphy of the Ediacaran Shuram Excursion at Oman (Miqrat-1 drill) (B), Death Valley, California, USA (C), and Three Gorges (Jiulongwan section), South China (D). Global paleogeographic map was modified from Merdith et al. (2017). Data sources: Oman–Fike et al. (2006); Death Valley–Kaufman et al. (2007); Three Gorges–Li et al. (2017), Shi et al. (2018) and Zhang et al. (2019). Abbreviations: Au, Australia; ANS, Arabian-Nubian Shield; Az, Azania; G, Greenland; Ka, Kalahari; Ra. Rayner; SF, São Francisco; Si, Siberia; SM, Sahara Metacraton. Fm., Formation; III-IV, Member III-IV; DOUNCE, DOUshantuo Negative Carbon isotope Excursion. Note: open diamonds represent unreliable data.

Fig. 2. Geological setting of the study sections containing the Ediacaran Shuram Excursion in South China and South Australia. (A) Paleogeographic map of the Yangtze Platform during deposition of the Doushantuo Formation (modified from Jiang et al., 2011) with the two study sections (Jiulongwan and Xiang'erwan) marked. (B) Geological map of the Huangling Anticline region, Yangtze Three Gorges area, showing locations of the Jiulongwan and Xiang'erwan sections as red stars. Modified from An et al. (2015). (C) Simplified map of the study area within the Adelaide Rift Complex, adapted from Harkins et al. (2008) with the Parachilna Gorge section shown as a red star. (D) Schematic section and $\delta^{13}C_{carb}$ dataset for the Parachilna Gorge section based on Husson et al. (2015) and Gong et al. (2023), which can be subdivided into 11 lithological units. Fm., Formation.

Fig. 3. Chemostratigraphic profiles of C-S-O-U isotopes through the Ediacaran Shuram-Wonoka interval at the Three Gorges (Jiulongwan and Xiang'erwan) (A) and Parachilna Gorge (B) sections. Published data sources: Jiulongwan–Li et al. (2017), Shi et al. (2018) and Zhang et al. (2019); Bunyeroo Gorge–Gong et al. (2023). Abbreviations: Fm., Formation; III-IV, Member III-IV. Note: relative stratigraphic position of Jiulongwan and Xiang'erwan sections are normalized to a range of 0 to 1 (details in Section 2.2); open diamonds represent unreliable data.

Fig. 4. Schematic showing H_2S reoxidation in the long-term C-S-O cycles of the COPSE model. Atmospheric-oceanic carbon (A) and sulfate (S) are removed into crustal reservoirs (G, organic carbon; C, carbonate; PYR, pyrite; GYP, gypsum) through burial (B) and seafloor weathering (*sfw*) fluxes, but

are returned by weathering (W) and degassing (D). Atmospheric oxygen (O_2) is sourced by the burial of organic carbon and pyrite but removed by weathering and degassing of the same species (blue arrows). Addition of a dissolved organic carbon (DOC) reservoir 30 times larger than the modern DIC reservoir is primed for coupling with the additional gypsum/evaporite weathering inputs via microbial sulfate reduction (MSR, magenta arrows); part of the MSR-derived H_2S flux is re-oxidized (Reox, orange arrow) to sulfate and the non-oxidized fraction is buried as pyrite to stabilize the marine sulfate reservoir. Burial of organic carbon is fueled by nutrient (i.e., N and P) cycling, which are partly sourced from oxidation of the DOC reservoir. Abbreviation: de-N, denitrification. Modified from Mills et al. (2021).

Fig. 5. Diagenetic evaluation of geochemical data in the SE interval of the Xiang'erwan section (Three Gorges, South China). (A) Chemostratigraphic profiles of $\delta^{13}C_{carb}$, $\delta^{18}O_{carb}$ and Mn/Sr. (B) Crossplots of $\delta^{18}O_{carb}$ versus $\delta^{13}C_{carb}$, $\delta^{18}O_{carb}$ versus $\delta^{34}S_{CAS}$ and $\delta^{18}O_{carb}$ versus $\delta^{18}O_{CAS}$, and Mn/Sr versus Mg/Ca, Mn/Sr versus $\delta^{34}S_{CAS}$ and Mn/Sr versus $\delta^{18}O_{CAS}$. (C) Crossplots of P/(Ca+Mg) versus Mg/Ca and P/(Ca+Mg) versus Mn/Sr. Shown in each panel are linear regressions, correlation coefficients (r), statistical significance (p) and sample size (n).

Fig. 6. Microphotographs showing uniform microcrystalline fabrics of the micritic carbonate with extremely negative $\delta^{13}C_{carb}$ values in the DOUNCE interval of the Jiulongwan (A-D) and Xiang'erwan (E-I) sections. (A, E) Banded limestone showing uniform micritic calcite; (B-D, F-I) finely laminated dolostone showing homogeneous dolomicrospar. JLW-56 and XEW-I-01 represent the pre-SE interval while JLW-35 and XEW-I-24 represent the P-rich intervals. Darker-colored samples have higher concentrations of organic matter.

Fig. 7. Biogeochemical processes related to H_2S reoxidation in the local water column (A) and its S-O isotope effects on carbonate-associated sulfate (CAS) as indicated by the crossplot of $\delta^{34}S_{CAS}$ versus $\delta^{18}O_{CAS}$ spanning the Ediacaran to lower Cambrian (B). In (A), the dissolved organic carbon (DOC) reservoir is oxidized by microbial sulfate reduction (MSR) using sulfate from weathering, while part of the derived H_2S is re-oxidized by Fe^{3+} or free oxygen back to marine sulfate. Abbreviations: $[CH_2O]_x$, fresh organic carbon; DIC, dissolved inorganic carbon; Reox, reoxidation; WSI, water-sediment interface. In (B), grey-square data are sourced from Crockford et al. (2019); green- and brown-symbols represent the pre-to-early Shuram steady state and the middle-to-late Shuram Excursion, respectively.

Fig. 8. COPSE model results for dissolved organic carbon (DOC) oxidation via microbial sulfate reduction (MSR) with a forced weathering sulfate input and varying fractions of H_2S reoxidation. (A) Weathering sulfate pulse and size of the DOC reservoir in moles of carbon. (B) Calculated seawater dissolved inorganic carbon (DIC) $\delta^{13}C$ (given as $\delta^{13}C_{carb}$). (C) Calculated seawater sulfate $\delta^{34}S$ (given as $\delta^{34}S_{SO4}$). (D) Calculated seawater sulfate $\delta^{18}O$ (given as $\delta^{18}O_{SO4}$). (E) Relative atmospheric oxygen concentration [(given as pO_2 in present atmospheric level (PAL)]. (F) Concentration of marine bioavailable phosphorus. (G) Degree of ocean anoxia. One (1) in Y-axis means completely anoxic while

0 means completely oxic. (H) Calculated δ^{238}U of seawater. Note: green shaded fields show possible model output under enhancements from 0 to 1 in f_{reox}. Time represents million years relative to the start of the Shuram Excursion (~575 Ma).

Fig. 9. Rates of δ^{13}C$_{carb}$ change (A and C) and bulk accumulation fluxes of pyrite sulfur (F_{pysb}; B and D) through the Shuram Excursion interval of the Miqrat-1 drillcore (Oman) and Jiulongwan section (Three Gorges, South China). Data sources: Miqrat-1–Fike et al. (2006); Jiulongwan–Li et al. (2017) and Shi et al. (2018).